HESS OIL VIRGIN ISLANDS CORP.

Brian Epperson
Director, EHS
Phone: (713) 496-7296
E-Mail: bepperson@hess.com

1501 McKinney Street
Houston, Texas 77010

April 26, 2021

Mr. Adolph Everett, Chief
Hazardous Waste Programs Branch
US Environmental Protection Agency, Region 2
290 Broadway
New York, New York 10007-1866
Via: Electronic Copy

Re: St. Croix Alumina Site Administrative Order Docket No. RCRA-0202001-7301
Revised LNAPL Natural Source Zone Depletion Work Plan
EPA Facility ID No. VID090302084

Dear Mr. Everett:

The St. Croix Alumina (SCA) Project Operating Committee (POC) submitted a Light Non-aqueous Phase Liquid (LNAPL) Natural Source Zone Depletion (NSZD) Work Plan on November 11, 2020. After receiving a series of comments and questions from EPA, the POC is submitting this Revised LNAPL NSZD Work Plan. This revised document addresses EPA's comments and questions. Please feel free to contact me if you have any questions or comments.

Sincerely,

Brian Epperson
Remediation Manager

Cc: Carol Stein (Electronic Copy)
Environmental Engineer
Hazardous Waste Programs Branch
EPA Region 2
290 Broadway
New York, New York 10007-1866

POC (Electronic Copy)

LNAPL Natural Source Zone Depletion Work Plan

St. Croix, U.S. Virgin Islands

Prepared for:

St. Croix Alumina Site

Prepared by:

EHS Support

April 2021

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Acronyms

°C	degrees Celsius
µmol	micromoles
AC	assimilative capacity
ALCOA	ALCOA World Alumina, L.L.C.
AOC	Administrative Order on Consent
ANOVA	analysis of variance
bgs	below ground surface
Ca	calcium
CFR	Code of Federal Regulations
CH_4	methane
CO_2	carbon dioxide
C-O-C	chain-of-custody
COC	chemical of concern
CRC CARE	Cooperative Research Centre for Contamination Assessment and Remediation of the Environment
CSM	conceptual site model
DCC	dynamic closed chamber
DIC	dissolved inorganic carbon
DO	dissolved oxygen
DOC	dissolved organic carbon
DPPHC	Dissolved Phase Petroleum Hydrocarbon Constituents
DQA	data quality assessment
DQO	data quality objective
DUE	data usability evaluation
DUP	duplicate
EB	equipment blank
Eh	Oxidation/Reduction Potential (hydrogen electrode)
FB	field blank
Fe	iron
g/mol	grams per mole
gpd	gallon per day
H_2S	hydrogen sulfide
HASP	Health and Safety Plan
HAZWOPER	Hazardous Waste Operations and Emergency Response
HCO_3	bicarbonate
HOVIC	Hess Oil Virgin Islands Corp.
ITRC	Interstate Technology & Regulatory Council

K	Kelvin
kJ	kilojoules
L/min	liter per minute
L	liter
LNAPL	light non-aqueous phase liquid
m^2	square meters
m^3m	meters cubed per meter
Mg	magnesium
mg	milligram
min	minute
mL	milliliter
mm^3	cubic millimeters
Mn	manganese
MNA	monitored natural attenuation
mol	moles
msl	mean sea level
mV	millivolt
N_2	dinitrogen gas
Na	sodium
NaCl	sodium chloride
NAPL	non-aqueous phase liquid
NH_4	ammonium
NO_3	nitrate
NOM	natural organic matter
NSZD	natural source zone depletion
NTU	Nephelometric turbidity unit
O_2	oxygen
ORP	oxidation-reduction potential
OSHA	Occupational Safety and Health Administration
POC	Project Operating Committee
PPE	personal protective equipment
PSPH	Phase Separated Petroleum Hydrocarbon
PVC	polyvinyl chloride
QA	quality assurance
QAPP	Quality Assurance Project Plan
QC	quality control
RCRA	Resource Conservation and Recovery Act
RL	reporting limit
ROD	Record of Decision

SCA	St. Croix Alumina, L.L.C.
SO_4	sulfate
SOP	standard operating procedures
TB	trip blank
TDS	total dissolved solids
TEA	terminal electron acceptor
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
VIALCO	Virgin Islands Alumina Company
VOC	volatile organic compound
VPH	volatile petroleum hydrocarbon

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1 Introduction and Purpose

The following entered into an Administrative Order On Consent (AOC), with the United States Environmental Protection Agency (USEPA), Region 2, on May 14, 2001 with an effective date of May 24, 2001:

- St. Croix Alumina, L.L.C. (referred to as SCA)
- ALCOA World Alumina, L.L.C. (formerly known as ALCOA Alumina and Chemical, L.L.C.) (referred to as ALCOA)
- Virgin Islands Alumina Company (referred to as VIALCO)
- Century Aluminum Company, Inc.
- Lockheed Martin Corporation (referred to as "Lockheed Martin")
- Hess Oil Virgin Islands Corp. (referred to as HOVIC)
- HOVENSA L.L.C. (referred to as "HOVENSA")

Pursuant to the AOC, these companies have agreed to work together to address Phase Separated Petroleum Hydrocarbon (PSPH) and Dissolved Phase Petroleum Hydrocarbon Constituents (DPPHC) located beneath the St. Croix Alumina facility in St. Croix, U.S. Virgin Islands (**Figure 1** attached). As per the AOC, a Project Operating Committee (POC) was formed to design, install, and operate a monitoring and remediation system for the Site.

A Draft PSPH Work Plan was submitted to the USEPA on July 23, 2001 (HOVIC, 2001). USEPA approved the PSPH Work Plan on August 8, 2001. Implementation of the PSPH Work Plan has been initiated and both PSPH and DPPHC recovery is underway. The initial Draft DPPHC Work Plan was submitted to USEPA on September 21, 2001 (HOVIC, 2001a). The USEPA requested seven items be incorporated into a revised draft. This revised Draft DPPHC Work Plan was submitted to the USEPA on December 21, 2001 (HOVIC, 2001b). In a January 15, 2002 letter, the USEPA conditionally approved the work plan with proposed changes to timeline items (USEPA, 2002). An amended Draft was submitted to the USEPA on February 22, 2002 incorporating the requested USEPA timeline changes. The POC recommended that the quarterly status reports and the semiannual report be consolidated into one report submitted semiannually. The USEPA approved this recommendation in their March 3, 2005 letter.

The POC submitted a PSPH Pilot Study and DPPHC Sampling Plan Modification to USEPA on May 21, 2018. USEPA provided comments to the proposed plan, which were implemented by the POC, and a final PSPH Pilot Study (HOVIC, 2018) and DPPHC Sampling Plan Modification was submitted on June 11, 2018 (HOVIC, 2018). This recovery plan was implemented by the POC over 2018, 2019, and the first quarter of 2020.

Using historical data and the data collected from this modified light non-aqueous phase liquid (LNAPL) recovery program, a detailed assessment of LNAPL recovery/mobility and chemistry data was completed and reported in the July 2020 LNAPL Conceptual Site Model (CSM) and Remedial Action Work Plan (EHS Support LLC ["EHS Support"], 2020). This assessment demonstrated that the majority of LNAPL recovery wells have reached or are approaching a practicality endpoint. In addition, the July 2020 LNAPL CSM and Remedial Action Work Plan (EHS Support, 2020) proposed shutdown criteria for active recovery wells. However, due to uncertainties and data gaps, recovery operations are planned to continue through June 2021 (including well maintenance and semi-annual groundwater monitoring).

As a supplement to continued routine groundwater sampling activities and the extension of the program of LNAPL recovery activities, it was proposed that additional analysis be conducted to support the assessment of natural source zone depletion (NSZD) processes in the aquifer. Based on the Site geohydrology and limited geochemical data, a combination of sulfate reduction and methanogenesis processes appear to be active and significant contributors to mass losses at the Site. A program of works was proposed to further define and quantify the processes contributing to such natural mass losses.

Therefore, based on the above, the objective of this NSZD Work Plan ("Work Plan") is to provide the protocols and procedures for a geohydrology and geochemistry assessment to facilitate a better understanding of and quantify the natural attenuation degradation of the historical dissolved and phase-separated impacts in the groundwater at the Site. This will be an iterative process conducted over two phases of assessment utilizing existing monitoring well geochemistry data and soil gas flux analysis in accordance with established NSZD and monitored natural attenuation (MNA) technical guidance (Interstate Technology & Regulatory Council [ITRC], 2009; CRC Care, 2015 and 2018).

For completeness USEPA comments and POC responses to the draft of the NSZD Work Plan are provided in **Appendix A**. Revisions to this report incorporate both USEPA comments and POC responses.

1.1 Site Description and History

The Site consists of a former bauxite ore processing refinery that produced alumina, the raw material used to make aluminum. The facility was constructed in the mid-1960s. Historically, the refinery consisted of administrative offices, operations buildings, bulk storage containers (e.g., tanks, silos, and a bauxite ore shed), and various active bauxite processing operations including grinding, digestion, thickening, filtrations, precipitation, and calcination. Ancillary operations included oil-fired boilers, water desalination units, a warehouse, laboratories, maintenance facilities, and stormwater collection and cooling ponds. Bauxite solid waste residue (e.g., red mud) disposal areas, a dock adjacent to the ship channel, and recreational areas were also located on-site.

Prior to the refinery being constructed, portions of the Site were used for production of sugar cane under various owners. Circa 1900 structures associated with the sugar cane are currently located on the western and northeastern portions of the property. The West Indian Sugar Factory, Inc. sold the Site to a private owner in 1937. The United States government assumed ownership of the Site in 1942, later transferring it to the Municipality of St. Croix in 1949. The Site was purchased by Harvey Aluminum, Inc. from the Government of the Virgin Islands in 1962, when construction of the refinery occurred. Martin Marietta Alumina, Virgin Islands Alumina Company, and SCA were owners of the refinery from 1968 through 1995. ALCOA took over the facility in 1998 and operated it until December 2000.

Currently, the facility remains generally inactive and demolition of facility structures is ongoing. Former refinery bulk storage tanks (currently used for molasses storage by Diageo rum distillery since circa 2010) are located on the west side of the Site. **Figure 2** (attached) shows the Site Layout including major features.

1.2 Site Geology

An in-depth evaluation of Site geology, hydrology, and geochemistry is provided in the LNAPL CSM and Remedial Action Work Plan (EHS Support, 2020), and is summarized below.

The Site is located on the south-central St. Croix coastline (**Figure 1**, attached). The northern part of the Site is situated on the Kingshill Limestone, and the southern portion is overlain by younger alluvial deposits that fill erosional channels in the Kingshill Limestone and grade into recent (pre-Site development) reef and lagoon deposits principally of the former Krause Lagoon (Whetten, 1966). During Site development, areas of excavation and/or fill were established on the preexisting topography.

The Kingshill Limestone at the Site and vicinity is described as a buff- to white-colored soft marl (Graves, 1995). Deposits of the overlying Blessing Formation are reportedly absent at the Site, and the nearest occurrence was identified in test holes drilled in Barren Spot well field approximately 1-mile northeast of the Site (Graves, 1995). Deposits of the Jealously Formation that underlie the Kingshill Limestone are typically encountered between 85 to over 120 feet below ground surface (bgs) in the Site vicinity in south-central St. Croix and are considered the base of the freshwater aquifer (Graves, 1995). The Jealously Formation has not likely been encountered in Site borings for monitoring well installations.

An interval of gravels, sands, silt, and clay within the Kingshill Limestone is identified beneath the central portion of the Site that is broadly coincident with the location of the water table and intervals over which most Site wells are screened. Chert, caliche (calcium carbonate), and/or gypsum deposits are identified in the well screen intervals in Site borings logs in wells VW-13B, VW-33, VW-37, VW-35, and VW-37. Conceivably, these minerals are more widespread within the lagoon clay identified in several Site borings but were not abundantly sampled due to the drilling techniques that were employed. A cross-section showing the identified interval of gravels, sands, silts, clays, and evaporite mineralization within the Kingshill Limestone is provided in **Figure 3A** (attached). The identified deposits appear to be contemporaneous with an interval of reef deposits containing coral and mollusk fossils within the Kingshill Limestone exposed in the quarry directly west of former well GM-12 and on the hillside north of GM-4 (Geraghty and Miller, 1982). The occurrence of reef and sediment deposits within the Kingshill Limestone likely coincide with the global sea level lowstand in the Middle to Late Miocene that is commonly observed within the Kingshill Limestone (Gill et al., 1999).

Following uplift and subaerial exposure of the Kingshill Limestone, several alluvial channels formed. The more recent alluvial channels are characterized by various proportions of soft or loosely consolidated sand, gravel, silt, and clay. The alluvial channels are now largely present in the subsurface beneath anthropogenic fill, although the channels are evident on a geologic map that was drafted prior to extensive Site development (**Figure 3A**, attached). It is not clear how the channels are hydraulically connected to lagoon deposits within the Kingshill Limestone; however, available data suggest that the channels are largely above the water table on the northern half of the Site.

South of the eroded edge of the Kingshill Limestone and on the southern portion of the Site, soft to very stiff organic clays, silty clays, and clayey silt deposits are present that formed in the historic Krause Lagoon. Krause Lagoon and the surrounding mangrove swamps were drastically altered after about the 1960s following the construction of industrial facilities and dredging of the shipping channel. The Krause lagoon deposits overlie a 4- to 10-foot-thick sand and gravel layer from about 10 to 30 feet below sea level that is derived from limestone and coral fragments that weathered from the Kingshill Limestone. The hydraulic connection between the Krause lagoon and Kingshill Limestone deposits is uncertain (Geraghty and Miller, 1982; Gill and Hubbard, 1987).

1.3 Site Hydrogeology

The general direction of groundwater flow beneath the Site is to the south-southwest and south towards the sea (GMS, 2020), consistent with groundwater equipotential in the broader region (Graves, 1995). The groundwater elevation at the Site typically ranges from about 0.5 to 3.5 feet above mean sea level (msl) (**Figure 4**, attached). Groundwater at the Site is largely present within the Kingshill Limestone. A notable groundwater elevation high is present at well GM-22, and the cause is presently unknown, but is conceivably a perched or isolated groundwater zone.

Original permeability of the Kingshill Limestone is in part related to the depositional environment; deeper water bathyal deposits and shallow lagoon deposits generally had low original porosity owing to a higher fraction of clay-sized carbonate particles (micrite), whereas shallower reef and washover deposits generally had a higher original porosity and permeability due to larger grain size and the presence of coral and shell fragments (Geraghty and Miller, Inc., 1982). Therefore, the distribution of the lagoon deposits in relation to sand pack/well screen intervals at the Site places a strong control on hydraulic properties of the groundwater saturated zone, specifically, large variations in hydraulic conductivity and storativity are expected. The location of the lagoon facies in relation to Site well screens is provided as **Figure 5** (attached), which illustrates the high variability of hydraulic properties in the monitored saturated zone at the Site and associated controls on LNAPL mobility.

In addition to variations in primary porosity of deposits at the Site, percolation of precipitation and groundwater seepage at the Site has re-precipitated sand-sized particles as micrite and filled pore spaces with secondary calcite (Geraghty and Miller, Inc., 1982). However, a review of Site borings logs has identified numerous poorly cemented and permeable layers within the Kingshill Limestone that consist of sand, gravel, sandstone, and sandstone-marl mixtures. Indeed, the frequently encountered no recovery- zones during drilling at the Site likely reflect zones of extremely loose sediment. Whereas these zones may have been attributed to void spaces, the associated changes in drilling resistance suggest that not all of those intervals were indeed voids.

2 Current LNAPL Conceptual Site Model

The LNAPL CSM and Remedial Action Work Plan (EHS Support, 2020) provided a detailed assessment of LNAPL mobility and recoverability at the Site. In the context of Site conditions, the complex and heterogeneous Site geology/hydrogeology was identified to be a key determinant in historical LNAPL mobility, LNAPL extent, and recoverability.

The LNAPL plume at the Site is stable to receding with observed declines in LNAPL thickness and extent associated with the intense LNAPL recovery activities that have been conducted at the Site. Major declines in LNAPL recovery rates have been observed at the Site in response to past removal actions with a large number of wells recovering less than 1 gallon per day (gpd) of LNAPL. The areas of higher LNAPL recovery rates are concentrated in the eastern area of the LNAPL plume and are associated with more transmissive sandy/gravel deposits.

Key components of geology/hydrogeology, LNAPL extent, composition, and geochemistry are summarized in the following sections with more detail included in the LNAPL CSM (EHS Support, 2020).

2.1 Geology Controls on LNAPL Distribution, Mobility, and Recoverability

Consistent with the Site geology and hydrogeology described in **Sections 1.2** and **1.3** the following key geologic and hydrogeologic components were identified that impact LNAPL distribution, mobility, and recoverability:

- An interval variably composed of calcareous clay, silt, sand, and gravel was identified within the Kingshill Limestone that is broadly consistent with the location of the water table and screened intervals in many Site wells. This interval likely represents lagoon deposits that accumulated during a global sea-level low stand. The lagoon deposits are encapsulated by deeper marine limestone/marl rocks of the Kingshill Limestone that formed during sea-level high stands.
- Abundant zones of no recovery encountered during drilling at the Site may be attributed to loose sand/gravel wash-over deposits that were deposited in the Kingshill Limestone lagoon. These intervals, when present at the water table, represent high conductivity zones in which historical LNAPL migration occurred and are also present in wells with historically high LNAPL recovery rates.
- Abundant clay deposits that likely formed in the Kingshill Limestone lagoon are associated with the evaporite minerals caliche (calcium carbonate), gypsum (calcium sulfate), and are associated with chert (organism frustules composed of silicon dioxide).
- There is large lateral variability in hydraulic conductivity and LNAPL transport due to the heterogenous Kingshill Limestone lagoon deposits that are broadly coincident with well screen intervals. Both intervals of fine-grained clay deposits and coarse-grained sands and gravels are encountered at the water table in wells across the Site. The fine-grained limestone and marl are likely to exhibit low groundwater and LNAPL transmissivities and the presence of these materials has precluded LNAPL migration in select areas and facilitated lateral (cross-gradient) migration of LNAPL.
- There is likely large variability in LNAPL transmissivity and storativity due to the heterogenous Kingshill Limestone lagoon deposits. The presence of LNAPL within the limestone and its recoverability will likely be controlled by secondary porosity features, and areas of higher long-term recovery likely reflect areas dominated by more coarse-grained materials. Storativity is

also limited by the calcium-rich nature of groundwater (which likely is super-saturated with respect to calcium carbonate solubility) and calcification of the intergranular porosity.

- The presence of abundant gypsum deposits is important as this is a key source of sulfate that can support sulfate reduction and potentially high rates of NSZD.
- The groundwater elevation and gradients at the Site are relatively stable with only major seasonal rains resulting in significant water table fluctuations. Tidal fluctuations in the groundwater level are limited. The net result is that vertical residualization (smearing) of LNAPL is limited at the Site with impacts focused at the water table.

2.2 LNAPL Composition and Extent

Assessment of the LNAPL chemistry at the Site indicates that it is a middle distillate consistent with diesel or No. 2 Fuel Oil. As such, NSZD calculations presented in **Section 4** of this work plan are conducted for octadecane ($C_{18}H_{38}$). A detailed description of LNAPL composition at the Site is provided in the LNAPL CSM (EHS Support, 2020).

The extent of LNAPL impacts is currently limited to the interior portions of the Site as shown on **Figure 2-1** and **Figure 2-2** (note that the scale of **Figure 2-1** is almost twice that of **Figure 2-2**)**;** a chronology of LNAPL extent is shown in **Appendix B**. A simple comparison of historical maps for 2006 versus 2019 shows that the inferred LNAPL extent has decreased over time with notable reductions in LNAPL thicknesses in response to both LNAPL recovery activities and natural mass losses.

The geometry of the LNAPL-impacted area does not reflect groundwater gradients at the Site and historical maps show an east-to-west extension of the LNAPL except in the easternmost portion of the Site. As described in **Section 4**, the geology of the Site is complex and large contrasts in hydraulic conductivity are evident. The presence of marl and other low permeability lagoon deposits closer to the turning basin, which exhibit low to no LNAPL permeability, support the observed dissipation of LNAPL in an east-west direction, and prevent migration to the south.

The chronology of the LNAPL extent shows that despite seasonal variability in groundwater elevations the LNAPL extent is stable to declining, and consistent decreasing trends in recovery well LNAPL thickness measurements are observed over time. The major declines in LNAPL thickness over time are evident in the temporal plots of LNAPL thickness which are provided in **Appendix B** and discussed in further detail below.

This assessment is somewhat constrained by the limited LNAPL thickness monitoring data for some of the monitoring wells which have only been recently added to the gauging program. Major declines in LNAPL thickness over time are evident in monitoring wells VW4, VW7, VW19, and VW32, and in the majority of recovery wells (VW5, VW15, VW18, VW23, VW24, VW26, VW28, VW29, VW29, and VW31). The magnitude of these decreases in LNAPL thickness is significant and, in combination with the consistent decreasing trends of LNAPL recovery over time, demonstrate the success of past LNAPL removal actions and the decreasing benefits of ongoing recovery efforts. It should be noted that LNAPL thickness measurements at recovery well VW2 have been relatively stable, which may be related to its proximity to the groundwater depression associated with VW13B and its proximity to the source area on the eastern side of the property.

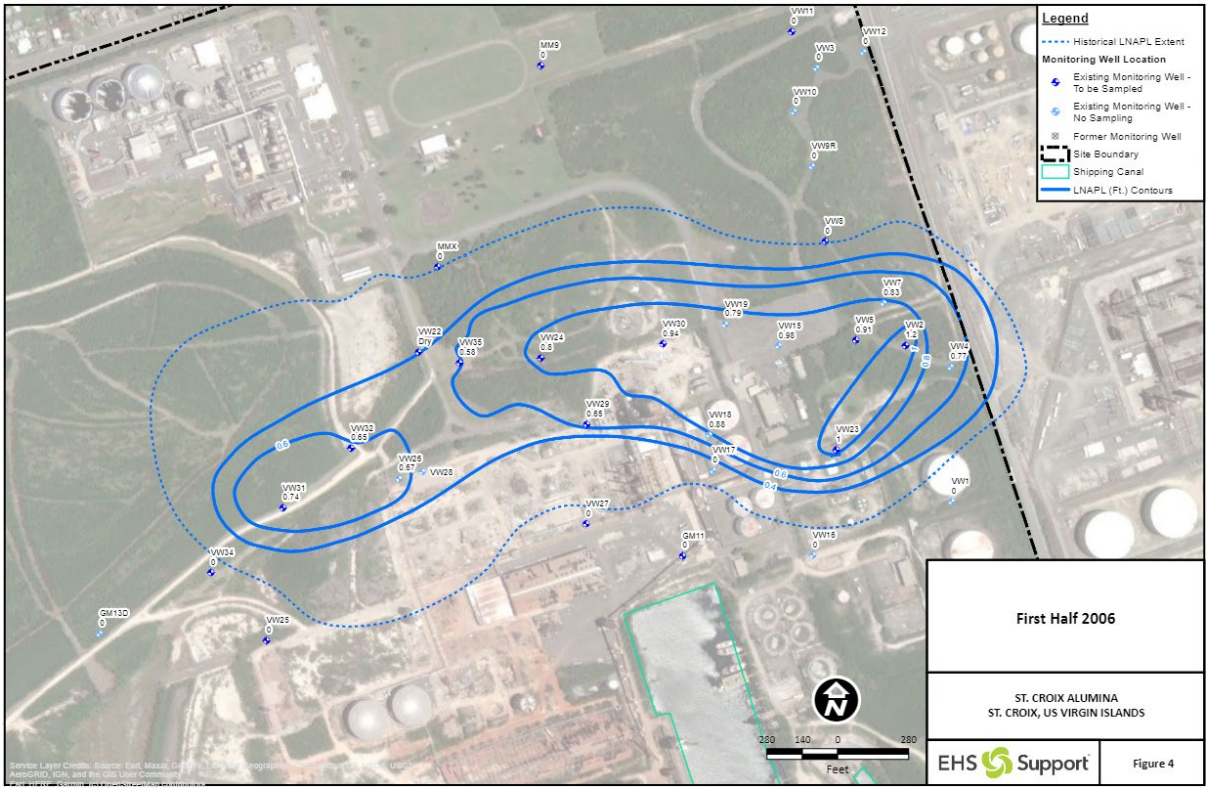


Figure 2-1 LNAPL Extent and Thickness 2006

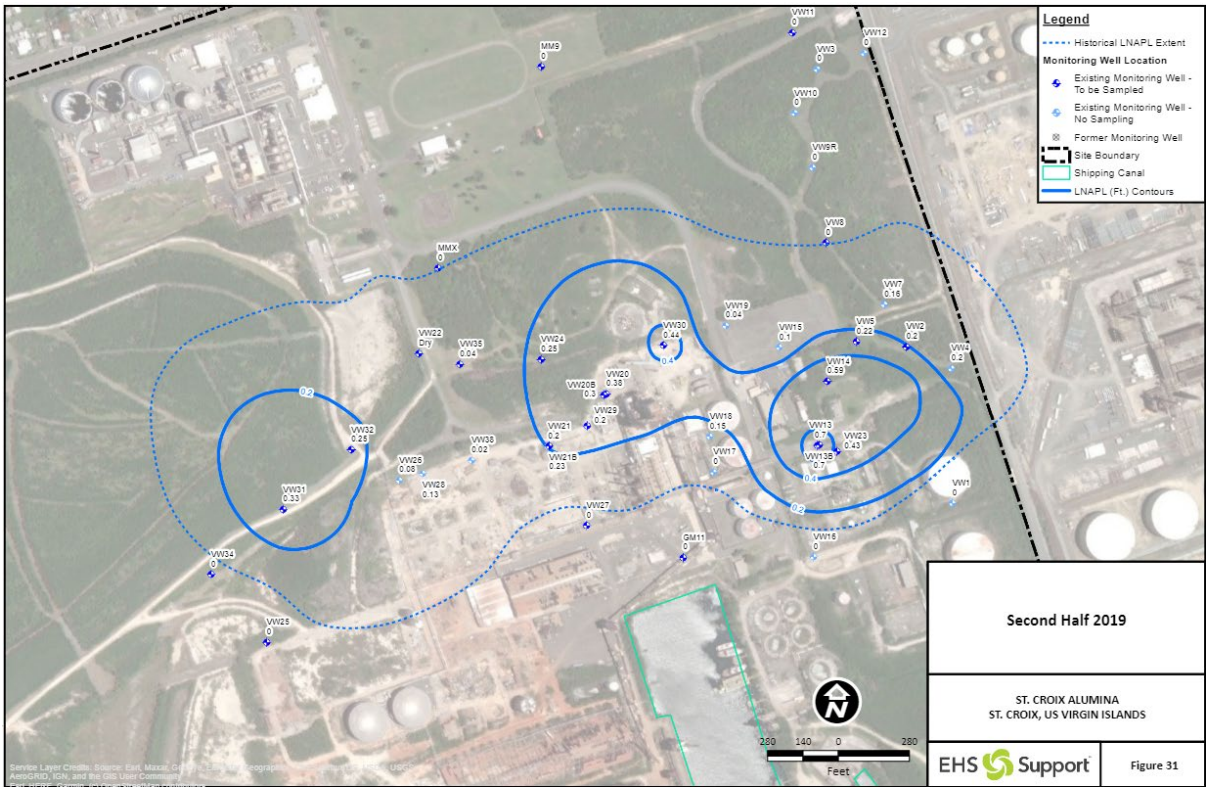


Figure 2-2 LNAPL Extent and Thickness 2019

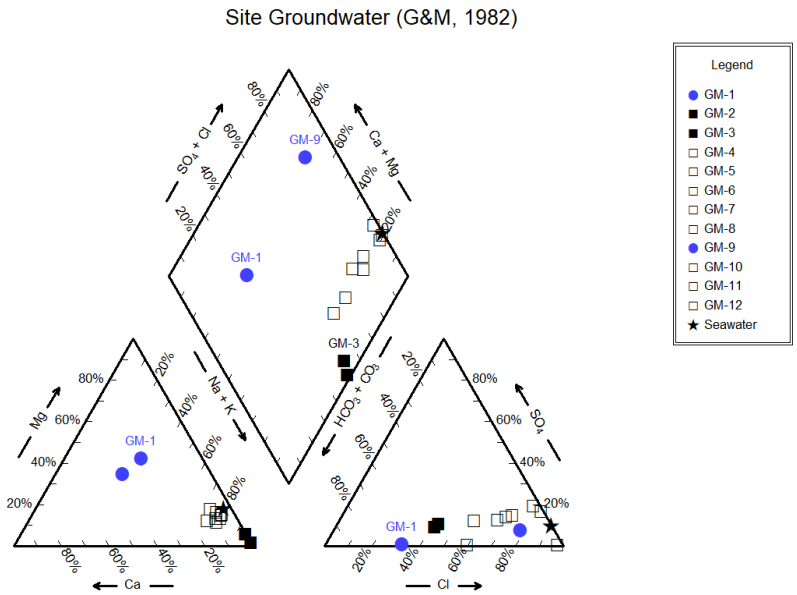
2.3 Geochemistry of Groundwater at the Site

Groundwater inorganic geochemistry data for fingerprinting water types at the Site is limited to the Geraghty and Miller, Inc., (1982) study. Groundwater in Kingshill Limestone is relatively fresh, although salinity increases sharply near the shoreline and in the vicinity of former wells GM-5, GM-6, and GM-10, which have chloride concentrations comparable to seawater.

In more detail, a Piper plot of the 1982 water samples (**Figure 2-3**) shows three main water types:

- Calcium/Magnesium-Bicarbonate (Ca/Mg-HCO_3) and Calcium/Magnesium-Sulfate (Ca/Mg-SO_4) waters with relatively low total dissolved solids (TDS), low Na, and Ca values equal to Mg at GM-1 and GM-9, along the upgradient site boundary. GM-1 has elevated phosphate and GM-9 has elevated nitrate, suggesting these samples were impacted by an off-site source of sewage effluent.
- Sodium-Bicarbonate (Na-HCO_3) water with low Ca and Mg much greater than Ca. This water type is represented by wells GM-2 and GM-3 along the upgradient property boundary. This water type likely reflects regional groundwater sourced from precipitation that has reacted with limestone aquifer rocks.
- Sodium Chloride (NaCl) water compositions fall on a mixing line between the Na-HCO_3 water type and mean seawater. This water type accounts for most groundwater at the Site and reflects the mild groundwater/seawater mixing across the Site that occurs in response to the mild tidal influence.

The historical evidence for seawater sulfate and an upgradient nitrate/phosphate source implies there may have been a supply of nutrients to support NSZD processes at one time. Consequently, NSZD rates based on aqueous geochemical data will potentially need to account for a spatially variable nutrient source. Therefore, additional groundwater geochemical characterization is planned.



Blue dots indicate samples likely influenced by sewage effluent (GM-1 and GM-9). Black squares indicate regional groundwater (GM-2 and GM-3). Open squares reflect mixing between groundwater and mean seawater.

Figure 2-3 Piper Plot of Groundwater Samples. Data from Geraghty and Miller (1982)

3 Objectives and Scope of Work

3.1 Objectives

The objective of the proposed work is to identify the presence and magnitude of LNAPL mass loss to NSZD processes. NSZD is a combination of naturally occurring processes that solubilize and volatilize LNAPL components accompanied with microbial degradation of the products over time (IRTC, 2009 and 2018). NSZD is recognized as a remediation pathway where microbial processes convert LNAPL into innocuous aqueous and gaseous by-products (ITRC, 2009). Peer-reviewed research confirms that NSZD processes are nearly always present and that they typically result in significant LNAPL mass destruction (Lundegard and Johnson, 2006: Sihota et al., 2012; McCoy et al., 2015; Boyd et al., 2016).

3.2 Scope of Work

Based on recovery data that indicate the majority of LNAPL recovery wells have reached or are approaching a practicality endpoint, the LNAPL CSM and Remedial Action Work Plan (EHS Support, 2020) provided shutdown criteria for active recovery wells that were developed based on a robust assessment of Site-specific conditions. However, due to uncertainties and data gaps, recovery operations are planned to continue through June 2021 (excluding well maintenance and semi-annual groundwater monitoring).

As a supplement to continued routine groundwater sampling activities, it is proposed that additional analysis be conducted to support the assessment of NSZD processes in the aquifer. Based on the Site geohydrology and limited geochemical data, a combination of sulfate reduction and methanogenesis processes appear to be active but require confirmation. The standard operating procedures for the fieldwork are provided in **Appendix C**

As presented in the LNAPL CSM and Remedial Action Work Plan submitted to the USEPA on July 8, 2020 (EHS Support, 2020), two phases of NSZD assessment will be conducted to identify and define uncertainties and data gaps in the current understanding of the geohydrology and chemical processes in the subsurface at the Site.

As outlined in detail in **Section 4**, the key components of the program will consist of the items listed in **Sections 3.2.1** through **3.2.3**.

3.2.1 Phase 1 Program of Works

For the Phase-1 program of works, source area wells were selected as those that most recently had LNAPL present (last quarter of 2019). Upgradient and downgradient wells were selected to be representative geology/hydrogeology variations across well screen intervals, historical chemistry data, and provide geographical coverage. More detailed description of well selections is provided on Table 3 and communicated visually in Figure 5.

The Phase 1 work consists of the following:

- **Groundwater Geochemistry** – Sampling and analysis of groundwater for petroleum hydrocarbon and MNA parameters in 17 wells located beneath the LNAPL-impacted area (VW2,

VW5, VW6, VW13, VW13B, VW14, VW20, VW20B, VW21B, VW22, VW23, VW24, VW29, VW30, VW31, VW32 and VW35), 4 upgradient wells (MMX, VW8, MM9 and VW11), and 7 downgradient wells (VW25, VW27, VW34, VW37, GM11, GM14 and GM-22) (refer to **Figure 6** and **Table 3**). This sampling will be conducted in conjunction with the next semi-annual groundwater sampling event (wells VW25, VW27, VW34, VW37, GM11, GM14, and MMX are already part of groundwater sampling). Note: VW22 has been dry for several sampling events but will be checked and sampled if possible.

- **Temperature Profiling for NSZD** – Completion of a downhole temperature profiling assessment in the unsaturated and saturated zones to determine ΔT (temperature gradient for each well). This will comprise a minimum of five unsaturated zone temperature readings (2 feet from ground surface, 1 foot above groundwater, and three intervals equally spaced in between) and a minimum of three saturated zone temperature readings (1 foot below the groundwater interface, 5 feet below the groundwater surface, and 10 feet bgs; where wells are deeper additional temperature readings will be collected). In addition to the wells in which groundwater sampling is being conducted, temperature profiles will also be obtained from wells VW3, VW9R, VW10, and GM22 to aid with defining background conditions and wells VW4, VW7, VW15, and VW18 to capture spatial variability in and around the source area.
- **Well Head Space Soil Gas** – Measurement of deep vadose methane (CH_4), carbon dioxide (CO_2), and hydrogen sulfide (H_2S) gas concentrations will be completed in all wells where temperature profiles are to be measured. This will consist of covering the well annulus and measuring the headspace gas concentration 1 foot above the water level in the well casing following the technique of Sweeney et al. (2017).

We anticipate completing a report within 90 days of completion of the Phase 1 field work.

3.2.2 Phase 2 Program of Works

The Phase 2 work involves the use of advanced methods to quantify mass depletion rates. The Phase 1 work (as described above) is designed to inform the study design for Phase 2 with a specific focus on the following:

1. Assess the gas composition in the subsurface and determine if methane is degraded to carbon dioxide prior to release to the atmosphere and if the Licor (which can measure methane and carbon dioxide) or passive E-Flux system (carbon dioxide only) is the most appropriate methodology.
2. Identify natural sources of carbon dioxide (sourced from limestone) and justify methods of correction to eliminate high bias.
3. Make modifications to optimize the grid layout and spacing based on the heterogeneity and variability observed in the Phase 1 scope of work.
4. Provide supporting data to provide multiple lines of evidence and sensitivity analysis for calculations of natural mass losses which ultimately will be compared to engineered, i.e., active recovery, mass losses.
5. Provide support for an approach that utilizes groundwater temperature and head space soil gas measurements as a means to demonstrate the long-term success and persistence of NSZD processes.

At this time, the preliminary scope of the Phase 2 Comprehensive Grid Soil Sampling Assessment will include the following:

- Advance up to 25 grid soil gas sampling locations and collect associated monitoring wellhead space readings immediately above the water table (**Figure 7**)
- LI-COR 7810, E-Flux, CO-2 (or other equivalent) field instrument/collection
- Carbon-13 (^{13}C) and carbon-14 (^{14}C) laboratory analysis, as required

3.2.3 Reporting

It is proposed after completion of both the Phase 1 and Phase 2 scopes of work that an NSZD evaluation report will be submitted to USEPA. The reporting of results in a Phase 1 Assessment submittal will include recommendations for necessary location and analytical adjustments for Phase 2 assessment activities. This will include the following:

- Map the distribution of soil gases based on wellhead measurements.
- Map the distribution of electron acceptor and geochemical parameters.
- Calculate assimilative capacity and assimilation rates in groundwater based on changes in electron acceptor and CH_4 concentrations (upgradient to under plume).
- Calculate mass loss using the thermal differences and enthalpy of reactions.
- Characterize the differences in estimated mass losses or byproduct concentrations based on geology and hydrogeology.
- Evaluate general groundwater chemistry across the Site as a means to validate geologic/hydrogeologic conceptualization and address artifact at GM22.

The Phase 2 NSZD report will integrate the findings from the Phase 1 report and provide a complete weight of evidence assessment (leveraging the Phase 2 testing results) of NSZD processes including quantification of mass losses across the Site (and potentially subareas of the Site).

3.3 Key Study Questions

EPA's 7-step data quality objectives (DQOs) process was used to identify decisions that will be made and the required level of data quality with corresponding acceptance criteria (**Table 1**).

Key study questions were developed to guide assessment activities and to aid in developing DQOs provided in **Table 1**. DQOs are also presented in the draft Quality Assurance Project Plan (QAPP) (**Appendix D**). The draft QAPP is a revised document intended to capture routine monitoring tasks and the work proposed herein, following the Uniform Federal Policy for Quality Assurance Project Plans (UFP-QAPP) format

Project objectives and key data gaps are discussed in **Sections 3.1** and **3.2** of this work plan, respectively. The work tasks and assessment program were developed to address the key questions listed in **Table 3-1**. This Site assessment is intended to be an iterative process, with subsequent data needs identified based on results and observations from the previous phase of work (e.g., Phase 1). The results of the activities described in this Work Plan will be used to guide additional scopes of work and, ultimately, to prepare the final LNAPL CSM and Management Plan.

Table 3-1 Key Investigation Questions

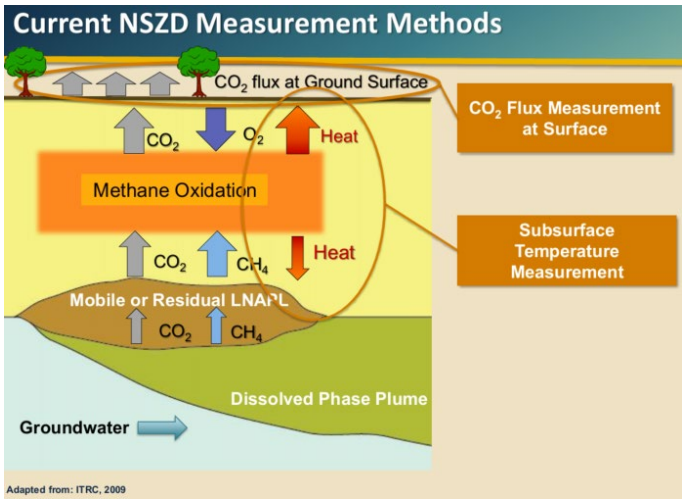
Topic	Key Investigation Questions to Answer as Part of NSZD/MNA Assessment Activities
Soil Gas Flux Assessment	Are soil gas locations representative of the geological and hydrological Site conditions? If not, is further assessment and evaluation warranted? If statistically significant differences in gas concentrations at multiple adjacent wells are identified, additional soil gas monitoring points between monitoring wells may be necessary. Statistically indistinguishable soil gas concentrations between sampling points will provide confidence that geological variations have little effect on soil gas measurements.
	Do groundwater MNA data results indicate that methane sampling is required during subsequent phases? If so, what instrumentation and methods will be used to collect methane (e.g., LI-COR 7810 meter)? If methane is detected above the method detection limit in groundwater samples, then use of a LI-COR meter or installation of soil gas probes will be recommended.
	Have Site conditions at sample locations (e.g., gravel, concrete) affected the gas readings (CO_2, etc.), requiring additional evaluation (e.g., probe sampling)? If there is a correlation between well headspace gas concentrations and cemented areas, then installation of soil gas probes may be recommended in cemented areas as they will be inaccessible to DCC or passive trap methods.
	Have Site hydrogeologic conditions (e.g., limestone, perched groundwater) affected soil gas flux results and if so, to what extent? What supplementary methods have been applied to existing data results and is further assessment required? If cation/anion fingerprinting results from GM-22 and Site wells indicate variable groundwater conditions at the site, then soil gas flux spatial variability will be assessed.
Groundwater MNA Assessment	Have the monitoring wells selected for MNA analyses adequately met DQOs, and are MNA analyses representative of the potential range of NSZD rates at the Site? If DQO's are not met, then an additional round of sampling or additional lines of evidence for NSZD may be proposed.
	Do monitoring well locations include a minimum of one well in upgradient (background, clean) source and dissolved-phase impacted downgradient areas? If data indicate the background well(s) do not adequately reflect upgradient groundwater conditions, then an aqueous NSZD rate calculation may not be possible.

Topic	Key Investigation Questions to Answer as Part of NSZD/MNA Assessment Activities
	Have standard and appropriate practices been followed for groundwater sampling? If groundwater data fail QA/QC criteria contained within a revised QAPP, then the data will not be used to calculate an aqueous NSZD rate.
	Have monitoring wells screened solely across the stratigraphy where the NAPL smear zone exists, and wells demonstrated to provide representative water quality, been used to avoid bias in the analysis? If representative data for calculating NSZD rates is not available, then results for NSZD rate(s) will be flagged as having a high/low bias.
	Have seasonal changes in the groundwater table and quality been assessed to determine if multiple rounds of data collection are necessary? If data indicate substantial seasonal variability in the water table elevation, then an additional round of data collection may be proposed.
Overall NSZD Evaluation (Geochemistry and Stoichiometry)	Has the hydrogeochemistry been assessed and the primary mass transfer processes been determined? Have sufficient measures been performed to estimate the phase transfers (i.e., non-advection contributions)? If study results are inconsistent with the site CSM, an update to the CSM will be proposed.
	Are the magnitude of the results intuitive and consistent with expectations, published literature, and/or known Site conditions? If results for calculated NSZD rates are inconsistent with literature values, then underlying assumptions about key parameters and hydrogeologic conceptualizations will be revised.
	Has spatial variability been adequately explained? If the cause of spatial variability is inconclusive, additional data collection may be proposed.

CO2 = carbon dioxide
COCs = chemicals of concern
DQO = data quality objective
MNA = monitored natural attenuation
NAPL = non-aqueous phase liquid
NSZD = natural source zone depletion

4 Natural Source Zone Depletion Testing Program Rationale

NSZD may occur through LNAPL dissolution in groundwater and biodegradation in the saturated zone, and LNAPL volatilization and biodegradation within the vadose zone (IRTC, 2009 and 2018). Source zones below the water table dissolve (according to various LNAPL constituent aqueous solubilities) and exit the source zone via groundwater advection. In the saturated zone, NSZD by microbial metabolism is controlled mainly by constituent solubility, availability of electron acceptors, and groundwater flow dynamics (IRTC, 2009 and 2018). LNAPL sources within the vadose zone volatilize and migrate by diffusion and advection from loci of a higher concentration to a lower concentration (IRTC, 2009 and 2018). Reduced gases produced by LNAPL volatilization mix with downward percolating atmospheric oxygen which produces a redox disequilibrium environment that is favorable for aerobic biologically mediated and exothermic oxidation reactions. Manifestations of the various NSZD processes are summarized in **Figure 4-1**.



Source: Newell, et al. (2016)

Figure 4-1 NSZD Measurement Methods

Technical procedures for evaluating NSZD at LNAPL sites are summarized in ITRC documents (ITRC, 2009 and 2018). The ITRC documents were developed to provide a consistent approach to qualitative and quantitative evaluation of NSZD at LNAPL sites. The ITRC documents are intended to distill information on NSZD evaluation procedures from several published peer-reviewed research items; several of these key primary references are summarized in **Table 2** (attached).

A limitation of the ITRC documents is that primary research is not always developed in an accessible manner for the end user to adapt to specific site contaminants or conditions. Other international organizations, such as the Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE), have utilized the same body of primary research literature to develop LNAPL NSZD approaches that are adaptable to the nuances of different site conceptual models (CRC CARE, 2018). Therefore, this work plan leverages ITRC, CRC CARE, and primary literature documents based on the information source that are most applicable to an applied approach for work implementation.

The proposed work leverages several techniques to integrate multiple lines of evidence in assessing LNAPL NSZD mass loss in both the saturated and vadose zone. There are several regulatory methods for quantifying NSZD, including passive gas CO_2 flux, soil gas gradient assessment, temperature profiling, or dynamic closed chamber (DCC) gas measurements (ITRC, 2018). Each approach has inherent weaknesses potentially in response to the variable site hydrogeological and groundwater geochemical conditions. Therefore, we are proposing to utilize the broadly accepted practice of implementing a phased approach and leveraging multiple lines of evidence to both qualitatively and quantitatively quantify NSZD processes at the Site.

The need for multiple approaches stems from the inherent limitations in each of the proposed techniques. Rationale for each proposed technique, and the inherent limitations and justification for pursuing multiple lines of evidence, are outlined in **Table 1**, attached. The work is planned in two phases to utilize data collected from Phase 1 to further define the scope for Phase 2. A summary of the two work phases is provided in the following sections.

4.1 Phase 1 – NSZD Processes and Spatial Variability

The goals of Phase 1 are designed to better constrain Site hydrological complexity by assessing variations in groundwater geochemistry and qualitatively confirm the degree to which NSZD depletion is active at the site. Given the geologic heterogeneity and variability of historic groundwater geochemistry, the following multiple lines of evidence will be evaluated to establish evidence for active NSZD:

1. Depletion of terminal electron acceptors (TEAs) relative to background (upgradient) groundwater.
2. Groundwater quality parameter assessment to identify the presence of redox conditions favorable for and indicative of NSZD.
3. Identification of biogenic gases in source area wells (elevated CO_2, CH_4, and/or H_2S; depleted oxygen [O_2]).
4. Elevated temperature at and below the water table as an indicator of aqueous and volatile phase exothermic NSZD reactions.

A consequence of the described qualitative approach is that sufficient geochemistry data will be available to calculate aqueous NSZD mass depletion rates, and sufficient temperature data will be available to calculate aqueous and vapor-phase NSZD rates.

A decision flow chart for how data collected during Phase 1 will be interpreted is provided in **Figure 4-2**.

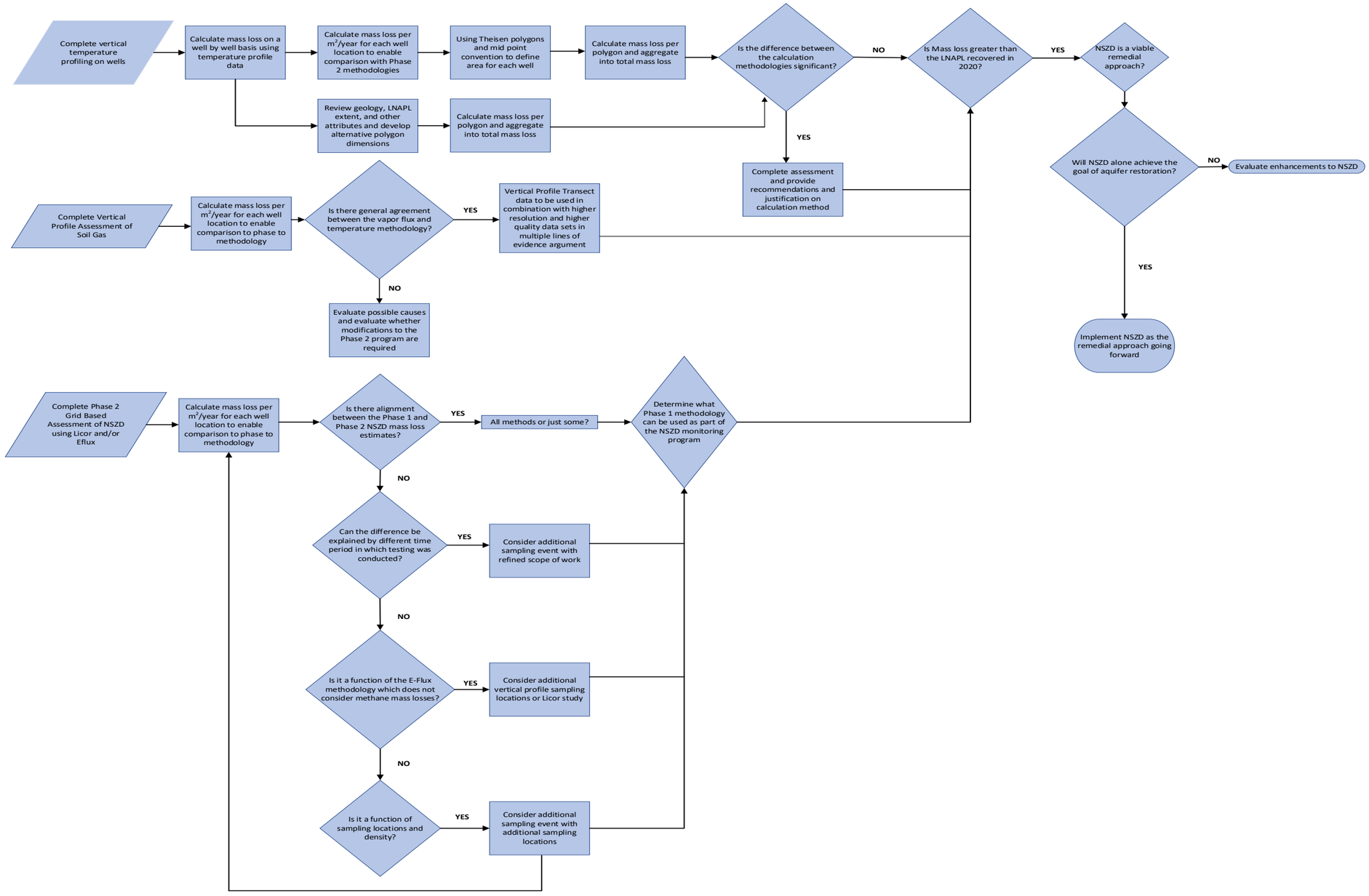


Figure 4-2 Decision flow chart for interpreting Phase 1 Results

4.1.1 Groundwater Geochemistry – Saturated Zone LNAPL Mass Loss

Microbial transformation of LNAPL (biodegradation) in the saturated zone utilizes and depletes TEAs, which are redox sensitive compounds (including O_2, nitrate $[NO_3]^-$, SO_4^{2-}, iron $[Fe]^{3+}$, and manganese $[Mn]^{4+}$) that are consumed as they are reductively transformed to a lower oxidation state (CRC CARE, 2015). O_2 tends to be consumed first, resulting in anoxic conditions. Following O_2 depletion, the next most energetically favorable naturally available electron acceptor is NO_3^-, followed by Mn^{4+}, Fe^{3+}, SO_4^{2-}, and finally CO_2. This order of preferential electron acceptor utilization — $O_2 > NO_3^- >$ Mn(IV) >Fe(III) > $SO_4^{2-} > CO_2$ — is referred to as the ecological succession of TEA processes (McMahon and Chapelle, 2008). Given the sequential nature of TEA utilization, identification of the end products of redox processes (dinitrogen gas $[N_2]$, ammonium $[NH_4^+]$, ferrous iron [Fe(II)], H_2S, and CH_4) through water quality sampling can be used to assess ambient redox processes that are occurring (e.g., Jurgens et al., 2009). Additionally, reductive transformation of TEAs can be identified using field parameter measurements, as the sequential redox reactions lower dissolved oxygen (DO) and lower the oxidation-reduction potential (ORP).

Phase 1 of the testing program is designed to further define the general Site geochemistry and identify if conditions that reflect NSZD are present at the Site. Additionally, the processes which are contributing to the natural degradation of petroleum hydrocarbons, and the locations where this is occurring, will be identified. The program of work is planned to be conducted concurrently with routine groundwater sampling to streamline field work efforts. The objectives of this phase of work are as follows:

1. Characterize site groundwater geochemistry using concentration plots and Piper diagrams, to:
    a. Verify the hydrogeological CSM by identifying complexities in groundwater flow pathways.
    b. Assess the presence of different background groundwater chemistries that should be accounted for in the assessment of aqueous phase LNAPL mass depletion rates.
    c. Identify locations of groundwater recharge or seawater from tidal flux that may indicate zones of high permeability or recharge water with a different composition. The results will have implications for interpreting the effectiveness of subsequent NZSD indicators and mass depletion rates.
2. Qualitatively identify locations with favorable redox conditions for NSZD using field parameter measurements, specifically:
    a. Locations where DO is depleted in the source area relative to background groundwater.
    b. Locations where ORP is lower than background groundwater.
3. Confirm active NSZD of LNAPL and calculate aqueous mass removal rates using measurements of TEAs and their byproducts.
    a. Confirm active NSZD by assessing spatial variations in TEA concentrations (e.g., O_2, NO_3^-, SO_4^{2-}), byproducts of TEA depletion reactions (e.g., nitrite, N2, NH4+, Fe(II), Mn(II), H2S, CH4), and alkalinity.
    b. Identify preferred aqueous biodegradation reactions.
    c. Calculate aqueous NSZD rates.

Groundwater sampling will be conducted by low-flow purging and sampling procedures to comply with the guidelines provided by Puls and Barcelona (USEPA Low-Flow [Minimal Drawdown] Groundwater Sampling Procedures, 1996) as summarized in standard operating procedures (SOPs) included as

Appendix C. Groundwater samples will be analyzed for the following (**note:** some parameters are included under multiple headings; however, only a single measurement of each parameter will be made):

- Field parameters for qualitative assessment of NSZD:
  - Temperature
  - pH
  - Conductivity
  - DO
  - ORP
  - Turbidity
- Geochemical fingerprinting parameters:
  - Alkalinity by EPA Method SM2320B
  - Cations (sodium, potassium, calcium, magnesium) by EPA Method SW-846 6020A
  - Anions (chloride, sulfate, nitrate, nitrite) by EPA Method 300.0 (note; separate sample containers are to be used chloride + sulfate (unpreserved) and nitrate + nitrite (preserved with sulfuric acid)
- Parameters for aqueous mass depletion rate calculations (TEAs and byproducts):
  - DO (field)
  - Dissolved organic carbon (DOC) by EPA Method SW-846 9060A
  - Nitrate-N, nitrite-N, and sulfate (by EPA Method 300.0)
  - Total and dissolved iron and manganese by EPA Method SW-846 6020A
  - Sulfide by EPA Method SM4500 S2-D
  - Ammonia (as N) and Total Kjeldahl Nitrogen (TKN) by EPA MethodsSM4500 NH3 B-F and SM4500 NH3-D
  - Dissolved gases (methane and carbon dioxide) by RSK-175
  - Alkalinity by EPA Method SM2320B

A detailed description of sample locations, bottle ware, and laboratory hold times is provided on Table 3. Data will be assessed as described in **Section 4.3.1**.

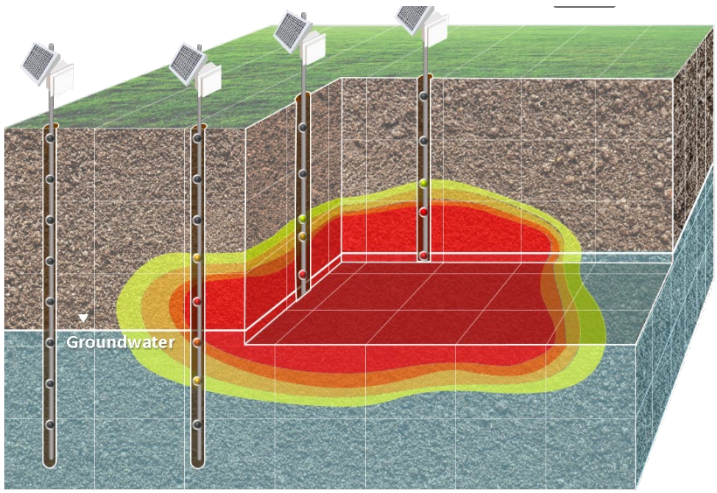
4.1.2 Monitoring Wellhead Space Readings

In addition to the aqueous-phase LNAPL degradation effects discussed above, NSZD is also manifested in vadose gases. CH_4, CO_2, and H_2S may be produced by aqueous phase methanogenesis and microbial TEA utilization reactions in the LNAPL smear zone, whereas O_2 is consumed (CRC CARE, 2015). In overlying aerobic soil zones, CH_4 may also be oxidized to CO_2. The identification of these gases provides a qualitative line of evidence for active NSZD.

To confirm active NSZD at the Site, head space readings in monitoring wells situated within the LNAPL footprint will be compared to measurements in wells outside of and upgradient of the LNAPL footprint. Upon removing caps on monitoring wells, a calibrated hand-held multi-gas meter capable of measuring H_2S, CO_2, and CH_4 will be inserted in each well. The maximum concentration in each well will be recorded in a field notebook.

4.1.3 Temperature Profiles – Vadose Zone LNAPL Mass Loss

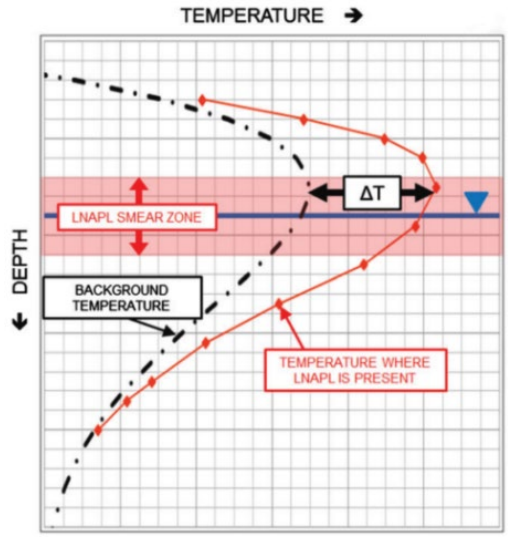
Biologic oxidation reactions from upward percolating LNAPL volatilization reactions and downward percolating atmospheric gases are exothermic in nature (CRC CARE, 2015). Temperature measurements may be used to identify elevated temperatures near source zones relative to background locations as evidence for NSZD attributable to biogenic (metabolic) heat resulting from biodegradation. The concept is illustrated in **Figure 4-3**.



Source: https://www.thermalnszd.com

Figure 4-3 NSZD Temperature Measurements in Monitoring Wells

The utility of using thermal gradient (temperature) measurements to assess LNAPL depletion accurately and inexpensively is gaining traction, as evidenced by recent abundant technical publications on the subject (e.g., Garg et al., 2017; Newell et al, 2016; Suthersan, 2015; Warren and Bekins, 2015; Sweeney and Ririe, 2014). The concept behind using thermal gradients is illustrated in **Figure 4-4**.



Source: Suthersan et al. 2015

Figure 4-4 Thermal Gradient Conceptualization

Temperatures in background, LNAPL source area, and downgradient locations at the Site will be measured using a thermocouple lowered down the well. A minimum of three unsaturated zone temperature readings (2 feet from ground surface, 1 foot above groundwater, and three intervals equally spaced in-between) and a minimum of three saturated zone temperature readings (1 foot below the groundwater interface, 5 feet below the groundwater surface, and 10 feet below the groundwater surface; where wells are deeper additional temperature readings will be collected). Thermocouples will be lowered to the specified monitoring depths within the vadose zone for a minimum of 3 minutes and groundwater for a minimum of 1 minute before lowering to the subsequent monitoring depth, following the procedure of Sweeney et al. (2014). Data assessment methods are outlined in **Section 4.3**.

4.2 Phase 2 – Assessment and Quantification of In-situ Biodegradation Rates

The Phase 2 assessment will focus on CO_2 flux measurements at the ground surface in the source area and background locations to calculate NSZD rates. The specifics of the Phase 2 implementation will be based on the findings of the Phase 1 assessment (confirmation of active NSZD). The density of flux measurement locations and background areas will be determined based on the outcome of Phase 1 results, specifically the identification of NSZD loci and hydrological complexities. The method employed to measure vadose gas flux will be based on the outcome of Phase 1 results and may include a passive trap method or a DCC method. A key determinant will be the necessary grid spacing of the CO_2 monitoring network to capture representative hydrogeochemical variability in background and source area locations. Given the expense of deploying passive traps, a highly variable site hydrogeochemical framework may support use of the portable DCC method. A fixed number of background passive gas trap locations may be utilized if the DCC method is selected, in order to calculate background CO_2 contributions using the ^{14}C correction method, as recommended in CRC CARE (2018).

Additionally, wind speed and duration downloaded from the National Oceanic and Atmospheric Administration (NOAA) data base for the site area will be assessed to determine if engineering controls are warranted to minimize the effect on results on the passive trap method, or if typical winds exceed

the threshold that would trigger use of the DCC method. Note that a NOAA weather station (LTBV3 - 9751401 - Lime Tree Bay, St. Croix, VI) is located less than 1.5 miles southeast of the site.

Should the monitoring wellhead space readings conducted during Phase 1 prove indicative of NSZD, a multiple lines of evidence approach will be used to confirm the soil gas CO_2 efflux NSZD rate calculations by using a soil gas gradient flux calculation approach based on Fick's first law of diffusion.

Preliminary E-Flux sampling locations are provided on **Figure 7**. Background location ESG-1 though ESG-3 were selected to provide spatial coverage of the area upgradient of the source zone and to encompass a broad range of vegetation cover types (Forest at ESG-1, unvegetated developed land at ESG-2, and manicured surface vegetation at ESG-3. Source area locations (ESG-4 through ESG-25) were selected to maximize coverage of different lithology types present at the well screen (as depicted on **Figure 5**), and to provide spatial coverage in the three main LNAPL lobes.

A decision flow chart for how data collected during Phase 2 will be interpreted is provided in **Figure 4-5.**

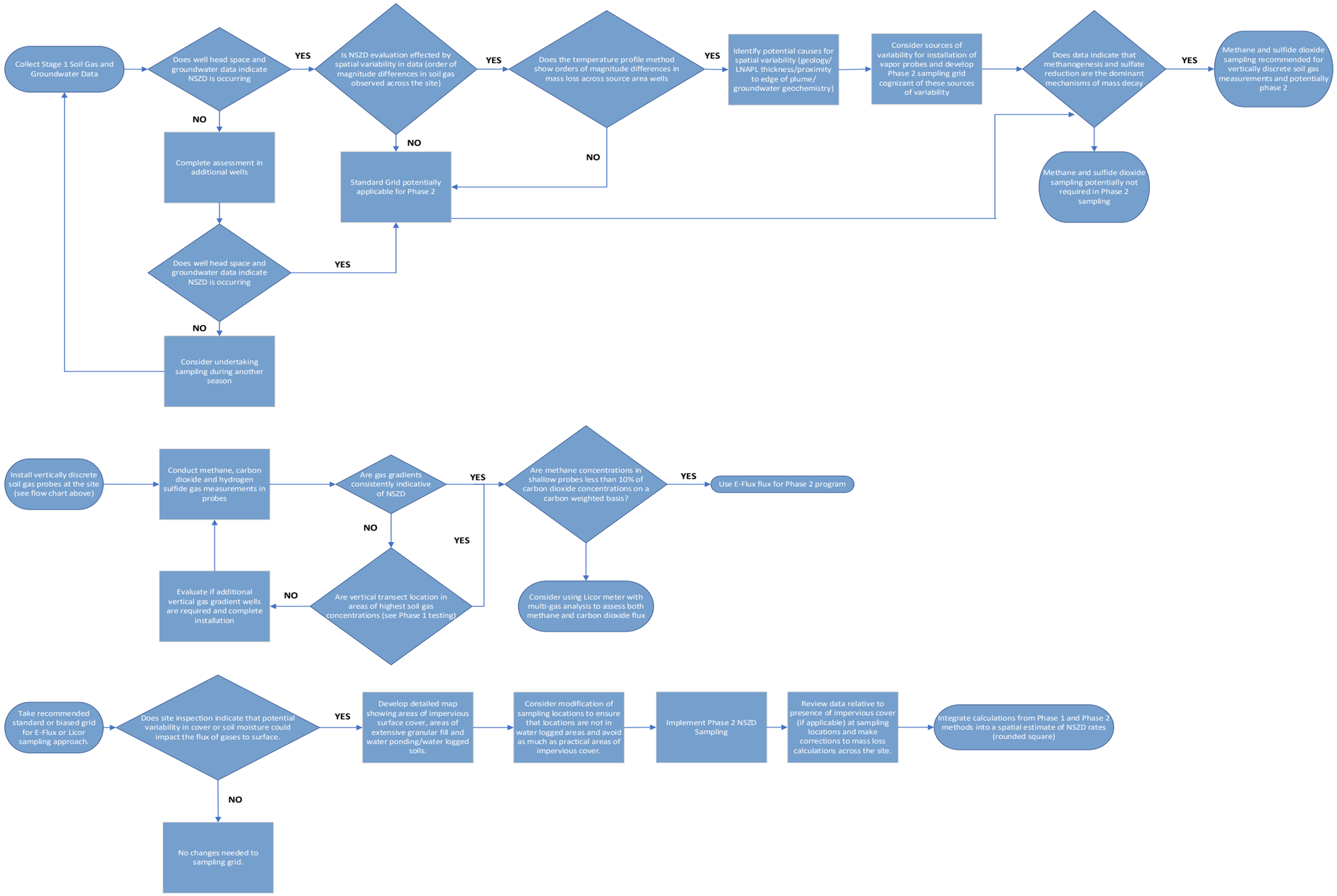


Figure 4-5 Decision flow chart for interpreting Phase 2 Results

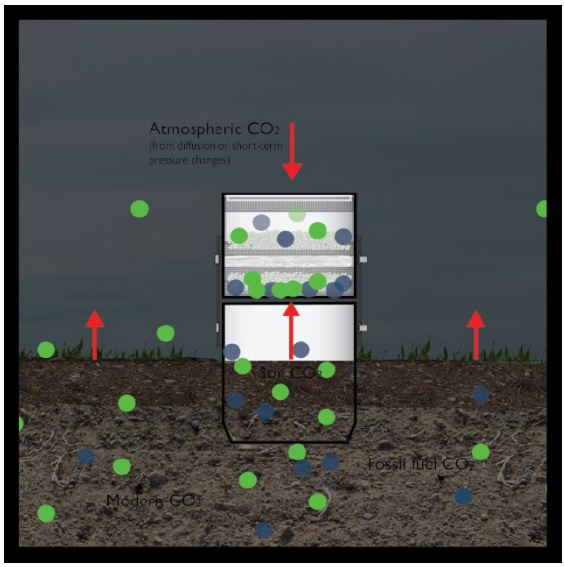
4.2.1 Soil Gas Efflux Measurement

As described in **Section 4.1**, LNAPL constituents are subject to volatilization into the vadose zone where the vapor-phase hydrocarbons may biodegrade. As the biodegradation of hydrocarbons proceeds, methane (via methanogenesis) and carbon dioxide (via aerobic respiration, nitrate/ferric iron/sulfate/manganese reduction and methanogenesis) are produced (ITRC, 2009;2018). In addition, methane and carbon dioxide are also produced via LNAPL and dissolved-phase degradation within the saturated zone. The produced methane and carbon dioxide partition from groundwater into the vadose zone. Therefore, the presence of methane and carbon dioxide above baseline concentrations within the vadose zone provide a strong line of evidence that hydrocarbon degradation and mass loss are occurring. The mixture of gaseous undegraded hydrocarbons (e.g., volatile organic compounds [VOCs] or volatile petroleum hydrocarbons [VPHs] and excluding methane), biogenic methane, and biogenic carbon dioxide tend to migrate towards land surface by concentration gradient-driven diffusion and barometric pumping. Time-integrated measurement of CO_2 flux (and potentially methane also if the DCC system is also utilized) provides a means to estimate vapor-phase NSZD rates.

One of the two methods outlined below (passive flux trap or DCC) will be employed to estimate volatile phase NSZD rates.

4.2.1.1 Passive flux trap method

The passive flux method is the preferred approach as it provides time-integrated flux estimate, whereas other NSZD rate estimates are snapshots in time that may not capture effects from combined external variables such as diurnal weather variations. The passive flux method is described in detail by McCoy et al. (2014). The passive flux method involves installation of a grid of CO_2 traps in background and source area locations. The traps are commercially available from E-Flux, LLC in Fort Collins, Colorado. The passive traps collect CO_2 moving from the subsurface to the atmosphere over a multi-day time period, determined based on results of CO_2 screening during Phase 1 (i.e., sufficient duration to exceed the CO_2 detection limit but not exceed saturation of the trap with gas). Trap installation involves installing a pipe into the ground as a housing for the main trap body. The trap body is sealed into the pipe housing with a rubber sleeve and protected with a rain cover. The trap body consists of an upper and lower layer of the caustic sorbent that traps CO_2. The upper layer of sorbent is open to the atmosphere as a measure to prevent atmospheric CO_2 from entering the lower trap from CO_2 flux reversals due to changes in barometric pressure. A schematic of the passive trap assembly is shown in **Figure 4-6**.



Source: www.soilgasflux.com

Figure 4-6 Passive CO_2 trap schematic

Traps are deployed in locations cleared of vegetation/organic debris and large pieces of gravel or cobbles. The housing pipe is installed approximately 1 to 3 inches bgs, with sufficient depth to provide a good seal and prevent short-circuiting of atmospheric gases. The pipe may be pushed or installed with a rubber mallet, ensuring minimal disturbance to the ground to minimize disturbance to efflux conditions. The pipe is installed as close to vertical as possible to minimize variations in the cross-sectional area of sorbent material exposed to CO_2 flux. Stabilizers may be used as needed to secure the pipe. The main body of the CO_2 trap is then attached to the pipe and sealed with a rubber sleeve and hose clamp.

Following the deployment period, passive flux traps are removed and shipped to the manufacturer-recommended specialty laboratory for CO_2 quantification and carbon isotope measurements. The procedures for performing background corrections and quantifying CO_2 flux are provided in **Section 4.3**.

4.2.1.2 Passive flux Carbon Isotope Background CO_2 Correction

By combining stable carbon isotope ($\delta^{13}C$) and radiogenic carbon isotope (^{14}C) measurements, multiple biotic (i.e., microbial transformation of modern natural organic matter [NOM] and LNAPL) and abiotic (i.e., carbonate equilibria in limestone aquifers) CO_2 sources may be identified (Coffin et al., 2008; Nowak et al., 2016). This type of model may be used to assess if the magnitude and variability of background inorganic CO_2 precludes accurate use of the ^{14}C correction method and a simpler means of correction is warranted. A major constraint on this method will be the variability of pH in groundwater across the site; substantially different background and source area pH values may lead to variable background CO_2 contributions, and the magnitude of these effects on background CO_2 generation from limestone may require assessment using geochemical modeling techniques. Complications from the predominantly limestone lithology may ultimately preclude the use of this method and this approach, and the applicability of the method will be evaluated following the results of the Phase 1 wellhead gas measurements.

When using passive CO_2 traps to estimate gas flux, background is corrected for using measurements of the radiogenic carbon-14 isotope (^{14}C) (McCoy et al., 2014; Boyd et al., 2016). The method relies on radiogenic decay of ^{14}C, which has a half-life of approximately 5,600 years and is detectable in less than 30,000-year-old modern NOM and CO_2 produced from its oxidation. In contrast, ^{14}C is depleted in fossil-sourced hydrocarbons and CO_2 derived from hydrocarbon NSZD processes. By determining the ^{14}C content in a background location, a binary mixing model can be used to determine the CO_2 contribution from NSZD depletion of a fossil hydrocarbon.

The ^{14}C background correction method is complicated in limestone and dolostone aquifers, where ^{14}C is also depleted in dissolved inorganic carbon (DIC) (and equilibrium gas-phase CO_2) produced from dissolution of ancient carbonate (Landmeyer and Stone, 1995). This may be overcome using stable isotope carbon isotope ratio ($\delta^{13}C$) measurements to distinguish the relative contributions from limestone and NOM in the background locations with a binary isotope mixing model (e.g., Schindlbacher et al., 2015).

4.2.1.3 Dynamic closed chamber method

The DCC method is described in detail by Shiota et al. (2011). This is an active method that uses real-time CO_2 flux measurements with a portable field gas analyzer, typically the LI-8100A (Li-COR Biosciences, Inc., Lincoln, Nebraska). The analyzer measures the change in CO_2 concentration over a fixed period (usually 90 seconds) to calculate the soil gas efflux. Typically, three or more measurements are performed at each location. An added benefit of the DCC method is that instruments are typically equipped with methane sensors also, which allow assessment of the completeness of microbial conversion of CH_4 to CO_2. In situations where CH_4 is not fully converted to CO_2, NSZD may be underestimated by assessing CO_2 concentrations alone.

The DCC method utilizes a collar installed approximately 1 to 3 inches below the ground surface, with sufficient depth to provide a good seal and prevent short-circuiting of atmospheric gases. The pipe may be pushed or installed with a rubber mallet, ensuring minimal disturbance to the ground to minimize disturbance to efflux conditions. Collars are not to be sampled within 16 hours of installation.

Efflux measurements are made by placing the chamber onto the soil collar and activating a measurement cycle with the equipment software. The unit undergoes a purge cycle to clear the chamber and then reinitiates until the preset number of measurements are complete. Additional measurements may be required to ensure three sequential 90-second measurements that are within 10 percent of each other. Data is then processed as described in **Section 4.3**.

A field blank (FB) measurement is collected by installing a collar with a sealed bottom cap. The chamber is set upon the sealed collar in the field and allowed to run for a total of 60 measurements. The results of the FB are then averaged, three times the standard deviation is added, and the resulting value is assigned the limit of detection for the specific measurement event.

4.2.2 Soil vapor monitoring locations

As described above, changes in vadose zone gas concentrations may be indicative of NSZD. Where a gas concentration at two or more depths in the subsurface is known, a concentration gradient can be calculated and used to calculate the diffusive gas flux and converted to an NSZD rate (ITRC, 2009).

Four soil gas monitoring point clusters will be installed measure vadose gas concentration gradients. Soil gas monitoring clusters will be installed adjacent to a monitoring well near the center of each LNAPL 'lobe' (VW-13B, VW-20B, and VW-31) and in one background location (MMX). In addition to being located in the center of each main LNAPL lobe, these locations represent different lithologies at the well screen (fine grained lagoon/evaporites, sandy/clastic material, and limestone [see **Figure 5**]). The generalized construction of each soil vapor monitoring location will consist of sampling points installed 5 feet above the groundwater table (targeting the sand unit present at or above most screened intervals), midway between the ground surface and top of well screen (approximately 20 feet bgs in most locations) and one 5 feet bgs.

The drive rod and drive point (anchor point) will be advanced using direct push technology. At the desired depth, the implant probe and tubing will be inserted through the drive rod and the implant probe will be locked to the anchor point by rotating the threaded joints. Once the implant probe has been secured, the rods will be retrieved, and the annulus will be backfilled in accordance with the manufacture's producers. A schematic of a typical permanent soil gas implant probe and a nested well construction is provided in Section D.4.2 of ITRC (2007).

The implant probe will be constructed of a six-inch length stainless steel wired meshed screen (86 Series) or equivalent. Based on the preferred specifications noted below, either low-density polyethylene (LDPE) or Teflon tubing will be used. The annular space surrounding the sample screen will be backfilled with a sand pack. Next, a dry bentonite powder mix will be added to fill the annular space above the screen. Once the drill rod is fully extracted, the bentonite will be hydrated and allowed to set for approximately 48 hours. Each sample point probe will be finished flush with ground surface. Each implant probe will be finished with a stainless-steel tube fitting (Swagelok®) to enable sample collection. The connections will be inter-changeable with a threaded cap/plug to protect the sample point between sampling events. Permanent sampling probes will be maintained until such time as all field work is completed and then abandoned. A description of the methods used to install each sample point will be recorded in the field log book, including details of concrete slab thickness, headspace readings, and sample point construction details.

Soil gas will then be monitored using a portable multi-gas meter capable of measuring CO_2, CH_4, O_2, and H_2S. The maximum concentration will be recorded in a field notebook.

To address possible bias due to soil vapor diffusivity coefficient (D_v^{eff}) variation and soil moisture content, site-specific D_v^{eff}, will be determined using a one-time tracer gas (SF_6 or helium) tests at each vadose gas monitoring point using the procedure described by Johnson et al. (1998) and summarized in CRC CARE (2018). The method involves injecting a volume of air spiked with a known concentration of tracer gas is injected into a soil vapor monitoring point. The concentration of tracer gas is then measured after a known interval of time. The procedure is as follows:

1. Prepare a mixture containing approximately 10 parts per million by volume (ppmv) of the selected tracer gas (i.e., dilute the supplied gas in a tedlar bag filled with air). Verify the gas concentration using the hand held meter.
2. Inject 5 mL of 1 ppmv SF6 into a 1-L Tedlar bag containing 1-L of SF6-free air.
3. Measure the resulting concentration in the 1-L Tedlar bag (should be approximately 5 ppbv); record and denote this value as Cmax.

4. Inject 5 mL of 1 ppmvSF6into the desired location in the vadose zone through small diameter tubing (1/8" stainless steel tubing is preferred). Follow this injection with sufficient SF6-free air to ensure that the 5 mL of SF6 has just been flushed from the tubing into the vadose zone (it is desired that the total injected volume be minimized; approximately 1 mL/ft for 304 SS 1/8" tubing with 2.1 mm i.d.).
5. Immediately withdraw enough soil gas to fill a 1-L Tedlar bag. Analyze and record the SF6 concentration in the 1-L Tedlar bag.
6. Inject 5-10 L of clean air into the vadose zone at this sampling point before conducting a longer test.
7. Repeat Steps 4, 5, and 6 except wait for periods of 15, 60, and 120 min before withdrawing the soil gas sample for analysis.

Reduce the data by dividing the measured concentrations by C_{max} (this is equivalent to determining η, the fraction of mass recovered).Sweeney and Ririe (2017) determined that low-rate gas extraction from monitoring wells screened across the water table provides comparable results to soil vapor probes installed 1 foot above the water table. This work suggests that low-flow collection of soil gas from short, unflooded monitoring well screens like those at the Site should provide satisfactory comparison points to shallow soil gas samples for NSZD rates calculated using the gradient method. The method requires installation of a cap on the well that allows tubing within the well to be connected to the gas analyzer. The small purge volume method (Sweeney and Ririe, 2017) requires that monitoring well gas be purged at a rate of 1 liter per minute (L/min) for a minimum of 12 seconds while the tubing is situated 1 foot above the groundwater/LNAPL interface.

Gas gradient calculations will be made following the procedure described in ITRC (2008,2019) and CRC Care (2018) to provide an estimate of an NSZD rate using the gas gradient method, to provide a check on NSZD rates calculated using the TEA/byproduct and Efflux methods, which may be affected by the complex site geologic and hydrologic conditions.

4.3 Means and Methods for NSZD Data Interpretation

The following section describes specific methodology that will be used to assess the proposed data.

4.3.1 Groundwater geochemistry characterization

Groundwater geochemistry characterization will utilize Piper diagrams and binary (X-Y axis) concentration plots to identify distinct water types to verify that background water samples are representative of plume conditions. If compositional differences are apparent, this will not necessarily indicate that background samples are unrepresentative. For example, alkalinity is routinely converted to bicarbonate or carbonate ion concentrations for plotting purposes as alkalinity is dominated by the carbonate system in most natural waters. However, LNAPL degradation leads to elevated alkalinity from the degradation process, which may cause apparent differences in background and source area chemistry. Likewise, sulfate utilization may lead to apparent differences in chemistry that should not be misinterpreted as indicative of different hydrogeologic zones. Therefore, an integral part of the geochemical assessment will be consideration of redox conditions determined from field parameters and TEA/byproduct results.

Areas of distinctive groundwater geochemistry (i.e., tidal flux, upgradient recharge) will be assessed in the context of well screen geology provided in the LNAPL CSM and Remedial Action Work Plan (EHS Support, 2020). Zones of enhanced permeability, groundwater flux, and/or distinctive groundwater chemistry will be used to assess locations where NSZD indicators using the various proposed techniques may not be representative.

Quality assurance and quality control (QA/QC) measures will include using manufacturer-recommended calibration procedures for all field instruments. Directions on the use, calibration, and tracking for standard field equipment is provided in EHS Support SOP-08: Field Equipment Operation and Calibration (**Appendix C**). Field and laboratory samples and analyses will comply with prescribed project specific field and lab duplicate and equipment blank (EB) requirements, as specified in the QAPP (**Appendix D**).

4.3.2 Identification of NSZD Using Field Parameters

DO and ORP measurements will be compared between background wells and source area wells. DO depletion in source area wells of more than 0.2 milligrams per liter (mg/L) (the standard precision of most instruments) relative to background values will be considered meaningful evidence of oxygen depletion and ongoing NSZD. DO values of less than or greater than 0.5 mg/L will be considered indicators of sub to anoxic conditions where TEA reduction reactions are likely (McMahon and Chapelle, 2008).

DO values greater than 0.5 mg/L will not preclude the possibility that NSZD is proceeding via TEA reduction reactions, as redox disequilibrium in groundwater frequently occurs where there is measurable oxygen coexisting with H_2S, CH_4, and Fe(II) (Nordstrom and Wilde, 2005). Additionally, elevated concentrations of CH_4 and H_2S are known interferences with many DO meters that may result in false readings. Therefore, the quality of DO measurements will be assessed by comparing measured values to TEA concentrations and by-products to identify redox disequilibrium using a United States Geological Survey (USGS) Excel Workbook (Jurgens et al., 2009).

ORP values less than +50 millivolts (mV) (relative to an Ag/AgCl electrode) will be used to suggest a reductive pathway is possible, and values less than -100 mV will suggest a reductive pathway is likely (Wiedemeier et al, 1998). Very generally, ORP values of +50 to -50 mV are indicative of NO_3^- reduction, -50 to -250 mV of SO_4^{2-} reduction, and -175 to -400 mV of CH_4 production.

ORP values greater than +50 mV will not conclusively indicate that NSZD is absent, due to potential O_2 introduced during sampling; and potential interferences from organic matter, sulfides, and methane on the ORP probe (Nordstrom and Wilde, 2005). Where suspect, redox potential may instead be calculated (using the USGS's PHREEQC software or The Geochemists' Workbench software) from the dominant redox pair (i.e., TEA and associated byproduct) for which data are available.

QA/QC measures will include using manufacturer-recommended calibration procedures for all field instruments. Directions on the use, calibration, and tracking for standard field equipment is provided in EHS Support SOP-08: Field Equipment Operation and Calibration (**Appendix C**) and in the QAPP (**Attachment D**).

4.3.3 Identification of Aqueous NSZD and Preferred Biodegradation Reactions

Decreases in TEA concentrations and elevated TEA byproducts and alkalinity in the source area relative to background groundwater will confirm that active LNAPL mass removal by NSZD processes are operating at the Site (e.g., Wiedemeier et al., 1995). Differences in TEA and byproduct concentrations between source area and background wells will be qualitatively assessed graphically by comparing mean and/or median concentrations using box and whisker plots (Beck and Mann, 2010). Additionally, a non-parametric statistical method (t-test, one-way analysis of variance [ANOVA], or Wilcoxon signed-rank test) will be used to determine if samples belong to the same or different populations, following the procedures outlined in USEPA (2009).

The results of the graphical and statistical tests will then be used to identify preferred biodegradation reactions, by identifying gains/losses in key TEA and byproduct concentrations as outlined on **Table 4-1** (source Beck and Mann, 2010).

Table 4-1 Preferred Biodegradation Reactions

Type of microbial respiration	Electron acceptor	Metabolic by-product	Geochemical indicator response		Redox potential, eH (mV @pH 7, 25 °C)	
Aerobic (Oxidation)	Oxygen	CO_2	O_2 ↓	CO_2 ↑	+820	Most preferred
Anaerobic (Reduction)	Nitrate (NO_3^-)	N_2	NO_3^- ↓	CO_2 ↑	+720	↓
	Manganese (Mn^{4+})	Mn^{2+}	Mn^{2+} ↑	CO_2 ↑	+520	
	Ferric iron (Fe^{3+})	Ferrous iron (Fe^{2+})	Fe^{2+} ↑	CO_2 ↑	-50	
	Sulfate (SO_4^{2-})	H_2S	SO_4^{2-} ↓	CO_2 ↑	-220	
	Carbon dioxide (CO_2)	Methane (CH_4)	CH_4 ↑	CO_2 ↑	-240	Least preferred

Source: Beck, P & Mann, B. 2010. A technical guide for demonstrating monitored natural attenuation of petroleum hydrocarbons in groundwater, CRC CARE Technical Report no. 15. CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.
°C = degrees Celsius
eH = Oxidation/reduction potential relative to hydrogen electrode
mV = millivolts

To facilitate aqueous NSZD rate calculations, the average NSZD indicator concentrations at background wells are compared to source and downgradient concentrations to give a plausible range of aqueous NSZD rates. The following three scenarios will be evaluated:

1. Values that give maximum concentration differences between background and source area/downgradient wells. These are minimum concentrations of NSZD indicators that are

consumed when biodegradation occurs (O_2, NO_3^-, SO_4^{2-}), and maximum concentrations of NSZD indicators that are produced when biodegradation occurs (CH_4, Fe^{2+}, CO_2, and alkalinity).

2. Mean NSZD indicator concentrations at the source and downgradient areas.
3. Values that give minimum concentration differences between background and source area/downgradient wells. These are maximum concentrations of NSZD indicators that are consumed when biodegradation occurs, and minimum concentrations of NSZD indicators that are produced when biodegradation occurs.

The three scenarios will be used to compute three different assimilative capacity (AC) values (described below) that will subsequently be incorporated into three different aqueous NSZD rate calculations. Note, Site complexities will potentially require a modified approach. Specifically, potential contributions from seawater will be evaluated during groundwater geochemistry characterization. To account for any identified seawater mixing at upgradient, source area, and downgradient locations, the effects of seawater mixing may be subtracted from sample analytical results using a conservative binary mixing model based on conservative ion (chloride) balance, or similar approach.

QA/QC measures will include using manufacturer-recommended calibration procedures for all field instruments. Directions on the use, calibration, and tracking for standard field equipment is provided in EHS Support SOP-08: Field Equipment Operation and Calibration (**Appendix C**) and in the QAPP (**Appendix D**). Field and laboratory samples and analyses will comply with prescribed project specific field and lab duplicate and EB requirements, as specified in the QAPP (**Appendix D**).

4.3.4 Identification of NSZD Using Well Head Space and Shallow Soil Gas Data

Wellhead space readings will be assessed both qualitatively and quantitatively. Qualitative assessment will compare head space readings in background and source areas to identify statistically significant values. Statistically significant differences in gas concentrations between source area and background wells will be assessed visually by comparing mean and/or median concentrations using box and whisker plots. Additionally, a non-parametric statistical method (t-test, one-way ANOVA, or Wilcoxon signed-rank test) will be used to determine if samples belong to the same or different populations, following the procedures outlined in USEPA (2009). The statistical method selected will depend upon the outcome of groundwater geochemical testing, specifically, the number of distinct sample groupings that is identified based on geologic, hydrologic, and geochemical variations.

Locations where gas readings within the LNAPL footprint are unexpectedly low or zero will be screened against the results of the groundwater geochemistry characterization and variations in subsurface geology to verify if results are valid indicators of NSZD or affected by complex subsurface geology or hydrogeology processes such as (but not limited to) areas of enhanced groundwater recharge or seawater flux.

QA/QC measures will be used to ensure the accuracy and precision of the data collected. Manufacturer recommended calibration procedures will be followed for all field instruments. Directions on the use, calibration, and tracking for standard field equipment is provided in EHS Support SOP-08: Field Equipment Operation and Calibration (**Appendix C**) and in the QAPP (**Appendix D**).

4.3.5 Identification of NSZD Using the Differential Temperature Method

Net temperature change (ΔT) will be calculated to qualitatively assess the presence of metabolic heat flux signatures by comparing the difference in groundwater temperature between source and background wells (ΔT = Ti – Tb, where Ti is the temperature of well I, and Tb is the temperature of background well). This calculation will be performed for the maximum, average, and minimum upgradient groundwater temperature for all three monitoring zones. Example tables that will summarize calculations are provided in **Table 4-2** and **Table 4-3**.

Table 4-2 Example Background and Downgradient Well Statistics (Tb)

Well	T Minimum (°C)	T Average (°C)	T Maximum (°C)
Background wells (MMX, VW8, MM9, and VW11)			
Depth 1			
Depth 2			
Depth 3			
Downgradient wells (VW25, VW27, VW34, VW37, GM11, and GM14)			
Depth 1			
Depth 2			
Depth 3			

°C = degrees Celsius
T = Temperature
Tb = Temperature of background well

Table 4-3 Example Source Area Well Statistics Well Calculations (Tb)

Well	T. (°C) [Measured = Ti]	ΔT (Minimum) [Relative to Background]	ΔT (Av.) [Relative to Background]	ΔT (Max.) [Relative to Background]	ΔT (Minimum) [Relative to Downgradient]	ΔT (Av.) [Relative to Downgradient]	ΔT (Max.) [Relative to Downgradient]
Source Area Well VW-2							
Depth 1							
Depth 2							
Depth 3							
Source Area Well VW-5							
Depth 1							
Depth 2							
Depth 3							
etc.							

°C = degrees Celsius
ΔT = temperature difference
Av. = average
Max. = maximum
T = temperature
Tb = temperature in background well
Ti = temperature of well "i"

Tabulated data will then be plotted in histograms and/or temperature contoured maps to visually identify locations with temperature differentials indicative of NSZD.

Temperature data will be assessed in the context of the hydrogeological CSM and results of the groundwater geochemistry characterization to identify areas where biogenic heat signatures are potentially masked by enhanced groundwater or tidal flux, or locations with elevated hydraulic conductivity.

QA/QC measures will be used to ensure the accuracy and precision of the data collected. Manufacturer-recommended calibration procedures will be followed for all field instruments. Thermocouples are typically calibrated by the manufacturer prior to shipping, and calibration may also be checked in the field by immersing the thermocouples in an ice bath filled with distilled water (0°C). Directions on the use, calibration, and tracking for standard field equipment is provided in EHS Support SOP-08: Field Equipment Operation and Calibration (**Appendix C**) and in the QAPP (**Appendix D**).

4.3.6 Aqueous NSZD rate estimate

The aqueous NSZD rate will be calculated following the methods outlined in CRC CARE (2018) and IRTC (2009). The calculation utilizes the following equation:

$$R_{aq} = V_D(YZ)(AC)$$

Where:

R_{aq} = the aqueous NSZD rate (grams/day)
V_D = Darcy velocity of groundwater flow (meters/day)
YZ = the area perpendicular to groundwater flow (square meters)
AC = the assimilative capacity (grams/cubic meter)

The resulting aqueous NSZD rate (R_{aq}) is then computed in units of grams/day. R_{aq} is then divided by the estimated LNAPL density to obtain units of 'volume LNAPL depleted/year'.

Darcy velocity is calculated using the following equation:

$$V_D = \frac{K \times i}{\eta}$$

Where:

K = the average hydraulic conductivity (meters/day)
i = the hydraulic gradient (unitless)
η = the effective porosity (unitless)

Hydraulic conductivity values based on slug testing have previously been calculated for five site monitoring wells in different lithologies (GES, 2017), and the representative site value will be used to determine Darcy Velocity. The hydraulic gradient will be calculated using water level elevations determined during a recent Site-wide groundwater monitoring event. Effective porosity is not reported for the Kingshill Limestone, however total porosity data are available for a number of locations at and

around the Site and average about 15 percent (Gill and Hubbard, 1985). Given that fractured intervals contribute to the Gill and Hubbard (1985) porosity estimates for Kingshill limestone, effective and total porosity are not expected to differ greatly. Therefore, the total porosity estimate will be used in the Darcy velocity calculation in lieu of effective porosity.

The YZ term is calculated from the following information:

- Average width of the LNAPL footprint (*Y*)
- Average thickness of the LNAPL smear zone (*Z*)

Assimilative (or biodegradation) capacity calculations are based on the theory of Wiedemeier et al. (1995) and calculated using the method outlined in CRC CARE Technical Report 15 (Beck and Mann, 2010). Considering the dominant LNAPL components at the site are middle distillates (EHS Support, 2020), stoichiometric conversions for TEAs and byproducts based on octadecane ($C_{18}H_{38}$) will be employed in the AC calculation. The balanced biotransformation chemical reactions are summarized in **Table 4-4** through **Table 4-8**.

Table 4-4 Balanced biotransformation reactions

Biotransformation process	TEA/Byproduct	Balanced equation
Aerobic	O_2	$2C_{18}H_{38} + 55O_2 \rightarrow 36CO_2 + 38H_2O$
Denitrification	NO_3^-	$C_{18}H_{38} + 22NO_3^- + 22H^+ \rightarrow 18CO_2 + 11N_{2(g)} + 30H_2O$
Sulfate reduction	SO_4^{2-}	$4C_{18}H_{38} + 55SO_4^{2-} + 110H^+ \rightarrow 72CO_2 + 55H_2S_{(g)} + 76H_2O$
Iron reduction	$Fe(OH)_{3(s)}$	$C_{18}H_{38} + 110Fe(OH)_{3(s)} + 220H^+ \rightarrow 18CO_2 + 110Fe^{2+} + 294H_2O$
Methanogenesis	CO_2 and CH_4	$4C_{18}H_{38} + 34H_2O \rightarrow 17CO_2 + 55CH_4$

TEA = terminal electron acceptor

Table 4-5 Molecular weights

NSZD Indicator	Molecular weight (g/mol)
O_2	32
NO_3^-	62.01
SO_4^{2-}	96.06
Fe^{2+}	55.84
CH_4	16.05
CO_2	44.01
$CaCO_3$	100.09
$C_{18}H_{38}$	254.5

g/mol = grams per mole
NSZD = natural source zone depletion

Table 4-6 Stoichiometric ratio calculations for octadecane ($C_{18}H_{38}$) degradation

Biotransformation process	TEA/Byproduct	Moles $C_{18}H_{38}$	Grams $C_{18}H_{38}$	Moles TEA/byproduct	Grams TEA/byproduct	Grams $C_{18}H_{38}$
Aerobic	O_2	2	509	55	1760	0.29
Denitrification	NO_3^-	1	254.5	22	1364.22	0.19
Sulfate reduction	SO_4^{2-}	4	1018	55	5283.3	0.19
Iron reduction	$Fe(OH)_{3(s)}$	1	254.5	110	6142.4	0.04
Methanogenesis	CO_2 and CH_4	4	1018	55	882.75	1.15

TEA = terminal electron acceptor

Table 4-7 Stoichiometric ratio calculations for CO_2 and alkalinity production

Biotransformation process	TEA/Byproduct	Moles CO_2	Grams CO_2	Grams CO_2/ Grams TEA/byproduct	Moles $CaCO_3$	Grams $CaCO_3$ - C	Grams $CaCO_3$ /Grams TEA/byproduct
Aerobic	O_2	36	1584.36	0.90	0	0	0
Denitrification	NO_3^-	18	792.18	0.58	18	1801.62	1.32
Sulfate reduction	SO_4^{2-}	72	3168.72	0.60	72	7206.48	1.36
Iron reduction	$Fe(OH)_{3(s)}$	18	792.18	0.13	18	1801.62	0.29
Methanogenesis	CO_2 and CH_4	17	748.17	0.85	0	0	0

TEA = terminal electron acceptor

Table 4-8 Summary of utilization factors for octadecane ($C_{18}H_{38}$) degradation and CO_2 and alkalinity production from biotransformation processes

Biotransformation process	TEA/Byproduct	Grams $C_{18}H_{38}$ /Grams TEA	Grams CO_2 /Grams TEA	Grams $CaCO_3$ /Grams TEA
Aerobic	O_2 Consumed	0.29	-0.90	0.00
Denitrification	NO_3^- Consumed	0.19	-0.58	-1.32
Sulfate reduction	SO_4^{2-} Consumed	0.19	-0.60	-1.36
Iron reduction	Fe^{2+} Produced	0.04	0.13	0.29
Methanogenesis	CH_4 Produced	-1.15	0.85	0.00

TEA = terminal electron acceptor

The total amount of available electron acceptors for biological reactions is then estimated by:

- Calculating the difference between upgradient concentrations and source zone concentrations of O_2, NO_3^-, and SO_4^{2-}.
- Measuring the concentration of metabolic by-products (Fe(II), CH_4, and alkalinity) in the source zone. Results for dissolved iron will be assumed equal to Fe(II).

The computation is completed for a lower end, mean, and upper end estimate of TEA/byproduct utilization across the LNAPL source area. The computation is based on the results of the difference between aqueous NSZD indicators in background and source are wells that are described in **Section 4.3.3**. AC is then calculated using the following equation:

Assimilative or biodegradation capacity (mg/L) =
[(av. upgradient O_2 concentration)–- (source zone O_2 concentration)] ÷ O_2 $C_{18}H_{38}$ UF
+ [(av. upgradient NO_3^- concentration)–- (source zone NO_3^- concentration)] ÷ NO_3^- $C_{18}H_{38}$ UF
+ [(av. upgradient SO_4^{2-} concentration)–- (source zone SO_4^{2-} concentration)] ÷ SO_4^{2-} $C_{18}H_{38}$ UF
+ [(Fe(II) concentration in source area) ÷ Fe(II) $C_{18}H_{38}$ UF
+ [(CH_4 concentration in source area) ÷ CH_4 $C_{18}H_{38}$ UF

Alkalinity provides a lumped estimate of AC. Therefore, alkalinity provides a primary check on the AC calculated from TEAs and by-products.

4.3.6.1 Aqueous NSZD Quality Assurance/Quality Control

The primary QA/QC check compares measured changes in CO_2 and alkalinity concentrations between background and source area wells to calculated changes in CO_2 and alkalinity concentrations. Calculated CO_2 and alkalinity changes are based on the sum of NSZD ratios given in **Table 4-7** for each TEA.

- If the theoretical estimate for CO_2 and alkalinity produced falls within the observed range of measured values, AC and NSZD rate calculations will be assumed valid.
- If the theoretical estimate for CO_2 and alkalinity produced is higher than the observed concentrations, the calculated NSZD rates will be assumed estimates with potential high bias.
- If the theoretical estimate for CO_2 and alkalinity produced is lower than the observed concentrations, the calculated NSZD rates will be assumed estimates with potential low bias.

Consequently, the measured lower end, mean, and upper end estimate of TEA/byproduct utilization across the LNAPL source will be compared to the calculated values to qualitatively determine which estimate mostly aptly reflects the aqueous hydrocarbon degradation at the site.

4.3.7 NSZD Rate Estimate Using the Differential Temperature Method

As an additional line of evidence, NSZD rates will be calculated using the differential temperature method as described in CRC CARE (2018) and IRTC (2009 and 2018). The method assumes homogenous and isotropic soil, a steady-state biogenic heat source, conductive heat transfer, and instantaneous and complete reaction. Complications with this method as applied to the Site may require 'parceling' areas for distinct calculations based on areas of distinct lithology.

Heat flux is estimated using Fournier's first law of conduction, that is modified to estimate heat flux (q_H [J/m^2-soil/s]:

$$q_H = K_T \left(\frac{\Delta T}{\Delta Z}\right)$$

Where:

$\frac{\Delta T}{\Delta Z}$ = the temperature gradient (^{o}K/m)

K_T = the thermal conductivity of the soil (J/m/s/^{o}K) in the hydrocarbon oxidation zone

Thermal conductivity for carbonate rocks will be taken from Thomas Jr. et al. (1973) (see **Table 4-9**) for representative lithologies in source zone wells and converted to the appropriate units.

Table 4-9 Thermal conductivity of carbonate rock samples

Sample no.	Rock Type	Pore Volume* (mm^3/g)	Thermal conductivity ($W\ m^{-1}\ C^{-1}$ at 40.5 °C)	
			Dry (air-saturated)	Water-sorbed
1	Iceland Spar Calcite	0	3.2**	-
2	Translucent calcite spar	0.4	3.1**	--
3	Limestone	4	3.0	3.1
4	Limestone	17	2.9	2.9
5	Limestone	38	2.5	2.9
6	Limestone	53	2.4	2.9
7	Limestone (chalk)	216	1.2	1.7
8	Dolomite	7	5.1	5.5
9	Dolomite	31	3.1	4.2
10	Magnesite	14	5.0	5.1

* = Determined by mercury porosimetry
** = Determined perpendicular to the {1014} planes
Source: Thomas Jr. et al. 1973.
°C = degrees Celsius
mm^3/g = cubic millimeters per gram

The thermal gradient will be calculated from measured temperature profiles as shown in **Figure 4-7** (note: consideration of thermal effects at ground surface owing to the tropical climate will be assessed and excluded from the temperature gradient calculation, if identified):

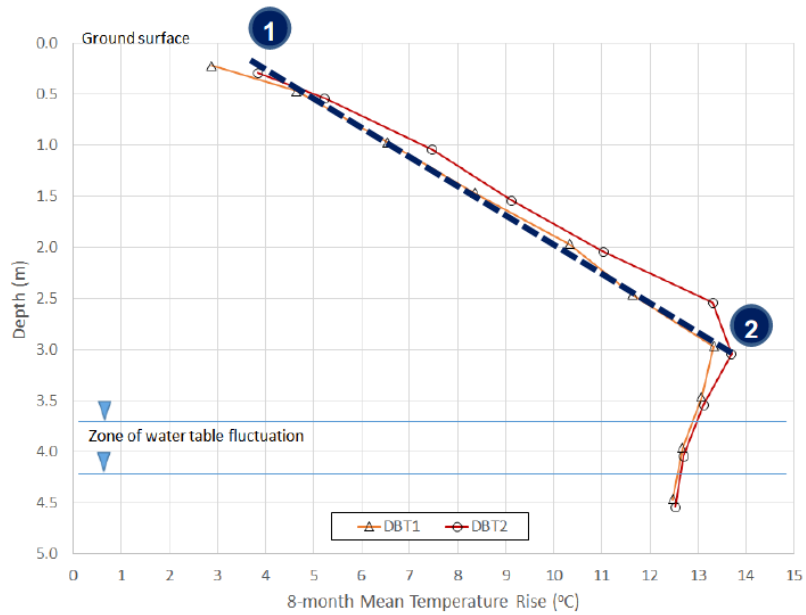


Figure 4-7 Temperature gradient calculation: $\Delta T/\Delta z = (T_2-T_1)/(z_2-z_1)$

The NSZD rate (R_{NSZD}) is then calculated by dividing the calculated heat flux by the enthalpy (ΔH^o) of octadecane ($C_{18}H_{38}$) oxidation. The enthalpy of octadecane oxidation is calculated following the method described in Sweeney et al (2014), which utilizes the stoichiometry of octadecane oxidation

$$C_{18}H_{38} + 27.5O_2 = 18CO_2 + 19H_2O$$

and the following enthalpies of formation at standard state of the reaction components (in kilojoules per mole [kJ/mol] at 298.15 Kelvin [K]): $\Delta H_f^o{}_{C18H38}$ = -414.6; $\Delta H_f^o{}_{O2}$ = 0; $\Delta H_f^o{}_{CO2}$ = -393.5; $\Delta H_f^o{}_{H2O}$ = -285.8. By solving for the standard enthalpy of the reaction, (i.e. $\Delta_r H^\circ = \Sigma v\, \Delta_f H^\circ$(products)–– $\Sigma v\, \Delta_f H^\circ$(reactants), ΔH_r^o of the above reaction is -12092.9 kJ/mol, which when divided by the molar weight of octadecane (254.5 g/mol) gives 47.5 kJ/g of heat released. Therefore, the NSZD degradation rate (in grams/m^2/day) is:

$$R_{NSZD} = \frac{q_H}{47500\ kJ/g} \times \frac{86{,}400\ s}{1\ d}$$

QA/QC measures will be used to ensure the accuracy and precision of the data collected. Manufacturer-recommended calibration procedures will be followed for all field instruments. Thermocouples are typically calibrated by the manufacturer prior to shipping, and calibration may be checked in the field by immersing the thermocouples in an ice bath filled with distilled water (0°C). Directions on the use, calibration, and tracking for standard field equipment is provided in EHS Support SOP-08: Field Equipment Operation and Calibration (**Appendix C**) and in the QAPP (**Appendix D**).

4.3.8 NSZD rate estimate using the vadose gas gradient method

Given the geologic and hydrologic complexities at the site and inherent limitations of NSZD rate estimates using other methods, an alternative line of evidence is proposed to verify NSZD rates should the results of Phase 1 determine it is warranted. Paired wellhead space and shallow soil gas concentrations will be used in a screening-level calculation of the NSZD rate used to verify results of passive gas flux stations using a modified procedure for the gradient method described in CRC CARE (2018) and IRTC (2009).

The procedure will utilize Fick's first law of diffusion:

$$J = D_v^{eff}\left(\frac{dC}{dZ}\right)$$

Where:

J = the steady-state diffusive flux (g/m^2-soil/second)
D_v^{eff} = the effective soil vapor diffusion coefficient (m^2/second)
v = gas specific (i.e. O_2, CO_2, or CH_4)
$\frac{dC}{dZ}$ = the soil gas concentration gradient (gram per meters cubed per meter [g/m^{3}m])

The modified method will involve the following steps:

1. Sample headspace for O_2, CO_2, and CH_4 in monitoring wells immediately above the water table using a calibrated hand-held multi gas meter. Headspace gas readings will be attributed to a depth corresponding to the water table/LNAPL surface measured with a water level meter or oil/water interface probe.
2. Sample headspace for O_2, CO_2, and CH_4 at 1 foot below ground using the procedure described in **Section 4.2** using a calibrated hand-held multi-gas meter.
3. Estimate soil vapor diffusion using empirical means. The empirical equation of Millington and Quirk (1961):

   $D_v^{eff} = D_v^{air}\left(\frac{\Theta_v^{3.3}}{\Theta_T^2}\right)$; where $\frac{\Theta_v^{3.3}}{\Theta_T^2}$ can be estimated from literature values (Johnson et al., 1998). The soil type will be selected based on monitoring well logs.

4. Estimate the concentration gradient: $\frac{dC}{dZ} = \frac{C_2 - C_1}{Z_2 - Z_1}$; where C_1 and C_2 are the concentrations and Z_1 and Z_2 are the depths of samples 1 (shallow) and 2 (deep), respectively.
5. Compensate for background fluxes. This will be accomplished by subtracting average background concentrations of gases from source area and downgradient locations.

Differences in soil gas concentrations will provide qualitative indicators of active NSZD, that is:

- Elevated CH_4 near the hydrocarbon-impacted soil interface indicates that anaerobic biodegradation is occurring.
- Lower O_2 and elevated CO_2 indicates aerobic biodegradation and hydrocarbon oxidation.

Gradient concentrations will be compared to NSZD rates determined from the soil gas efflux method as a means for QC.

QA/QC measures will be used to ensure the accuracy and precision of the data collected. Manufacturer-recommended calibration procedures will be followed for all field instruments. Directions on the use, calibration, and tracking for standard field equipment is provided in EHS Support SOP-08: Field Equipment Operation and Calibration (**Appendix C**) and in the QAPP (**Appendix D**).

4.3.9 Soil Gas Efflux NSZD Rate Quantification Methods

4.3.9.1 NSZD rate calculation – passive CO_2 trap method

NSZD rate calculations are typically completed by the trap supplier and analytical laboratory. The laboratory reports the results in grams per square meter per year by simply quantifying the mass of the carbon dioxide on the trap and standardizing this to a unit of area (based on the cross-sectional area of the pipe and the time period over which the trap was deployed in the field. Data manipulation and corrections may be required at this site due to background carbon dioxide associated with the limestone geology. . The procedures are outlined in the EHS Support 'NSZD Passive Trap SOP' included in the QAPP (**Appendix D**) and summarized below.

The rate calculation method conducted by E-Flux involves subtracting the trip blank (TB) CO_2 contribution from the sorbed CO_2 mass for each sample. The corrected CO_2 mass is converted to a total CO_2 efflux (J_{total} in $\frac{\mu mol}{m^2 s}$) using the following equation:

$$J_{Total} = \frac{M_{CO_2\ (TB\ corrected)} \times \left(\frac{1\ mol\ CO_2}{44\ g\ CO_2}\right) \times \left(\frac{1000000 \mu mol\ CO_2}{mol\ CO_2}\right)}{days\ deployed\ \times 24 \frac{hr}{day} \times 3600 \frac{s}{hr} \times 8.11 \times 10^{-3} m^2}$$

Where the cross-sectional area of the receiver pipe is $8.11 \times 10^{-3} m^2$. The background CO_2 efflux is corrected for by multiplying J_{total} by the fraction of fossil fuel CO_2 (Ff_{CO_2}):

$$J_{NSZD} = J_{Total} \times Ff_{CO_2}$$

The utility of the ^{14}C correction method will be determined as described in **Section 4.2**, and alternate methods for addressing the background correction (i.e. the fraction of fossil fuel CO_2) will be evaluated based on the outcome of this assessment, but may include geochemical modeling (The Geochemists' Workbench or PHREEQC) based on geochemistry characterization and field parameters to assess inorganic CO_2 contributions from limestone weathering, or a simple background concentration subtraction.

Lastly, the NSZD rate (R_{NSZD}) is calculated as follows:

$$R_{NSZD} = \left(\frac{J_{NSZD} \times m_r \times MW}{10^6}\right) \times \frac{86400s}{d}$$

Where R_{NSZD} is in units of g/m^2/d, m_r is the stoichiometric molar ratio of hydrocarbon degraded (see **Section 4.3.3**), and MW is the molar weight of the representative hydrocarbon. The value of R_{NSZD} may be presented in alternate units, calculated using standard conversion factors.

The spatial distribution of NSZD rates is then compared spatially using contouring or Thiessen polygon assessment technique, with consideration of geologic and hydrologic controls on NSZD rates.

4.3.9.1.1 QA/QC and data validation for the passive trap method

QA/QC and data validation for the passive trap method involve:

1. Checking accuracy of laboratory reports
2. Utilizing a background location to account for variations in wind/weather or background sources not captured in the isotope analysis.
3. Using one duplicate trap for every 10 samples (within 1 foot of the primary sample) with a target of +/- 25% agreement 9 No formal quality control metrics have been proposed in the guidance or by the vendor.).
4. Using a TB
5. Establishing a CO_2 detection limit

The goal is a 30 percent relative percent difference between primary and duplicate samples; however, heterogeneities in the subsurface may preclude achieving this criterion.

The detection limit is dictated by the analytical method and deployment time. Laboratory QA/QC and internal calibration criteria are provided in **Appendix D**. As described in CRC CARE (2018) the detection limit is typically 0.1 micromoles per square meter per second (µmol/m^2/second) for a 15-day deployment time, a cross-sectional diameter of 10.16 centimeters of the Schedule 40 polyvinyl chloride (PVC) receiver pipe, and 40 grams of sorbent material. A decrease in deployment time of four days would result in approximately a five-fold increase in the detection limit (0.5 µmol/m^2/second). Note that if laboratory results are less than the specified analytical detection limit, the resulting detection limit of the CO_2 traps must be considered non-detect.

QA/QC procedures are important in evaluating the accuracy and precision of the data collected. One duplicate trap location every 10 locations is recommended to evaluate consistency between installation procedures and replication of results. Place the duplicate trap approximately 0.3 m from the parent location and install it in an area of similar ground cover. Statistics such as the calculation of a relative percent difference (RPD) from the parent and duplicate sample data can be performed to assess data quality. An elevated RPD of greater than 30% is typically used as a criterion to re-evaluate the soil receiver pipe installation procedures to ensure a good seal with the subsurface was attained. However, heterogeneities in the subsurface impact the ability to achieve an RPD of less than 30% at many sites, therefore the 30% criterion may not be achieved in all cases.

As discussed above, a TB must be provided by the passive flux trap supplier and analyzed along with the samples for each field event. The TB accounts for CO2 not associated with flux from the subsurface that either came from manufacturing or sorbed from atmosphere (through the caps) during the shipment.

The detection limit of a passive CO_2 trap is dictated by the detection limit of the analytical method. The detection limit of the analytical method is found by multiplying a typical coefficient of variation of 3% on trap CO_2 analyses, and a typical blank trap CO2 content of 1% by weight by five (i.e., 3% cv * 1% CO2 by weight * 5). The detection limit of the analytical method of CO2 trap is approximately 0.15% CO2 by weight of the sorbent (API 2017). Then using deployment time, the area exposed to efflux, and the quantity of sorbent material the detection limit of the CO2 trap can be determined. The detection limit is typically 0.1 µmol/m2/s for a 15-day deployment time, a cross-sectional diameter of 10.16 cm of the Schedule 40 polyvinyl chloride (PVC) receiver pipe, and 40 g of sorbent material A decrease in deployment time of 4 days would result in approximately a 5-fold increase in the detection limit (0.5 µmol/m2/s). Note that if laboratory results are less than the specified analytical detection limit, the resulting detection limit of the CO_2 traps must be considered non-detect.

4.3.9.2 NSZD rate calculation – dynamic closed chamber method

The DCC method requires careful selection of background locations to adequately capture the range of site conditions (e.g., variations in soil thickness, vegetation) that may contribute CO_2 in addition to that derived from the NSZD processes.

A minimum of three sequential (approximately 90-second duration each, field optimized) CO_2 efflux measurements are performed at each sampling location. A deadband period of 10 to 20 seconds (adjusted and optimized in the field) is selected at the start of each run to ignore the initial period of data to account for mixing with ambient air in the chamber. After each measurement, the chamber is lifted off the sampling point and a post measurement purge cycle is run to minimize cross contamination between samples. Sequential samples are collected until they are within 10 percent of each other.

NSZD rate calculations are largely automated with the software supplied by LI-COR, Inc. Details of curve fitting corrections and calculation of R_{NSZD} broadly utilize similar equations and procedures to the passive efflux method described in **Section 4.3.9.1** and described in Appendix F of CRC CARE (2019), and considerations for determining detection limits, accuracy, and background corrections are described in the following QA/QC and data validation section.

4.3.9.2.1 QA/QC and data validation for the dynamic closed chamber method

Data validation consists of four steps:

1. Establish a detection limit
2. Data validation
3. Background correction and NSZD rate calculation
4. Data visualization

A collar with a sealed bottom cap is used for a FB. The chamber is used to obtain 60 measurements from the FB. The detection limit is calculated as the average + three times the standard deviation of the 60 FB measurements.

Data validation is accomplished by first assigning non-detect values to field data equal to or below the computed detection limit value. The remaining (detected) data are processed by optimizing R^2 values of the curves fitted to data values.

CO_2 efflux values determined by the LI-COR meter do not determine the CO_2 source. Therefore, background CO_2 efflux must be subtracted from measured values to determine the magnitude attributable to NSZD processes. Background CO_2 efflux values may be determined using a select number of passive traps and using the carbon isotope determination of CO_2 sources, or by directly utilizing the LI-COR meter at background locations. The specific background CO_2 determination method will be based on the outcome of the Phase 1 investigation. In selecting locations to use in background corrections, care will be taken to evaluate comparable surface vegetation and landcover.

Data visualization is then accomplished by mapping CO_2 efflux values. The primary data check during this step is that elevated CO_2 broadly corresponds to areas of known LNAPL, otherwise alternative explanations for CO_2 flux will be explored.

QA/QC procedures include duplicate collection at a collar installed no more than approximately 1 foot from the primary location (1 in 10 samples). Accuracy is typically within 1.5 percent of the measured CO_2 value, as specified by the manufacturer. Atmospheric conditions (e.g., fog, precipitation, pressure changes) have an influence of efflux measurements, therefore weather conditions on the day of collection are a key QA/QC consideration.

5 General Field and Sampling Procedures

Field and sampling SOPs are provided in **Appendix C**. The following procedures are included:

- SOP-02 Site Visit and Reconnaissance
- SOP-04 Field Documentation
- SOP-05 Sample Management and Shipping
- SOP-07 Investigation Derived Waste Management
- SOP-08 Field Equipment Operation and Calibration
- SOP-09 Field Equipment Decontamination
- SOP-12 Quality Assurance and Quality Control
- SOP-41 Fluid Measurement
- SOP-43 Low Flow Groundwater Sampling
- SOP-44 Volume-Purge Method for Groundwater Sampling
- SOP-46 Water Sampling for Chemical Analysis

5.1 Health, Safety, and Security

Site investigation activities will be performed by the POC lead contractor (Geomonitoring Services) in accordance with the Health and Safety Plan (HASP) developed for the Site. A copy of the Site-specific HASP for this project is included in **Appendix E**.

On-site personnel will be trained in accordance with Title 20 Code of Federal Regulations (CFR) 1910.120 requirements for hazardous waste Site operations. Subcontractor personnel will have 40 hours of the Occupational Safety and Health Administration (OSHA) Hazardous Waste Operations and Emergency Response (HAZWOPER) certification with current refresher training.

Personnel will attend a daily pre-work safety briefing. Sampling and other field activities will be conducted in modified level D personal protective equipment (PPE), which will include at a minimum, safety glasses or goggles, hard hat, gloves, steel-toed boots, a reflective safety vest (in heavy equipment or high traffic areas), and. PPE will be upgraded as necessary in accordance with HASP guidelines.

5.2 Monitoring Well Sampling

Groundwater samples may be collected in accordance with the USEPA Low Flow Groundwater Sampling guidance (USEPA, 1996) as summarized in EHS Support SOP-43: Low Flow Groundwater Sampling or EHS Support SOP-44 Volume-Purge Method of Groundwater Sampling as included in **Appendix C** and identified in the QAPP (**Appendix D** The water level in the well will be measured prior to sample collection following the procedures outlined in EHS Support SOP-41: Fluid Level Monitoring (**Appendix C**). Prior to sampling, the following parameters will be monitored until the specified stabilization threshold is achieved:

Water level drawdown	< 0.3 feet
pH	± 0.1 pH unit
Specific conductance	± 3%
Temperature	± 3%

DO	± 10% if DO is > 0.5 mg/L; if DO is < 0.5 mg/L, three consecutive measurements are considered stabilized.
Turbidity	± 10% for values greater than 5 Nephelometric turbidity unit (NTU)
ORP/Eh	± 10 millivolts

The parameters will be monitored using a flow cell with a volume no greater than 300 milliliters, and readings will be taken every 5 to 6 minutes until stabilization is achieved. Groundwater samples will be collected following stabilization from a point ahead of the flow cell. A positive-displacement bladder pump with disposable bladders, a Geotech controller, and Teflon® lined polyethylene tubing not greater than 3/8-inch inner diameter (1/4-inch inner diameter is preferred). Groundwater samples will be collected from least to most impacted wells (as applicable). Each sample will be collected from below the elevation of the LNAPL as measured by a dual phase level indicator prior to sampling. For wells where NAPL is present, disposable bailers may be used to purge and sample the wells. Water quality parameters described above will be collected from bailed wells at the beginning, in the middle, and at the end of purging and prior to sampling unless to do so would damage field equipment due to potential exposure to LNAPL. Water samples for laboratory analysis will be filtered in the field using a 0.45-micron filter.

5.3 Instrument Calibration

Field instruments used to collect data will be calibrated following manufacturer specifications and checked at least daily against a known standard prior to the commencement of use (if applicable). Calibration records will be transcribed on field forms or in logbooks. Directions on the use, calibration, and tracking for standard field equipment is provided in EHS Support SOP-08: Field Equipment Operation and Calibration (**Appendix C**), and for specialized equipment for NSZD rate determination in the QAPP (**Appendix D**).

5.4 Management of Investigative-Derived Waste

Waste materials generated through the completion of the investigation will be managed in accordance with Resource Conservation and Recovery Act (RCRA) waste regulations (Sections 22a-44I0-100 through -119, incorporating 40 CFR 124 and 40 CFR 260 to 279) including any hazardous waste or free product. General guidance for managing investigation derived waste is provided in EHS Support SOP-07: Investigation Derived Waste Management (**Appendix C**).

Waste will be placed into a recovery drum used in the solar sipper system. The purge water will then be pumped through the wastewater system at Limetree Bay terminals along with the other fluids recovered by the solar sippers.

5.5 Decontamination Procedures

To reduce the amount of cross contamination, dedicated or disposable equipment will be used when possible. Disposable equipment, including PPE, will be containerized and managed as investigation derived waste. Non-dedicated and/or non-disposable sampling equipment used will be decontaminated,

in accordance with the QAPP (**Appendix D**), prior to and after completion of the sampling activities at the Site.

The procedures for equipment decontamination will vary according to the type of equipment and equipment use. The objective of decontamination is to minimize the potential for cross-contaminating samples and media during the implementation of investigative activities. High-pressure and high-temperature water may be used to decontaminate downhole equipment. Downhole drilling equipment, and non-dedicated sampling or monitoring equipment (including flow through cells for water quality measurements) may also be cleaned manually (with appropriate use of PPE) using the following steps:

1. Remove as much of the affected media or, if present, visible contamination from the non-dedicated equipment, as possible prior to washing.
2. Wash the contaminated sampling and monitoring equipment with a non-phosphate detergent (i.e., Alconox or Liquinox) and tap water.
3. Rinse with tap or potable water.
4. Rinse with distilled water.
5. Air-dry to the extent practical on plastic sheeting (or equivalent) to ensure equipment remains decontaminated.

Following groundwater sample collection, pumps will be decontaminated using a detergent wash and distilled water rinse as outlined in EHS Support SOP-09: Field Equipment Decontamination (**Appendix B**). Decontamination fluid and spoils will be managed as investigation derived waste.

5.6 Groundwater Sample Collection, Labeling, Packaging, and Shipment

Groundwater samples will be collected from each monitoring well in accordance USEPA Low Flow Groundwater Sampling guidance (USEPA, 1996), and the QAPP (**Appendix D**). Certified commercially clean sample containers will be obtained from the contract analytical laboratory, in accordance with the QAPP (**Appendix D** Sample containers will be filled to minimize or eliminate headspace when capped. The sample volume, container type, preservative, and holding time (from the point of collection) for the analyses conducted in this work plan are listed in **Table 3**, attached**.**

Every sample container will be labeled with the following information:

- Site identification
- Sample identification
- Sample date and time
- Sampler's initials

Sample labels will be a unique alphanumeric label based on the well ID. Groundwater samples collected from each monitoring well will be identified using the following alphanumeric sequence: Well ID (e.g., VW2).

Sample containers will be checked for tightness as a measure of additional security and placed in re-sealable plastic storage bags. Samples will be placed upright and secured in a cooler containing ice packs to maintain the acceptable temperature range. Coolers will be shipped or transported by courier, and traceable by chain-of-custody (C-O-C) until analyzed or disposed of by the laboratory.

5.7 Quality Assurance and Quality Control Samples

The following groundwater QA/QC samples may be collected during the field investigation, as specified under each task in **Section 4.3**:

- Field duplicate (DUP) sample
- EB sample
- FB sample
- TB sample

QA/QC samples will be collected in general accordance with USEPA Groundwater Sampling Guidelines for Superfund and RCRA Project Managers guidance (USEPA, 2002b), SOP-12 (**Appendix C** and the QAPP (**Appendix C**). Field duplicate, EB, and TB samples will have unique identifiers that will be distinguishable from the normal sample label scheme (e.g., VW2-DUP, EB-01, or TB-01). QA/QC samples for potential Li-COR and/or passive CO_2 traps are discussed in the respective sections of **Section 4.3**, and passive trap (E-flux) laboratory analytical procedures and quality assurance documentation is provided in **the QAPP (Appendix D**).

5.7.1 Field Duplicate Samples

A field duplicate is a second sample collected at the same location as the original sample. Field duplicate samples are used to assess field and analytical consistency, and sample homogeneity, which includes variability associated with both the sample collection procedures and laboratory analysis. Field duplicate samples will be collected simultaneously with, or in immediate succession from, the original samples. Field duplicate samples will be collected using identical recovery techniques, and treated in an identical manner during storage, transportation, and analysis. The prescribed field duplicate sample is listed on **Table 3: Groundwater Sampling and Analysis Plan**

As per the QAPP (**Appendix D**), one duplicate will be collected per event. Duplicate samples will have the same ID as the original sample and will be qualified with "-DUP".

5.7.2 Equipment Blank Samples

EB sample will be collected during sampling event to evaluate potential cross contamination from sampling equipment and to assess the field decontamination process. EBs will be collected at a frequency of one blank per event as per the QAPP (**Appendix D**) on non-dedicated equipment. EBs will be analyzed for the same parameters as the associated soil or groundwater samples. EBs will be collected according to the following steps:

1. Non-dedicated sampling devices will be properly decontaminated prior to EB sample collection.
2. Proper sample containers and an appropriate quantity of analyte-free water (de-ionized or distilled) will be selected.
3. Sample labels will be completed with the appropriate information.
4. Analyte-free water will be slowly poured through or over the sampling device until the sample bottle is filled to the appropriate level.
5. The sample bottle cap will be securely tightened.
6. The sample bottle will be labeled and stored for shipment.

EB samples will be named as follows: "EB" followed by date (e.g., EB01).

5.7.3 Field Blank Samples

Field blanks are prepared by pouring laboratory-supplied analyte-free water from the original container into laboratory‐supplied sample bottles in the field between sampling locations. These samples will be clearly identified as field blanks on sample labels and in the C-O-C Record(s). These blanks are prepared to ensure that contamination of samples is not occurring from the sampling activities. A minimum of one field blank for each sampling event is required. FB samples will be named as follows: "FB" followed by date (e.g., FB01) (**Table 3**, attached).

5.7.4 Trip Blank Samples

A water sample trip blank is required for every event where water samples are collected for VOC analysis. At least one sealed preserved (or unpreserved if appropriate) 40 milliliter (mL) VOA vial will be transported to the field. These trip blanks will be handled and treated by sampling personnel in the same manner as the water samples collected for purgeable organic compounds analysis on that particular sampling event. These samples will be clearly identified on sample labels and C-O-C Records as trip blanks.

Any contaminants found in the trip blank could be attributed to:

- Interaction between the sample and the container;
- Contaminated rinse water; or,
- A handling procedure that alters the sample analysis.

TB samples will be named as follows: "TB" followed by date (e.g., TB01) (**Table 3**, attached).

5.8 Laboratory Analysis

Groundwater samples will be analyzed for geochemical parameters at ALS Environmental located in Houston, Texas. Analysis of soil gas samples will be conducted by E-Flux in Fort Collins, Colorado. The full list of analytes is provided in **Table 3** Groundwater Sampling Plan (attached)**.**

5.9 Soil Gas Sampling

Based on the results of the Phase 1 Assessment, soil gas samples will be collected from each location in accordance with E-Flux Fossil Fuel Trap SOP or the LICOR LI-7810 sampling procedure, as applicable, located in the QAPP (**Appendix D**). LICOR soil gas sampling will be conducted using the field meter model LI-7810 or equivalent.

5.10 Sample Documentation and Management

Samples collected for laboratory analysis will be handled and managed in accordance with C-O-C procedures, as described in QAPP (**Appendix D**). C-O-C forms will be completed for samples submitted to the laboratory for analysis. The form will include, at a minimum, the following information:

- Site identification

- Site contact person and phone number
- Sampler's name (include names for all samplers)
- Sample identification, location, time, and date
- Identification of QA/QC samples
- Analyses requested
- Number of samples
- Reporting requirements

A completed C-O-C form will accompany samples from the field to the laboratory to document sample transfer and handling. Upon transfer of custody, the number and condition of the samples and the information on the C-O-C form will be verified, then the C-O-C form will be signed by the party releasing the samples and the party receiving the samples. As typically provided by the laboratory, a copy of the C-O-C form will be kept with the sampler for documentation of samples and placed in the project file.

5.11 Project Documentation

Field activities will be recorded and documented in a field notebook and/or appropriate digital forms, in accordance with EHS Support SOP-04 (**Appendix C**). Information recorded will include the date and time activities are performed, weather observations, names of field personnel and Site visitors present, descriptions of the field activities performed, and field observations and measurements made.

Field form and logbook entries will be made in indelible and waterproof ink, and corrections to entries, if needed, will be made by single line strike-through marks. Corrections will be dated (if the occurrence is not the original record date) and initialed by the author. Copies of forms and logbooks will be kept in the project file.

6 Data Quality Evaluation and Usability Assessment

Analytical performance objectives based on analytical methods published by the USEPA to describe QA/QC procedures that ensure laboratories provide data of a known and documented quality will be applied to products of this study. As outlined in the 2021 QAPP (**Appendix D**), this objective will be achieved by requiring the laboratory to provide QA/QC methodologies, personnel qualifications, analytical methods, and holding times and a narrative that accompanies each laboratory report.

Project-specific DQOs will be communicated to the laboratory to ensure that laboratory reporting limits (RLs) are at or below the USEPA approved Minimum Action Levels. Data quality assessment and data usability evaluations (DQA and DUE) will be performed upon receipt of laboratory data by EHS Support to identify QC non-conformances, and to determine that the quality of analytical data is sufficient for the intended purpose. DQA and DUE packages will be prepared for all analytical environmental data associated with the present work. Specific details of the DQA and DUE will be followed according to the QAPP **Appendix D**).

7 Deliverables and Schedule

The proposed schedule is subject to change based on weather conditions, personnel availability, and USEPA approvals. Our intended plan for the Phase 1 work is to sample in June 2021, evaluate results during the third quarter of 2021, and then upon EPA approval implement Phase 2.

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Tables

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State the Problem:	•It is unknown if LNAPL NSZD is occurring at the St. Croix Alumina site. •The rates of LNAPL NSZD in the vadose zone and saturated zone at the St. Croix Alumina site are unknown.

Identify the Decision:	•The primary study question is: "What is the magnitude of NSZD mass losses at the site". •The alternative action is: "Potential pursuit of a NSZD remediation strategy". •The decision statement is: "Determine if an initial NSZD mass loss estimates support that a NSZD strategy is the most effective use of resources that is also protective of human health and the environment at the site".

Relevant Workplan Section	Goal	Information Inputs	Boundaries of the Study	Analytical Approach	Performance Criteria/Limits on Decisions	Optimize the Design	Anticipated Advantages	Potential Challenges
Phase 1								
4.1.2, 4.3.4	Obtain qualitative data to identify if vapor-phase NSZD is occurring in the vadose zone above the known extent of LNAPL at the site.	Well headspace gas (CH_4, CO_2, and H_2S) measurements from 1-foot above the liquid level in wells with well annulus covered using a calibrated hand-held gas meter.	A single data collection event at upgradient, source area, and downgradient monitoring wells specified on Table 3.	Gas concentrations in wells where LNAPL is present will be compared to upgradient and/or side gradient locations.	The threshold for a positive result will be a value that exceeds the instrument precision and accuracy thresholds as specified by the manufacturer and outlined in the UFP-QAPP Worksheets 22 & 24. A parametric one-way ANOVA statistical test will be used to determine if differences are statistically significant. Absence of a statistically significant difference may not imply the absence of NSZD and may indicate high background gas cocnetrations, thus, multiple lines of evidence must be used to support decisions.	The magnitude of background gas concentrations will factor into the decision to move into Phase 2, and the decision for methodology selection and optimization of Phase 2 • Data may indicate that background corrections to source area gas concentrations are needed/not needed. • Data may support decisions on the location, duration, and deployment density of in situ soil gas flux measurement devices deployed in Phase 2. • Data will be used to identify locations with favorable/unfavorable aqueous NSZD conditions	• Provides a rapid, cost effective screening method to confirm if NSZD is occurring. • Provides a baseline to assess effectiveness of soil gas measurement techniques deployed in Phase 2.	• Headspace gases may be affected by the carbonate lithology, which conceivably contributes to the background CO_2 soil gas flux. • Gas concentrations may be affected by municipal effluent or natural degradation of organic matter. • Instantaneous measurement that does not integrate temporal variations of soil gas flux.
4.1.1, 4.3.2, 4.3.3	Obtain qualitative data to identify if NSZD is occurring in the saturated zone beneath and downgradient of the known extent of LNAPL at the site.	Groundwater samples analyzed for cations, anions, nitrogen, ammonia, methane, sulfate, sulfide, carbon dioxide, total and dissolved iron and manganese.	A single data collection event at upgradient, source area, and downgradient monitoring wells specified on Table 3.	Depletion/accumulation of terminal electron acceptors and NSZD byproducts will be compared between locations where LNAPL is present and upgradient/side gradient locations.	The threshold for a positive result will be a value that exceeds precision as evaluated from the RPD of a primary and duplicate sample, and accuracy as specified in the UFP-QAPP worksheets 22 & 24. Absence of a statistically significant difference may not imply the absence of NSZD and instead indicate complexities in site hydrogeology.	The magnitude of concentration differences will factor into the decision to move into Phase 2. • Data may support decisions on the location, duration, and deployment density of in situ soil gas flux measurement devices deployed in Phase 2. • Data will be used to identify locations with favorable/unfavorable aqueous NSZD conditions.	• The same dataset may be used to directly calculate quantitative NSZD rates.	• Results may be affected by timing of sampling relative to the tidal cycle, or a rapid recharge during a major precipitation event that is not representative of typical site conditions.
		Field parameters (ORP, DO, temperature) measured on groundwater samples.	A single data collection event at upgradient, source area, and downgradient monitoring wells specified on Table 3.	Field parameters of groundwater from beneath LNAPL in the source area will be compared to upgradient and/or side gradient locations.	The threshold for a positive result will be a value that exceeds the instrument precision as specified by the manufacturer, and accuracy as determined by measurement of standard solution as as specified in the UFP-QAPP worksheets 22 & 24.	• Data may support decisions on the location, duration, and deployment density of in situ soil gas flux measurement devices deployed in Phase 2. • Data will be used to identify locations with favorable/unfavorable aqueous NSZD conditions.	•Field parameters are already measured at several locations during routine groundwater sampling events. •Cost effective and readily available technique.	•Hydrogeologic variability and complexity, such as tidal flushing may lead to unrepresentative readings. •Potential interferences from dissolved gases (particularly CH_4, H_2S). •Redox disequilibrium may yield DO values that are not representative of *in situ* conditions.
4.1.3 and 4.3.5	Obtain qualitative data to identify NSZD in the saturated and vadose zone at the site.	Temperature profiles measured in the vadose zone 1 foot above liquid, midway between groundwater and ground surface, and 1 foot below ground surface using a thermocouple. Groundwater 1 foot below the interface with LNAPL, 5 feet below the interface, and 10 feet below the interface.	A single data collection event at upgradient, source area, and downgradient monitoring wells specified on Table 3.	Temperature data from wells where LNAPL is present will be compared to upgradient and/or side gradient locations.	The threshold for a positive result will be a value that exceeds the instrument precision as specified by the manufacturer, and accuracy as specified in the UFP-QAPP worksheets 22 & 24. Absence of a difference may not imply the absence of NSZD and instead reflect soil properties, thus, multiple lines of evidence must support decisions.	The magnitude of temperature differences between source-zone and background locations will factor into the decision to move into Phase 2. • The magnitude of data variability may support decisions on the locations and grid density of methods employed during Phase 2. • Data will be used to identify locations with favorable/unfavorable NSZD conditions.	•Relatively small diurnal, seasonal, and background temperature fluctuations due to the tropical climate will minimize climate-related uncertainties. •Temperature difference accounts for vapor phase mass depletion, which is the dominant fraction of NSZD.	•Hydrogeologic variability and complexity may obscure temperature anomalies in locations with high hydraulic conductivity, tidal flux, or groundwater mixing. •Affected by groundwater recharge zones, which may be identified using general geochemistry and field parameter measurement assessment. •May be variable in areas of geologic complexity, and require assessment of thermal gradients in each unique geologic environment.

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Relevant Workplan Section	Goal	Information Inputs	Boundaries of the Study	Analytical Approach	Performance Criteria/Limits on Decisions	Optimize the Design	Anticipated Advantages	Potential Challenges
4.1.1 and 4.3.6	Use data to quantitatively determine aqueous-phase NSZD rates in the saturated zone at the site.	Groundwater samples analyzed for cations, anions, nitrogen, ammonia, methane, sulfate, sulfide, carbon dioxide, total and dissolved iron and manganese.	The same samples and data used to provide qualitative evidence for aqueous-phase NSZD.	Assess changes in electron acceptors in up- and down-gradient wells to calculate aqueous phase LNAPL NSZD mass depletion rates using the methods described in the relevant workplan section.	Data will only be used if the data is deemed usable following QQA/QC as specified in the UFP-QAPP worksheets 22 & 24. Rates will only be calculated using data that show a difference between source and background locations that exceeds analytical precision as determined by comparison of a primary and duplicate sample.	The magnitude of concentration differences will factor into the decision to move into Phase 2. • The magnitude of data variability may support decision on the locations and grid density of methods employed during Phase 2. • Data will be used to identify locations with favorable/unfavorable aqueous NSZD conditions.	•Existing monitoring well network provides access, and sampling can be readily piggy-backed with existing field monitoring/sampling events.	• Variability of electron acceptor concentrations may be affected by the presence/absence of evaporites (e.g. gypsum). • Results may be affected by sheen or LNAPL globules entrained in samples. • Impacts from effluent or tidal flushing with sea water may obscure electron acceptor concentrations. • Accounts for aqueous mass depletion only, which is a fraction of the overall mass depletion.
4.1.1, 4.3.1	Verify and validate current LNAPL CSM by assessing the spatial distribution of different groundwater types (e.g. perched) in the context of site geology, and identify potential groundwater recharge areas that may affect temperature profile results.	Groundwater samples analyzed for cations, anions, nitrogen, ammonia, methane, sulfate, sulfide, carbon dioxide, total and dissolved iron and manganese.	The same samples and data used to provide qualitative evidence for aqueous-phase NSZD.	Data will be assessed by comparing results from the source area to upgradient and/or side gradient locations using the method in the relevant section of the workplan.	Data will only be used if the data is deemed usable following QA/QC as specified in the UFP-QAPP worksheets 22 & 24. The threshold for a positive result will be a value that exceeds precision as evaluated from the RPD of a primary and duplicate sample.	The results will help better understand the source of the groundwater mound focused at GM-22, and help refine groundwater contour maps. The data will aid in confirming the stability of the LNAPL plume and utility of a NSZD approach.	• Piper, concentration and ion ratio plots are a robust means to identify hydrological variability due to the presence of different water types (e.g. background groundwater, municipal effluent, sea water), or variations in groundwater hydrogeochemistry due to different recharge loci.	• Results may be affected by timing of sampling relative to the tidal cycle, or a rapid recharge during a major precipitation event that is not representative of typical site conditions.
4.1		Gauge groundwater at GM-13D (simultaneously with other site wells).	A single data collection event.	Use data to update groundwater contour maps.	Data will only be used if requisite top of casing elevation data are available.	The outcome of contours will affect decisions about the effectiveness of NSZD, through consideration of LNAPL plume stability.	•Inexpensive data point that will provide large value in refining groundwater contours.	•Well may be inaccessible, or affected by local conditions that are not reflective of the site groundwater system.
		Sample well GM-22 for cations, anions, nitrate, and alkalinity.	A single data collection event coinciding with collection of the same parameters at other site wells for aqueous NSZD characterization.	Data will be plotted on a Piper diagram to identify if a distinct water type to groundwater at the site is present.	Data will only be used if the data is deemed usable following QA/QC as specified in the UFP-QAPP worksheets 22 & 24. The threshold for a unique source will be component concentration values that exceeds precision as evaluated from the RPD of a primary and duplicate sample.	The outcome of the groundwater contour revision will affect decisions about the effectiveness of NSZD as a strategy, through consideration of effects of the groundwater system on stability of the LNAPL plume.	•Similar data are to be collected from other site wells, so a unique mobilization or sampling plan does not need to be developed.	•Groundwater in this location may be compositionally indistinguishable from other locations that are recharging the site.
Phase 2								
4.2.1.1		Time-integrated soil gas (CO_2) flux measurements using passive traps.	A single deployment. Grid extent and spacing to be informed by results of Phase 1 work.	Methods are described in McCoy et al. (2014). Gas traps will be provided and analyzed by E-FLUX (www.soilgasflux.com). Carbon traps will be analyzed for: • ASTM D4373-14, Rapid Determination of Carbonate Content of Soils • ASTM D6866-18, Determination of the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis (includes carbon stable isotope analysis).	Key quality control measures include: • Collection of data from background locations and comparison to source area locations with consideration of analytical precision. • Analysis of a trip blank and comparison to source area results with consideration of analytical precision. Results will be considered reflective of NSZD rates if concentration thresholds are greater than the analytical precision and accuracy thresholds as determined by the vendor and specified in the UFP-QAPP worksheets 22 & 24.	Given the stable climate and limited seasonal variability, a single deployment is adequate to address the decision statement.	•Deployed for a period of time, therefore, integrate effects of all processes that contribute to temporal flux variability.	•Affected by gas contributions from soil organic matter degradation. •Site conditions (e.g. gravel, concrete) may affect gas (e.g. O_2) readings requiring additional stoichiometric conversions. •Carbonate lithology presents an alternate fossil CO_2 source that must be resolved from the LNAPL contribution using non-standard techniques. •May be prohibitively expensive if Phase 1 results indicate substantial geological/hydrochemical variability and a tight grid spacing is needed. •Expensive analysis, and calculations typically performed by labs that may not be familiar with corrections for carbonate lithology sites.

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Relevant Workplan Section	Goal	Information Inputs	Boundaries of the Study	Analytical Approach	Performance Criteria/Limits on Decisions	Optimize the Design	Anticipated Advantages	Potential Challenges
4.2.1.2	Obtain quantitative data to calculate vapor-phase NSZD rates in the vadose zone at the site.	Instantaneous soil gas flux (CH_4, CO_2) measurements using a dynamic closed chamber system (LI-COR meter model # LI-7810SC).	A single deployment. Grid extent and spacing to be informed by results of Phase 1 work.	Methods are described by Shiota et al. (2011). NSZD rate calculations are automated with the software supplied by LI-COR.	A key quality control measure will be analysis of a collar with a bottom cap installed to collect a field blank (FB). The chamber is used to obtain 60 measurements from the FB. The detection limit is calculated as the average + 3 times the standard deviation of the 60 FB measurements. Locations where gas flux is below the limit of detection will be considered in the context of localized hydrogeological/hydrogeochemical variations before determining the result is null for NSZD. Details are specified in the UFP-QAPP worksheet X.	Given the stable climate and limited seasonal variability, a single deployment is adequate to address the decision statement.	•Portable meter useful for multiple deployments or dense sampling grid network. •Established and robust method utilized in numerous NSZD evaluations elsewhere. •Rapid analysis with real-time data read out.	•Expensive up-front investment for equipment. •Does not directly distinguish contributions from different carbon sources (i.e. limestone, modern organic matter degradation in soil) and requires study of a large number of background locations. •Provides a snap-shot measurement that does not account for diurnal and temporal variations in gas flux. •Requires 3 sequential readings within an acceptable % threshold, which may prove challenging in complex settings.
4.2.2, 4.3.8		Measure soil gas (CH_4, CO_2, and H_2S) gradients in deep, intermediate and shallow levels of the vadose zone using a calibrated hand-held gas meter.	Install soil vapor probes at a density determined by the results of Phase 1 in source area and background locations at intermediate and shallow levels in the vadose zone. Use co-located and existing monitoring wells to obtain gas samples from the deep vadose zone. A single measurement event.	Procedures to calculate gas fluxes will leverage Fick's first law of diffusion and are described in Section 4.3.8 of the workplan. A key consideration will be subtraction of background gas concentrations.	The threshold for a positive result will be a value that exceeds the instrument precision and accuracy as specified by the manufacturer and outlined in the UFP-QAPP worksheets 22 & 24. A parametric one-way ANOVA statistical test will be used to determine if differences are statistically different between source area and background wells.	Given the stable climate and limited seasonal variability, a single deployment is adequate to address the decision statement. Defining future paths forward are beyond the scope of the proposed study.	•Portable meter useful for multiple deployments or use in a dense sampling grid network. •Established and robust method utilized in numerous NSZD evaluations elsewhere. •Rapid analysis with real-time data read out.	•Expensive up-front investment for installation of nested sampling points. •Does not directly distinguish contributions from different carbon sources (i.e. limestone, modern organic matter degradation in soil) and requires study of a large number of background locations. •Provides a snap-shot measurement that does not account for diurnal and temporal variations in gas flux.
4.2.1.2	Obtain quantitative data to correct for interferences that may overestimate NSZD rates.	Radiogenic carbon isotope (^{14}C) measurement of CO_2 in gas traps.	A select number of the gas trap samples polaced at a density informed by the results of Phase 1 work. A travel blank sample, a control sample, at minimum 3 background samples.	Comparison of the radiogenic carbon content between source area and background well locations.	Background correction for natural organic matter will be deemed unnessecary if radiogenic carbon content is within precision and accuracy limits(as specified by the lab and outlined on the UFP-QAPP Worksheets 22 & 24) between source area and background locations.	Results will provide confidence in NSZD rate estimates by accounting for contributions from processes other than NSZD.	•Is the gold standard for correcting CO_2 from modern sources and LNAPL NSZD. •Is a robust correction if there are no unimpacted areas for trap deployment to quantify background CO_2, if background locations have highly variable CO_2 flux, and if background locations have different natural processes (i.e. vegetation microbial activity) than impacted locations (McCoy et al. 2015). •May be used in conjunction with Lycor meter CO_2 measurement, should phase 1 results indicate passive trap method is prohibitively expensive due to the need for a tight grid spacing.	• A site with low ambient pH (> ~4.8) and considerable limestone ($CaCO_3$) may be a poor candidate for applying this technique as ancient carbonate deposits might dissolve at low pH and bias the analysis (Boyd et al., 2016). • Limestone lithology requires non-radiogenic ($\delta^{13}C$) data in addition, which may or may not identify limestone carbon contribution.

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Relevant Workplan Section	Goal	Information Inputs	Boundaries of the Study	Analytical Approach	Performance Criteria/Limits on Decisions	Optimize the Design	Anticipated Advantages	Potential Challenges
		Stable carbon isotope ($\delta^{13}C$) measurement of CO_2 in gas traps	Gas trap samples analyzed for ^{14}C	Comparison of the stable isotope ratio of background and source area wells using the approach described in the relevent workplan section	The method will be unnessecary if gases are absent at background locations. Isotopic differences between source area and background locations require values that exceed precision of the analytical method as determined by the laboratory.	Results will provide confidence in NSZD rate estimates by accounting for contributions from processes other than NSZD.	• Marine carbonates typically yield soil CO_2 $\delta^{13}C$ values more than -15 ‰ (VPDB) with small fractionation on conversion to CO_2 at ambient temperatures. In contrast, CO_2 from NAPL and modern soil organic matter degradation typically have $\delta^{13}C$ values less than -25 ‰ (VPDB). The difference may be sufficiently large that the three potential reservoirs can be resolved when assessed in conjunction with ^{14}C.	• Identification of abiotic carbonate weathering requires unimpacted background locations with similar hydrogeochemistry to impacted areas. • Identification of abiotic carbonate weathering from microbial LNAPL mass depletion requires that both processes result in distinctive stable carbon isotope signatures that can be demonstrated with site-specific samples (Coffin et al. 2008).

Notes
CSM = Conceptual site model
DO = Dissolved oxygen
LNAPL = Light non-aqueous phase liquid
NOAA= National Ocean And Atmospheric Administration
FB= Field Blank
QAPP=Quality assurance project plan
RPD = Relative percent difference
NSZD = Natural source zone depletion
ORP = Oxidation reduction potential
VPDB = Vienna PeeDee Belemnite
UFP=Unified Federal Policy

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Table 2
Key Literature References
LNAPL NSZD Work Plan
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Task	Data Use Objective	Key References
Phase 1		
Well headspace readings	Qualitatively assess active vapor-phase NSZD by verifying that CH_4, CO_2, and H_2S gases are present/absent, and identifying where NSZD is occurring spatially.	Sweeney and Ririe, 2017;
General geochemistry, cations, anions, nitrogen, ammonia, methane, sulfate, sulfide, carbon dioxide, total and dissolved iron and maganesese	Qualitatively assess active aqueous NSZD based on electron acceptor depletions relative to background locations.	Wiedemeier et al., 1995; Beck and Mann, 2010
Key field parameters (e.g. ORP, DO, etc.)	Identify locations with favorable aqueous NSZD redox conditions, specifically using dissolved oxygen (DO) and oxidation reduction potential (ORP) measurements	McMahon and Chapelle, 2008; Nordstrom and Wilde, 2005; Jurgens et al., 2009; Wiedemeier et al, 1998
Temperature profiles	Verify NSZD is occurring based on the presence/absence of a thermal response from active microbial LNAPL mass depletion. Calculate vapor phase LNAPL NSZD mass depletion rates.	Sweeney and Ririe, 2014; Warren and Bekins, 2015; Suthersan, 2015; Newell et al., 2016; Garg et al., 2017;
Electron acceptors	Quantitatively assess changes in electron acceptors in up- and down-gradient wells to calculate aqueous phase LNAPL NSZD mass depletion rates.	Wiedemeier et al., 1995; Beck and Mann, 2010
Phase 2		
Soil gas flux measurements using passive CO_2 traps	Provide soil gas flux measurements used to calculate vapor phase LNAPL mass depletion rates.	McCoy et al., 2014
Soil gas flux measurements using lycor meter	Provide soil gas flux measurements used to calculate vapor phase LNAPL mass depletion rates.	Sihota et al., 2011
Radiogenic carbon isotope (^{14}C) measurement of CO_2 in gas traps	Background correction to identify CO_2 from hydrocarbon degradation and modern soil organic matter degradation.	Landmeyerand Stone, 1995; Coffin et al, 2008; McCoy et al., 2014; Schindlbacher et al., 2015; Boyd et al., 2016
Stable carbon isotope ($\delta^{13}C$) measurement of CO_2 in gas traps	Background correction to determine additional potential sources of CO_2, including Kingshill Limestone.	Meckenstock et al., 2004; Nowak et al., 2016
CO_2 Gradient method calculated using Fick's first law of diffusion.	Provide soil gas gradient measurements used to calculate vapor phase LNAPL mass depletion rates.	Sweeney and Ririe, 2014

Notes
DO = dissolved oxygen
LNAPL = light non-aqueous phase liquid
NSZD = Natural source zone depletion
ORP = oxidation reduction potential

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Table 3
Groundwater Sampling and Analysis Plan
LNAPL NSZD Work Plan
St. Croix Alumina Site
St. Croix, U.S. Virgin Islands

Field Sample ID	Rationale for Well Selection	Laboratory Provided Sample IDs	TPH-DRO (SW-846 8015C)	BTEX (SW-846 8260C)	Naphthalene Only (SW8270)	Field Parameters	Alkalinity (SM2320B)	Cations (SW-846 6020A)	Total Fe & Mn (SW-846 6020A)	Anions (Cl and SO_4 by EPA 300.0)	Nitrate and Nitrite (EPA 300.0)	Dissolved Fe and Mn (SW-846 6020A)	Sulfide (SM4500 S2-D)	Ammonia and TKN (SM4500 NH3 B-F/NH3-D)	Methane (RSK-175)	Carbon Dioxide (RSK-175 (ALS Simi Valley)	DOC (SW-846 9060A)
Upgradient Ground Water Samples																	
MMX	Screened across limestone	MMX-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
VW8	Screened across fine-grained deposits	VW8-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
MM9	Screened across alluvium	MM9-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
VW11	Most upgradient site well	VW11-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
Source Area Ground Water Samples																	
VW2	LNAPL is typically present	VW2-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
VW5	LNAPL is typically present	VW5-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
VW6	LNAPL is typically present	VW6-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
VW13	LNAPL is typically present	VW13-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
VW13B	LNAPL is typically present	VW13B-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
VW14	LNAPL is typically present	VW14-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
VW20	LNAPL is typically present	VW20-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
VW20B	LNAPL is typically present	VW20B-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
VW21B	LNAPL is typically present	VW21B-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
VW22	LNAPL is typically present	VW22-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
VW23	LNAPL is typically present	VW23-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
VW24	LNAPL is typically present	VW24-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
VW29	LNAPL is typically present	VW29-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
VW30	LNAPL is typically present	VW30-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
VW31	LNAPL is typically present	VW31-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
VW32	LNAPL is typically present	VW32-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
VW35	LNAPL is typically present	VW35-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
Downgradient Ground Water Samples																	
VW25	Screened across alluvium	VW25-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
VW27	Screened across limestone	VW27-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
VW34	Screened across fine-grained deposits	VW34-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
VW37	Screened across evaporite deposits	VW37-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
GM11	Historically mixed with seawater	GM11-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
GM14	Furthest downgradient point	GM14-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
GM22	Groundwater mound is present	GM22-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
Quality Control Samples																	
EB-01	--	EB-01-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
FB-01	--	FB-01-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
TB-01	--	TB-01-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K
DUP-01	--	DUP-01-yyyymmdd		A		N	B	C		D	E	F	G	H	I	J	K

Table 3
Groundwater Sampling and Analysis Plan
LNAPL NSZD Work Plan
St. Croix Alumina Site
St. Croix, U.S. Virgin Islands

FB = Field Blank (1 per event; pouring clean water directly into lab sample containers)
EB = Equipment Blank (1 per event; non-dedicated and reusable equipment only)
DUP = field duplicate (1 per event)
TB = Trip blank (1 per container of volatile organic compounds which will be consolidated in final shipment)

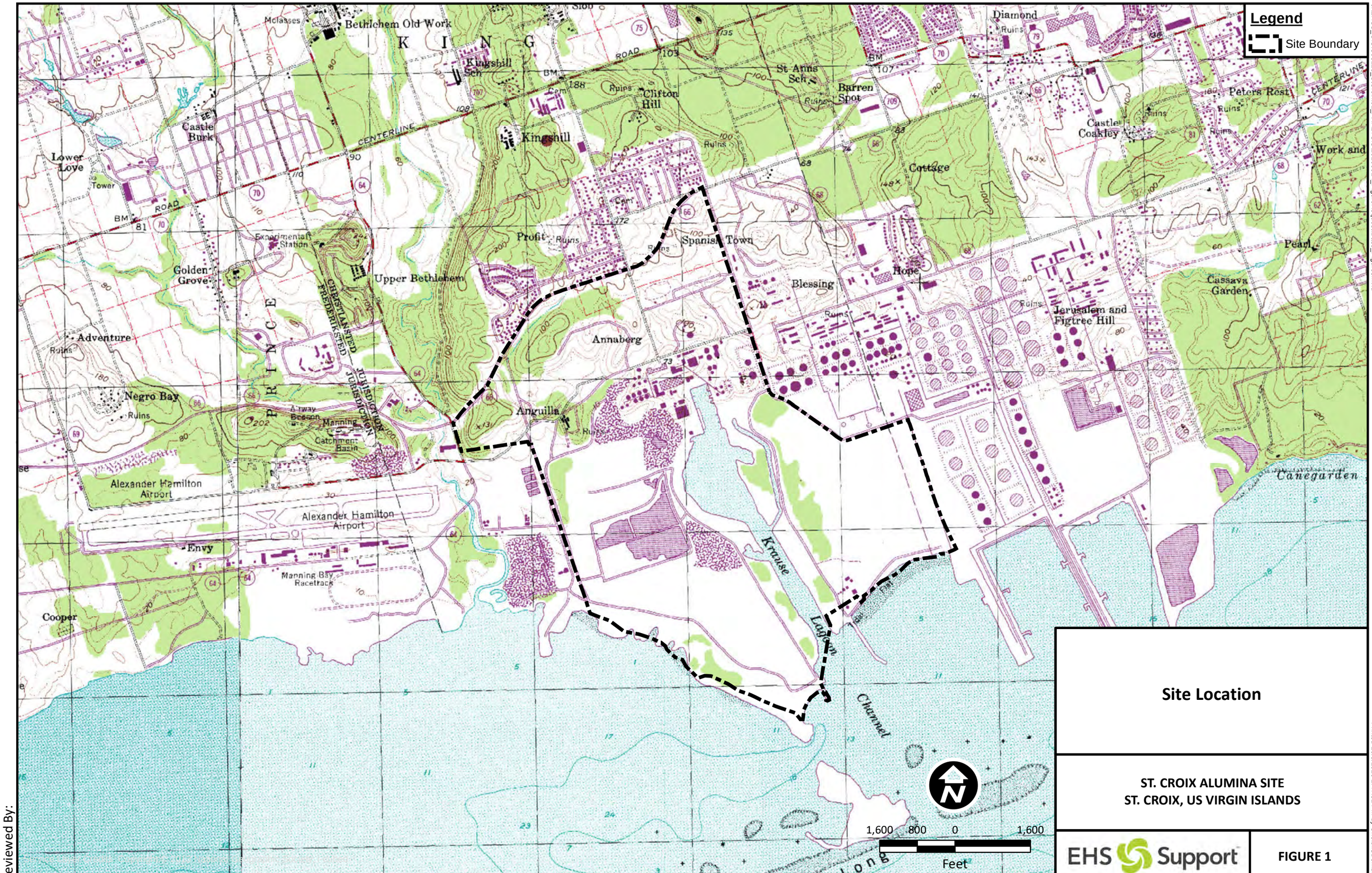
Field Parameters = temperature, pH, conductivity, dissolved oxygen, oxidation reduction potential, turbidity

DOC = dissolved organic carbon
HCl = Hydrochloric acid
HNO_3 = Nitric acid
H_2SO_4 = Sulfuric acid
mL = milliliter
MS = Matrix spike
MSD = Matrix spike duplicate
NA = Not applicable
BTEX = Benzene, toluene, ethylbenzene, xylenes,
TPH-DRO = Total petroleum hydrocarbons - diesel range organics
ZnAc = zinc acetate

Cations = Na, K, Ca, Mg
Anions = Cl, SO_4
Dissolved gases = methane and carbon dioxide

Recommended bottleware
(number of containers) container type - preservative; holding time
A: (3×) 40 ml glass vials - kept ≤6°C and unpreserved; 7 days (14 days for DRO and BTEX if collected in HCl preserved VOAs; do not acidify napthlaene sample)
B: (1x) 250 ml plastic - kept ≤6°C and unpreserved; NO_2 & NO_3 48 hours, Cl & SO_4 28 days, alkalinity 14 days
C: (1x) 120 mL plastic - HNO_3; 180 days
D: (1x) 125 ml plastic - kept ≤6°C and unpreserved; 28 days (halides and sulfate), 48 hours (nitrate, nitrite, phosphate)
E: (1x) 125 ml plastic - H_2SO_4; 28 days. If samples can be analyzed within 48 hours, nitrate and nitrate may be analyzed for from the SO_4 and Cl sample bottle.
F: (1x) 120 ml plastic - field filtered, HNO_3; 180 days
G: (1x) 500 ml plastic - NaOH/ZnAc and kept ≤6°C; 7 days
H: (1x) 250 ml plastic - H_2SO_4 and kept ≤6°C; 28 days
I: (3x) 40 ml glass vials - HCl and kept ≤6°C; 14 days (7 days if unpreserved)
J: (3x) 40 ml unpreserved glass vials - kept ≤6°C; no hold time specified but recommended within 5 days
K: (2X) 40 ml glass vials- filtered and kept ≤6°C, H2SO4; 28 days
N: None - field parameter

Figures



Site Location

ST. CROIX ALUMINA SITE
ST. CROIX, US VIRGIN ISLANDS

EHS Support

FIGURE 1

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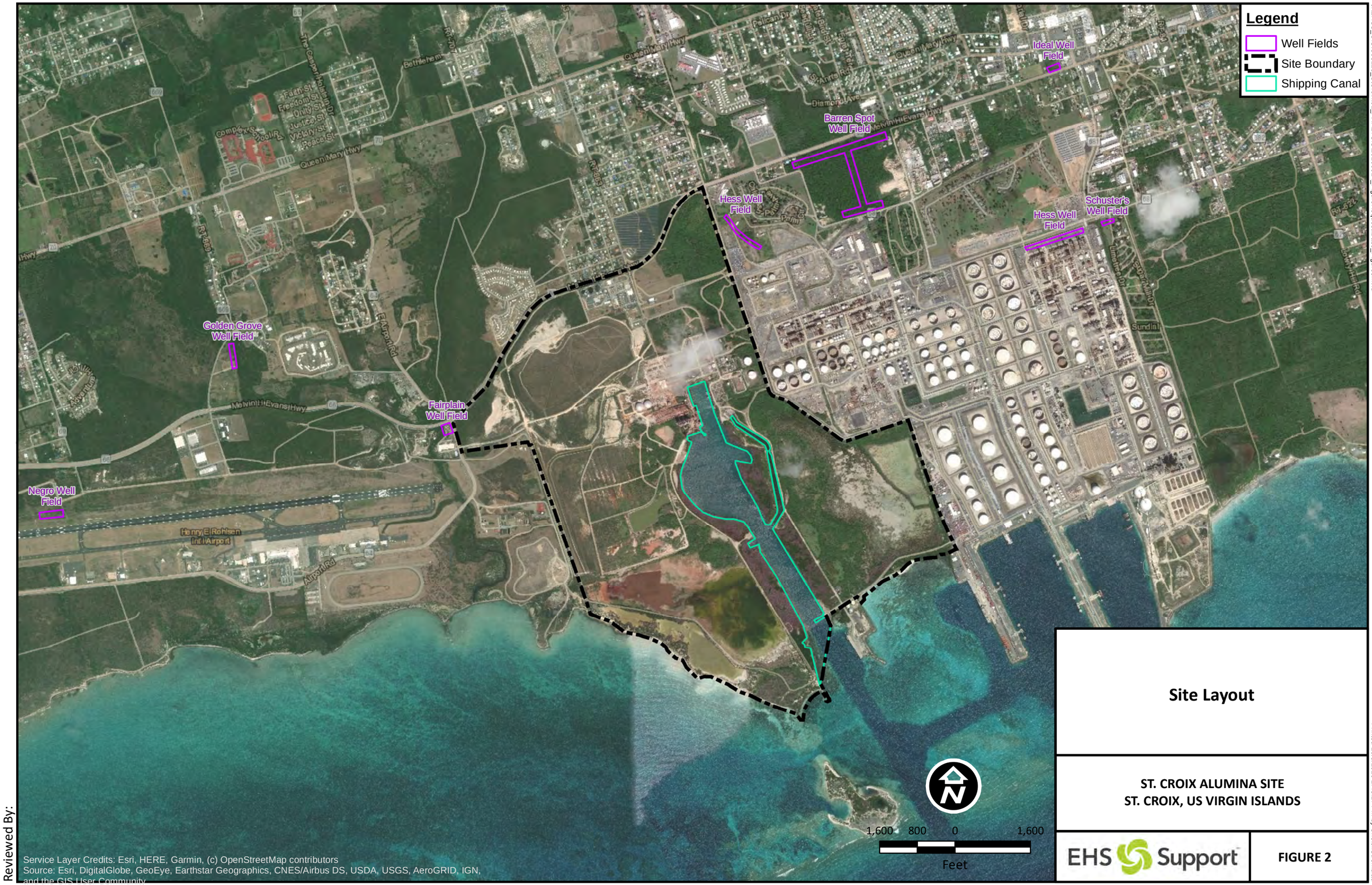

Site Layout

ST. CROIX ALUMINA SITE
ST. CROIX, US VIRGIN ISLANDS

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FIGURE 2

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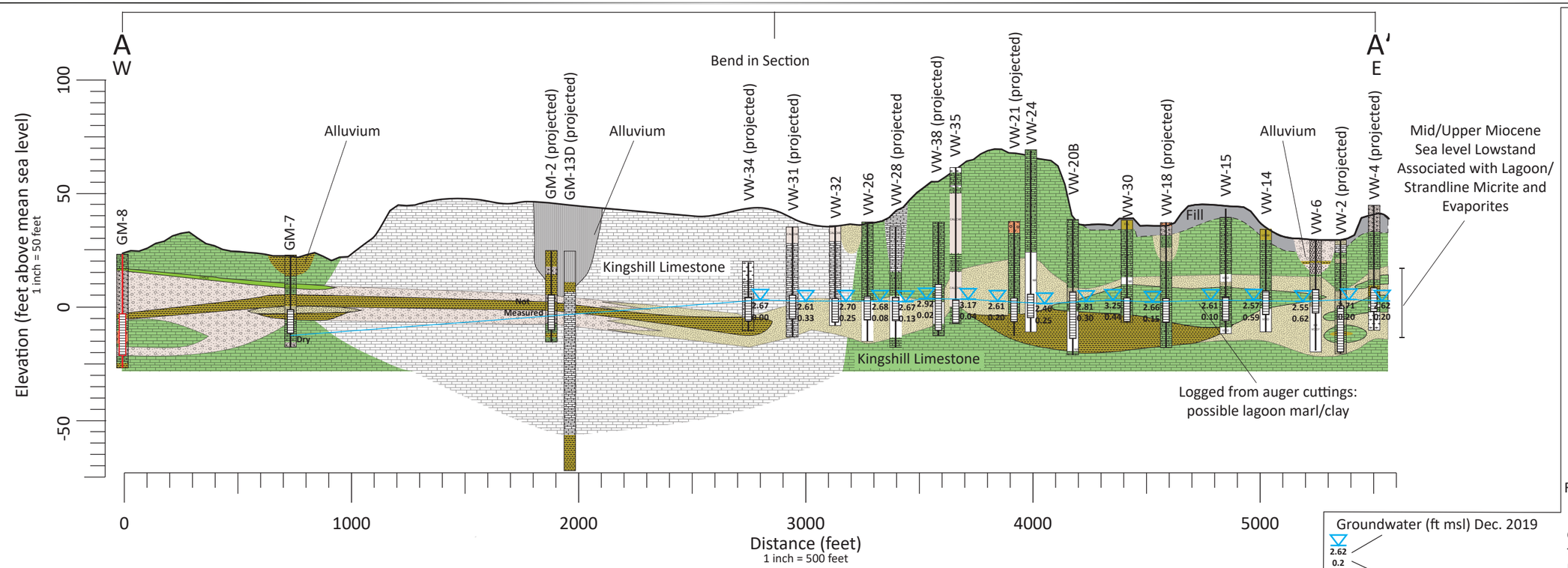


LEGEND

- Limestone
- Weathered Limestone
- Clay
- Clayey Silt
- Silt
- Sandy Clay
- Sand
- Gravel
- Sand and Gravel
- Interbedded evaporite minerals (termed 'caliche' where specific minerals not identified)

Well ID [*Elevation feet msl]

Asterisk indicates ground surface elevation not available; top of casing elevation used.

Borehole

Monitoring Well Screen/ Well Production Zone

Approximate GW elevation

Former well

Existing well

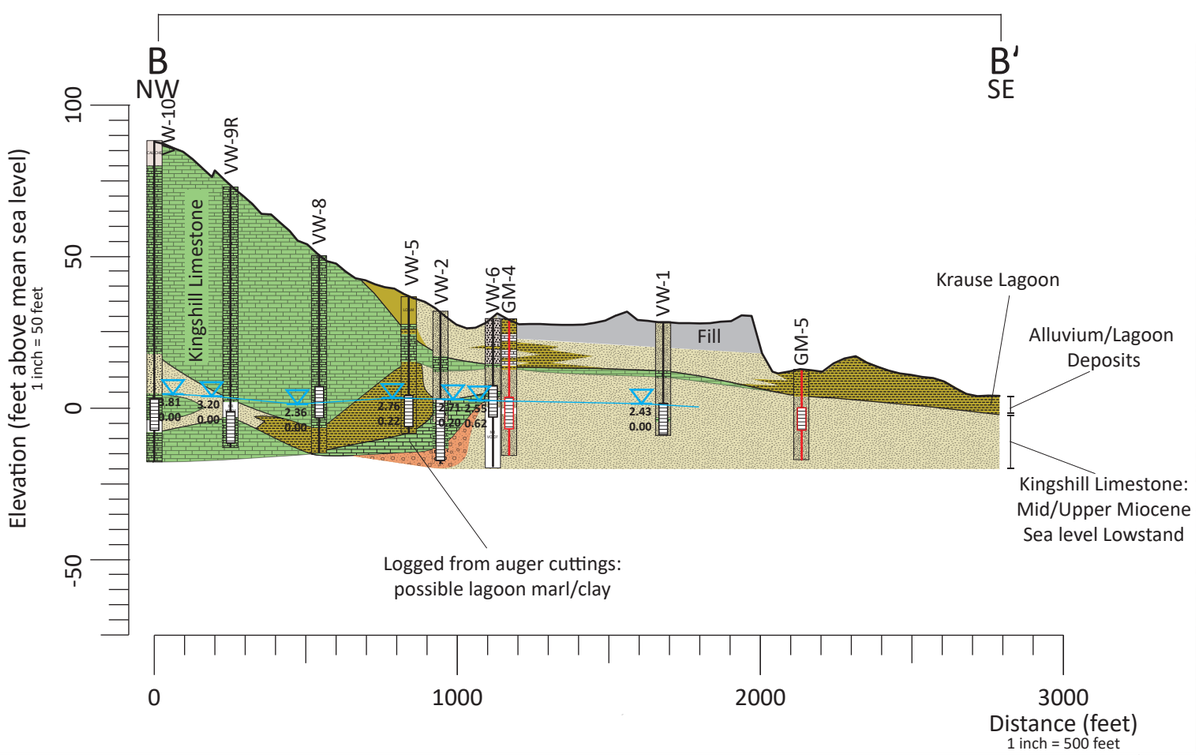
Groundwater (ft msl) Dec. 2019

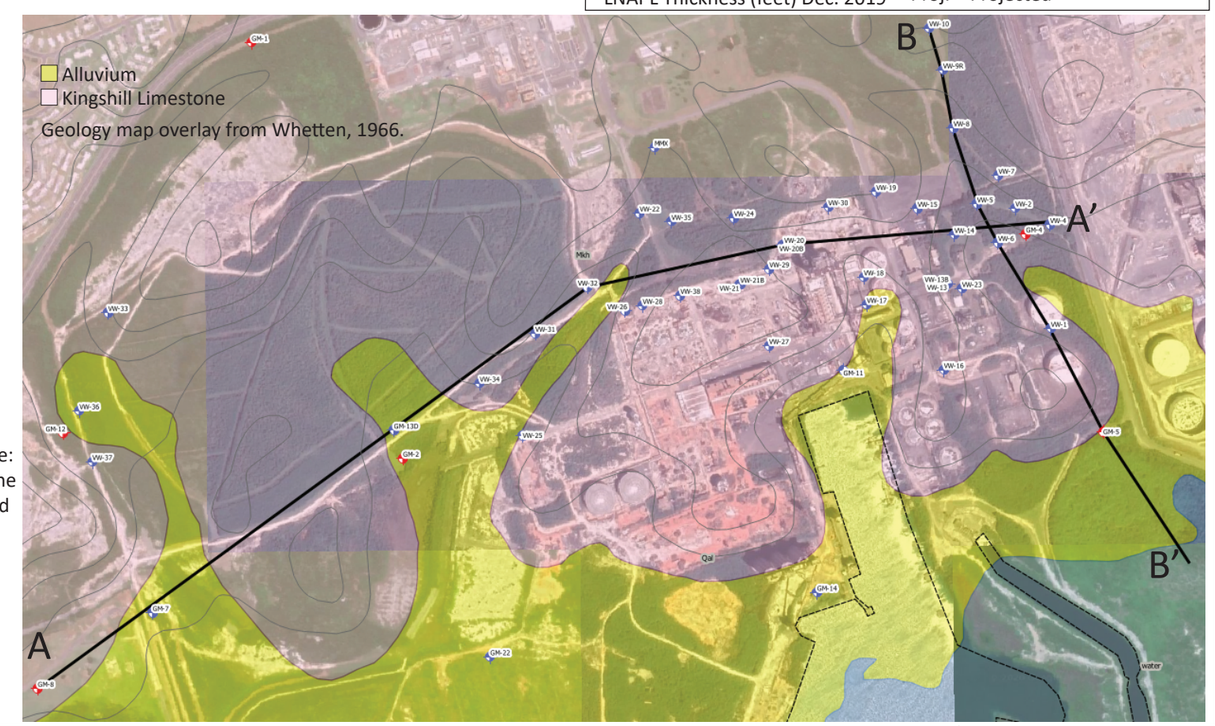
2.62

0.2

LNAPL Thickness (feet) Dec. 2019

GW = Groundwater
ft = feet
msl = mean sea level
Proj. = Projected





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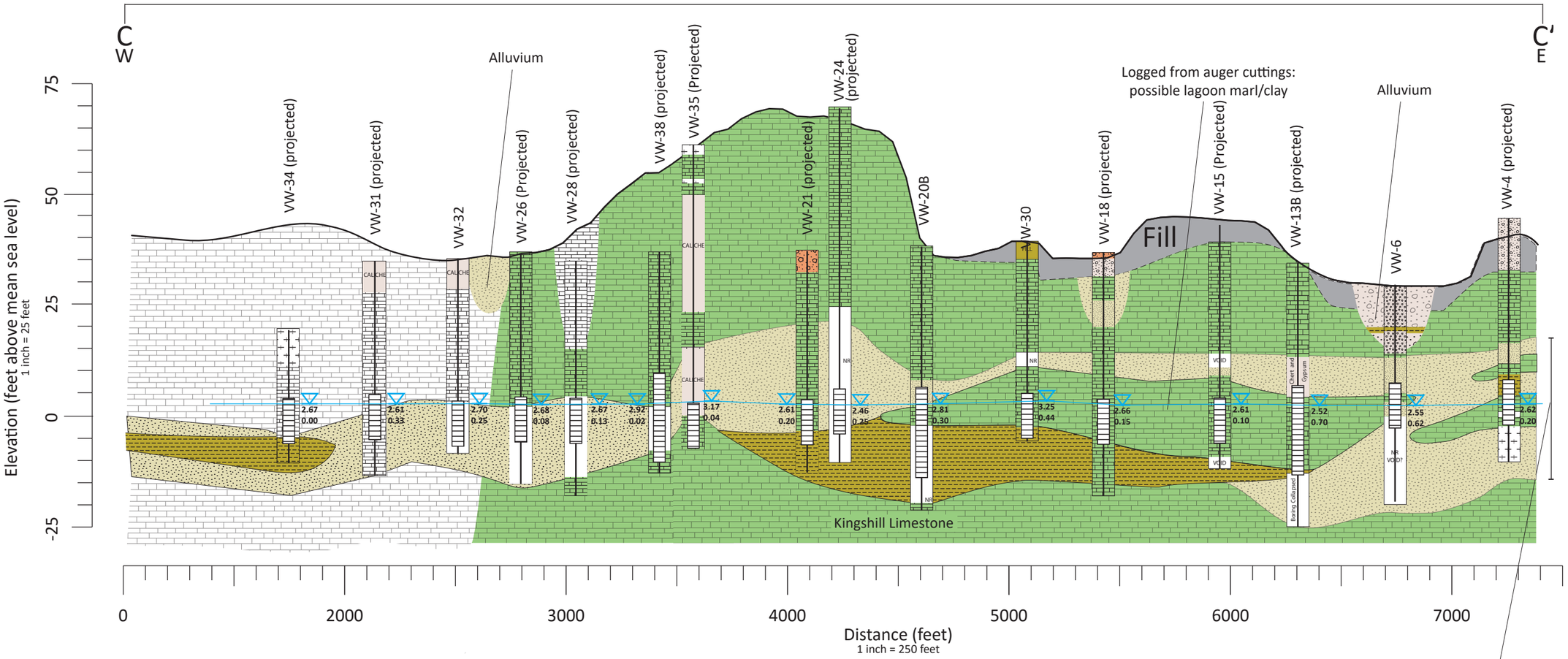
EHS Support

St. Croix Alumina Site
St. Croix, U.S. Virgin Islands

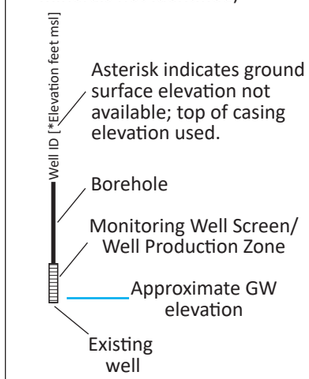
Cross Sections A-A' and B-B'
LNAPL Natural Source Zone Depletion Work Plan

Figure 3A



LEGEND

- Limestone
- Weathered Limestone
- Clay
- Clayey Silt
- Silt
- Sandy Clay
- Sand
- Gravel
- Sand and Gravel
- Interbedded evaporite minerals (termed 'caliche' where specific minerals not identified)



GW = Groundwater
ft = feet
msl = mean sea level
Proj. = Projected

Groundwater (ft msl) Dec. 2019
2.62
0.2
LNAPL Thickness (feet) Dec. 2019

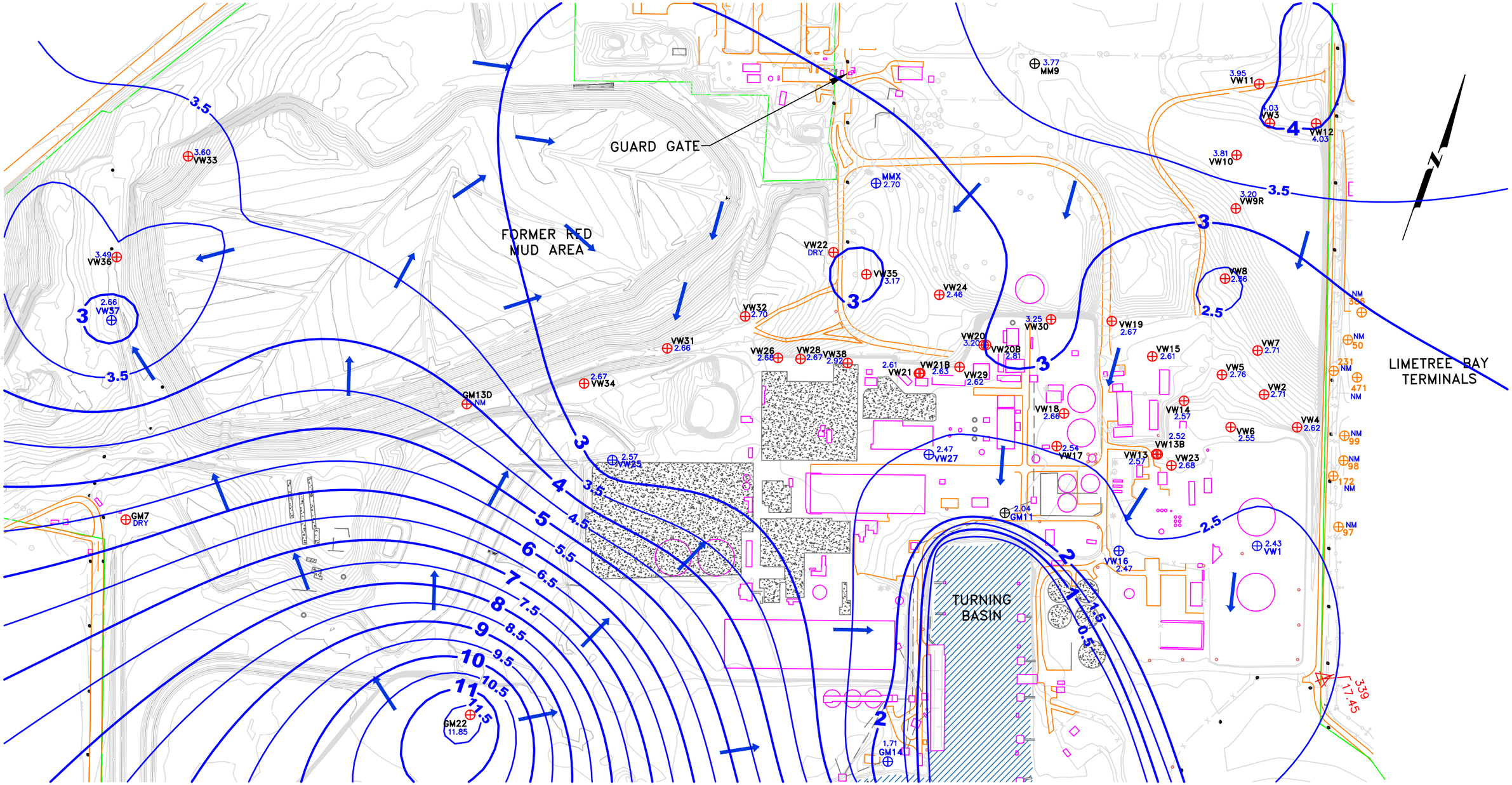
EHS Support

St. Croix Alumina Site
St. Croix, U.S. Virgin Islands

Cross Section C-C'
LNAPL Natural Source Zone Depletion Work Plan

Figure 3B

Developed by Andrew Fowler, EHS Support LLC - December 16, 2020



LEGEND

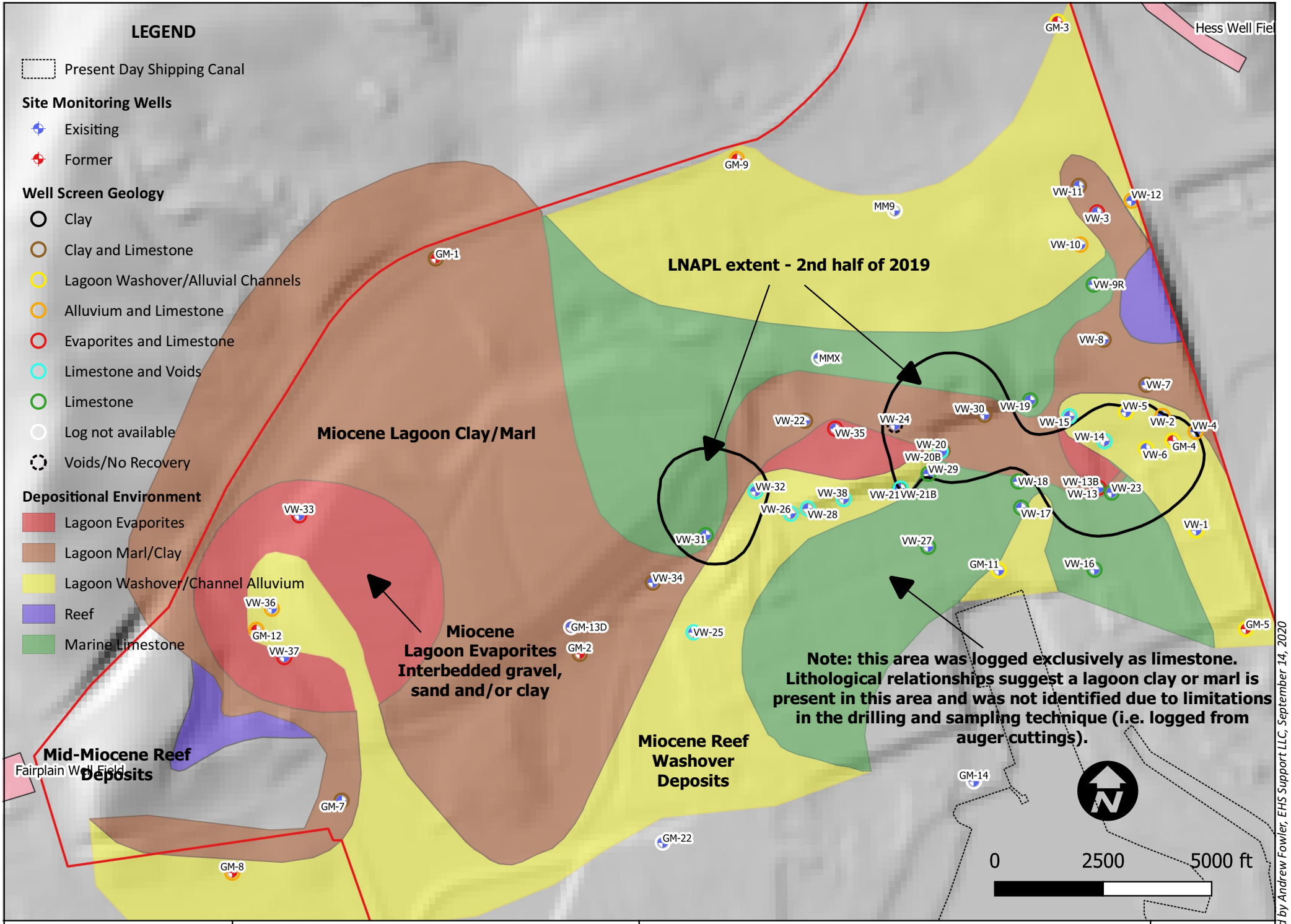
VW33	MONITORING WELL		GROUND SURFACE CONTOUR (IN FEET)
VW37	DPPHC PERIMETER MONITRORING WELL	1.93	STATIC GROUNDWATER LEVEL
386	LIMETREE BAY WELL		GROUNDWATER FLOW DIRECTION
		NM	NOT MEASURED
		4	GROUNDWATER CONTOUR LINE (FEET ABOVE MLS)
			INFERRED GROUNDWATER CONTOUR LINE

0 200 400 800
APPROXIMATE SCALE IN FEET

NOTE: TOPOGRAPHIC MAP PROVIDED BY ALCOA/2012 AND TETRATECH/2017

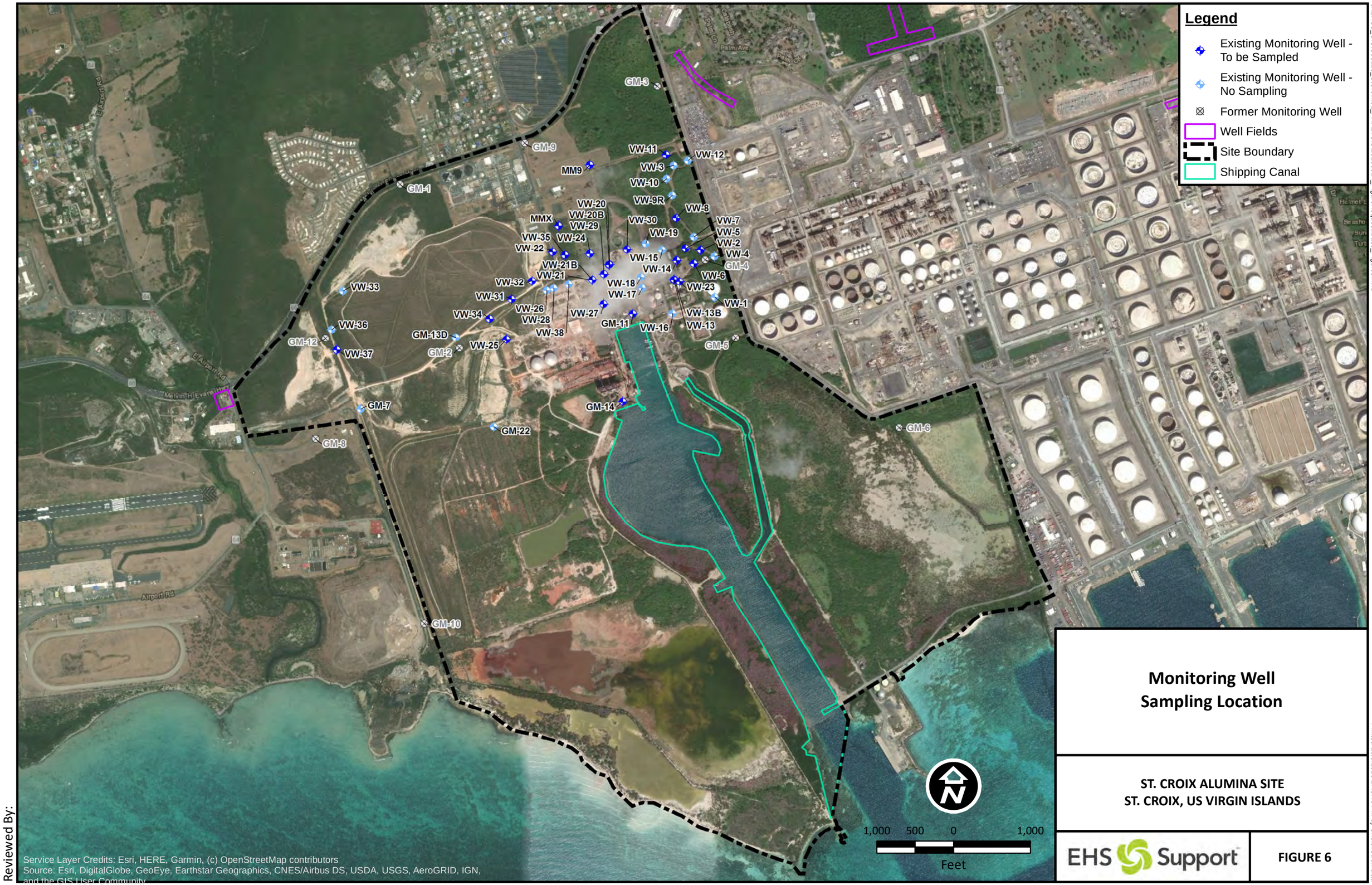
EHS Support	St. Croix Alumina Site St. Croix, U.S. Virgin Islands	Groundwater Elevations (Corrected for LNAPL Density), December 2019 LNAPL Source Zone Depletion Work Plan	Figure 4

Source: GMS, 2019. 36th Groundwater Monitoring Event and 2nd Semiannual 2019 Status Report for the St. Croix Alumina Groundwater Remediation Project. January 31.



EHS Support	St, Croix Alumina Site St. Croix, U.S. Virgin Islands	Well Screen Geology LNAPL Natural Source Zone Depletion Work Plan	Figure 5

Developed by Andrew Fowler, EHS Support LLC, September 14, 2020



Monitoring Well Sampling Location

ST. CROIX ALUMINA SITE
ST. CROIX, US VIRGIN ISLANDS

EHS Support

FIGURE 6

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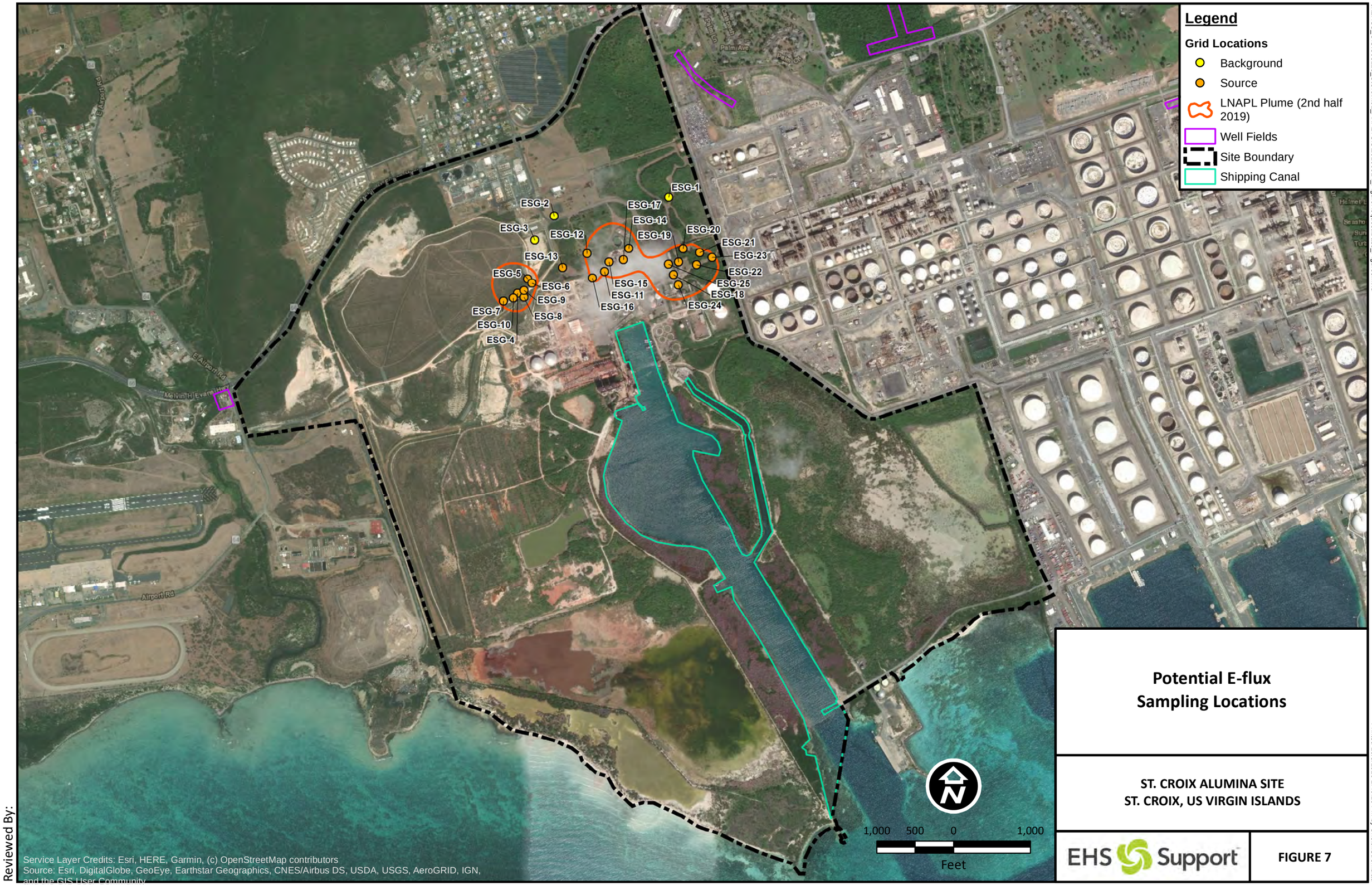

Potential E-flux Sampling Locations

ST. CROIX ALUMINA SITE
ST. CROIX, US VIRGIN ISLANDS

EHS Support

FIGURE 7

Reviewed By:

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Appendix A USEPA Comments and POC Responses on LNAPL CSM and NSZD Work Plan

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 2
290 BROADWAY
NEW YORK, NY 10007-1866

December 14, 2020

Mr. Brian Epperson,
Director, Environmental Health & Safety
HOVIC
1501 McKinney Street
Director, EHS Houston, Texas 77010

Re: Review of the draft LNAPL CSM and Revised Remedial Action Work Plan, St. Croix Alumina Groundwater Plume, U.S. Virgin Islands, dated July 2020,
EPA ID Number: VID090302084

Dear Mr Epperson:

EPA has reviewed the *LNAPL CSM and Remedial Action Work Plan* for the St. Croix Alumina groundwater plume, located in St. Croix, U.S. Virgin Islands. While we understand that many of our questions may have been addressed verbally at the November 18, 2020 conference call with the Project Operating Committee, the enclosed written comments address the report which is lacking the detail we need to evaluate the efficacy of the proposal.

Additionally, as discussed in our conference call of November 25, 2020, EPA would be interested in discussing with you several recommendations for optimizing the solar sipper system. Finally, as noted in the enclosed comments, EPA is not in concurrence at this time with a final goal of 80% removal of recoverable LNAPL, or with the final transmissivity and corresponding 1-gallon per day recovery criteria for discontinuation of active remediation. These assumptions are dependent upon the plume being stable, which has not yet been established for this site. Further coordination with EPA would be warranted to evaluate the proposed criteria following collection of supporting data.

Should you have any questions, please feel free to contact me via telephone at 212-637-4181, or via email at stein.carol@epa.gov

Sincerely,

Carol A. Stein

Carol A. Stein, PE
Environmental Engineer
Land and Resources Programs Branch

Enclosure

cc: Austin Callwood, Director, USVI-DPNR-DEP (electronic copy)
Syed Syedali, USVI-DPNR-DEP (electronic copy)
Brad Martin, Toeroek (electronic copy)

TECHNICAL REVIEW
LNAPL CSM AND REMEDIAL ACTION WORK PLAN
ST. CROIX, U.S. VIRGIN ISLANDS
ST CROIX ALUMINA SITE
DATED JULY 2020

GENERAL COMMENTS:

General Comment 1*:* The *LNAPL CSM and Remedial Action Work Plan, St. Croix, U.S. Virgin Islands, St. Croix Alumina Site*, dated July 2020 (Work Plan), summarizes the Tier I and Tier II risk assessment reports that were prepared in 2002 and 2003 for the St. Croix Alumina Site. EPA is reviewing these risk assessments to determine whether updates are warranted to reflect both the current Conceptual Site Model (CSM) and the potential for vapor intrusion impacts for any projected or potential reuse of the property. EPA will be contacting you regarding the results of this review. Additionally, please ensure the references to the risk assessments are accurate. In at least one instance (page 45, last paragraph), the date of the Tier 1 risk assessment is incorrectly cited as ES&T 2012 which leads the reader to assume the risk assessment is more recent; However, the date of the reference needs to be corrected to read ES&T 2002.

General Comment 2*:* The Work Plan does not provide specific actionable remedial goals in Step 4 of Section 6.2 for the proposed transition from LNAPL recovery to natural source zone depletion (NSZD) that accounts for the anticipated uncertainty and variability in NSZD, including the variability of a calculated NSZD depletion rate in a well-by-well basis. Without this information, the adequacy of the Work Plan cannot be assessed, and a complete list of data gaps cannot be determined to transition from phase separated petroleum hydrocarbon (PSPH) recovery to NSZD. Please revise the Work Plan to incorporate more details on Step 4 and a cross-walk showing how the proposed NSZD will be evaluated against LNAPL recovery. Also, please note that the transmissivity and corresponding 1-gallon per day criteria (noted in Section 6.2 and elsewhere in the document) is a starting point for evaluating when sippers may no longer be effective tools for removing LNAPL. However, this is dependent on the plume being stable, which has not yet been established at this site. The reason for the apparent instability of the plume may be related to the secondary porosity features present at the site and the buoyancy

changes in the system created by LNAPL pumping activity. We anticipate that further information regarding NSZD and plume stability may be available after additional vapor probe investigations are conducted.

General Comment 3*:* The Work Plan proposes to provide additional visual comparisons of the LNAPL plumes. To ensure the information is readily comparable, ensure the images provided include the following:

Consistent presentation of information in sufficient size and scale to allow for direct comparison of historical and current LNAPL extent.

Consistent labeling of LNAPL contour intervals for ease of understanding of the information presented.

Development of current figures for all information presented.

Revise the Work Plan to address this issue.

General Comment 4*:* Throughout the Work Plan, reference is made to the potential impacts of calcification and an apparent reduction in the inherent porosity of the limestone beneath the Site. However, boring logs are generally poor quality and there are no data provided which substantiate that porosity and permeability in the limestone is restricted to secondary porosity features. Evidence for the statements made regarding secondary porosity is not provided in the Work Plan. The presence of evaporites is only indicated on Figure 4-6 in wells outside the LNAPL treatment areas (specifically in wells VW-33, VW-37, VW-35, VW-3), yet the extent of mapped evaporites is shown near extraction well VW-13B. Based on the data shown on Figure 4-6, it is unclear how the extent of the potential infilling of reef carbonate porosity because of evaporite deposition and calcification was developed.

Also, large scale geologic cross-sections shown in Figure 4-3 do not cut through the majority of the LNAPL treatment area and do not show the juxtaposition or even the presence of any evaporite facies. Smaller scale treatment-area specific geologic cross-sections that show the relationship between the limestone and evaporite

facies are needed. Cross-sections are needed along with the salient extraction well completions showing the LNAPL extent to support the project specific CSM for the Site.

Further, the cross-sections need to indicate the approximate location of the water table in critical extraction wells such that the thickness of LNAPL can be evaluated relative to changes in the relationships between geology and well completions and the apparent thicknesses of LNAPL. The relationship of geology to well screens and the water table can have major impacts on LNAPL removal efficiencies and apparent thicknesses of the LNAPL measured in the field. Please revise the Work Plan such that it incorporates site-specific data capable of supporting the LNAPL CSM as discussed above. In the event such data do not exist, then identify the necessary steps to fill the data gaps to ensure the presented CSM is substantiated by site-specific data.

General Comment 5*:* Throughout the Work Plan the weathered nature of the LNAPL at the Site is noted as potentially impacting viscosity and the transmissivity of the LNAPL, but no viscosity data is provided. The authors imply that the effective solubility data for the LNAPL at the Site resembles a fresh diesel and No.2 fuel oil as provided in Tables 5-2 and 5-3. Please explain how the effective solubilities for the LNAPL at the Site can be similar to fresh diesel and No.2 fuel oil while the LNAPL can be described as highly weathered. Viscosity data for the LNAPL and other geochemical information is needed to substantiate that weathering has impacted the transmissivity of the LNAPL at the Site. Further, if the geochemical data substantiate that the hydrocarbons are weathered, additional lines of evidence regarding the appropriate effective solubility for the site hydrocarbon releases is needed.

General Comment 6*:* In Section 5.5, LNAPL Mobility and Recoverability, reference is made to previous studies that indicate seepage rates at the Site for LNAPL are 0.1 foot/day. Reference to dissolved phase monitoring results as an indication of plume stability also is cited. Substantiation of the mobility of the LNAPL plume needs

to be presented separately from any determination of the stability of the dissolved phase plume. LNAPL buoyancies and the orientation of main secondary fracture zones will control LNAPL mobility and host rock storativity. Neither of these two factors are adequately defined for the Site. Without information regarding the orientation of the primary and secondary fracture zones or LNAPL buoyancy, the recoverability of the LNAPL and the stability of the LNAPL plume cannot be adequately established. Please revise the Work Plan to address these data gaps.

Additionally, in Appendix B, NAPL Thickness Maps, the extent of LNAPL is shown for 2002 and 2003, and then from 2006 through 2019. A review of the plume maps indicates the LNAPL thickness has varied over time. The shifting LNAPL thicknesses shown on these images do not support the interpretation that the plume is stable. Revise the discussion of plume stability to address the shifting configuration of the LNAPL plume.

General Comment 7: The presence of reducing conditions capable of substantiating the potential for reductive MNA processes to act on the LNAPL were only measured in dissolved phase monitoring wells shown in Table 5-4. The results in monitoring wells are variable as shown in Table 1 of the *37th Groundwater Monitoring Event and 1st Semiannual 2020 Status Report for the St. Croix Alumina Groundwater Remediation Project, Geomonitoring Services (GMS), August 31, 2020.* Some data presented in this table suggest the presence of reductive conditions while other wells have values for oxygen reductive potential (ORP) and dissolved oxygen (DO) which are positive and higher respectively, which is indicative of more oxygenated conditions in the groundwater sampled. It is noted in the first sentence of the second paragraph on page 45 of the Work Plan that "Extensive assessment of natural attenuation processes has not been conducted at the site." Additional ORP and DO measurements are needed from wells and associated groundwater beneath the LNAPL plume to evaluate geochemical conditions in groundwater beneath the LNAPL plume and the potential for MNA processes to reduce LNAPL volumes over time. Currently, the lack of geochemical data represents a significant data gap in

substantiation that transition to NSZD and MNA is warranted. Ensure the Work Plan adequately addresses this data gap.

General Comment 8*:* In section 5.5.1, Bail Down Tests Assessments of Transmissivity and Mobility, second to the last paragraph, in the last sentence on page 48, the Work Plan notes that additional bail down testing both spatially and temporally is required. Presumably, this is because current modeling results are only based on bail down tests from three out of approximately 21 wells inside the mapped LNAPL plume. The Work Plan calls for bail down tests at the extraction wells in the proposed network. It is unclear how many, where, and in what wells additional bail down tests will be performed. Please revise the Work Plan to present the locations of additional bail down testing and ensure the selection of those locations considers geologic setting, the presence or absence of fractures, LNAPL thickness, and water table elevation.

General Comment 9*:* LNAPL recoveries shown in Table 5-6 show inconsistent expected LNAPL transmissivity values that exceed the practicality limits provided in the ITRC (2018) guidance and calculated by the authors of greater than 1 gallon per day (gpd) based on an expected transmissivity value of 0.8 foot squared/day. Based on this data. it is unclear how long it might be before individual wells might consistently fall below this estimated practical recovery limit. Many more wells have consistent recovery values that exceed the 0.5 gallon per day recovery limit in this table. Optimization of the solar sipper systems followed by operation of the systems for an additional period of time is warranted before the system can be established as not providing additional value in terms of LNAPL removal rates and total volumes. Solar sippers that can be cycled more regularly allowing for recharge of LNAPL and the addition of additional fluid storage at each location may change the observed recoveries. EPA would be interested in further exploring with the ERT ways to optimize the solar sipper systems. Additionally, changes in the LNAPL removal methods may also change LNAPL recoveries shown in Table 5-6, which is attached at end of the draft Work Plan.

General Comment 10*:* Section 6.2 discusses the proposed framework for LNAPL recovery well shutdown. Four steps are listed, but Step 4 indicates that Steps 2 and 3 would not have to be met when the POC concludes that the active remediation is no more effective than NSZD, or 'where NSZD processes are particularly robust'. Please note that any deviation to the listed steps would require EPA approval. Please revise the Work Plan to note that the POC is not authorized to discontinue active remediation of the system without prior approval from EPA.

SPECIFIC COMMENTS:

Specific Comment #1 *- Table 5-4, Groundwater Parameters, Page 45:* Data presented in Table 5-4 of the Work Plan indicates that reducing conditions are present in key wells. No basis is provided for how the wells were identified as key in terms of the potential for MNA to occur at the site. The Work Plan suggests that the reducing conditions in these key wells are capable of supporting nitrate and sulfate reduction and methanogenesis of LNAPL constituents. Section 5-4 (p. 45) also cites the GES/ES&T model results which indicate that there are 3,379 barrels of oil remaining in the ground, and that there has been a 91.1% decrease in estimated hydrocarbons. However, insufficient information is provided to substantiate that a 91.1% reduction has occurred as stated in the text. If the POC is interested in continuing to refer to the results of this model, the Work Plan would need to provide sufficient detail about how these modeled estimates were derived to allow for concurrence with the stated results. The oxidation reduction conductivity (ORP) and the dissolved oxygen (DO) data would need to be provided for all wells where LNAPL or dissolved phase contamination is present. Furthermore, the work plan would need to be revised to provide the requested information, to provide the decision logic for the selection

of key wells, and to provide sufficient detail regarding the model used to determine the stated percent reduction to allow for an independent assessment of the information provided.

Specific Comment #2 *Table 5-7, Summary of Recovery August 2018 through to May 2020, Page 53:* Under Section 5.5.3, Table 5-7 provides LNAPL recovery rankings for different wells. However, the Work Plan needs to clarify how theses rankings were established and whether these rankings are based on geological conditions and the resulting amount of PSPH recovered from these wells over time. Additionally, details regarding the calculations of "% of total LNAPL" and "oil/water cut (%)" need to be presented as well as the data used needs to be provided.

Specific Comment #3*: Section 6, Updated Remedial Action Work Plan, Page 63:* Section 6 discusses the scope of the Work Plan, which is an updated version of the previously EPA approved July 23, 2001 document. One of the stated objectives of the Work Plan (a.k.a., the updated work plan) is the optimization of LNAPL recovery efforts in order to cease LNAPL recovery. How "optimization" will be determined, what lines of evidence will be used to perform the optimization, and how it will be determined that the system has been optimized to the degree possible is not defined. Site specific performance goals and decision thresholds need to be defined to achieve consensus for the proposed approach. A decision tree and a contingency plan are recommended for integration into the Work Plan, to help determine which decision criteria to use to move the site forward through the optimization process. A decision tree is outlined in *" A Decision-Making Framework for Cleanup of Sites Impacted with Light Non-Aqueous Phase Liquids (LNAPL), EPA 542-R-04-001, March 2005* [and a similar decision tree is outlined in LNAPL-3: LNAPL Site Management: LCSM Evolution, Decision Process, and Remedial Technologies, ITRC, March 2018).

Specific Comment #4: Section 6.1, LNAPL Recovery Activities, first paragraph, Page 63: The Work Plan indicates that active measures to manage the LNAPL at the Site should only proceed until June 2021. No rationale is presented for this date. Revise the Work Plan such that the firm date of June 2021 is removed, and lines of evidence are presented that will be attained prior to the cessation of LNAPL recovery.

Specific Comment #5 - Section 6.1, LNAPL Recovery Activities, Bullet 1 Page 64: In the second to last paragraph, it is noted that solar sipper systems will be visited monthly. Because of the low transmissivities of wells at the site, sippers should be checked and cycled more often and on a regularly frequency during the optimization process to assure maximum recoveries are obtained. Weekly assessments, at least during start up, could potentially increase system efficiencies and be used to evaluate the viability of reducing the frequency of system checks and optimization activities. Revise the Work Plan to allow for more frequent initial visits for optimization related activities.

Specific Comment #6: Section 6.2, Proposed Framework for LNAPL Recovery Well Shutdown, Bullet 3, Page 65; and Section 6.2.1, Rationale and Methodology for Reservoir Decline Curve Analysis, Page 66: In Section 6.2, a goal of 80 percent removal of the recoverable LNAPL is proposed. However, few details are provided regarding how this criterion will be applied to the Site. The Work Plan needs to be revised to include specifics regarding how this criterion would be developed and used for decision making purposes before it can be adopted for use at the Site. Additionally, EPA is not in concurrence that this should be the end goal for removal. We would be interested in exploring with the POC ways to increase the removal of recoverable LNAPL beyond 80% removal.

Specific Comment #7 Section 6.2.1, Rationale and Methodology for Reservoir Decline Curve Analysis, Page 66: In Section 6.2.1, in the second to the last sentence, a criterion for R^2 squared of 0.1 is suggested for use when

deciding to perform data analyses and estimating trends. The basis for suggesting this criterion is presented as being based on the inherent variability within geostatistical data sets. Provide a literature reference indicating that use of 0.1 is preferred for analyzing geostatistical data trends. A review of the current regression analyses, provided in Appendix C, Reservoir Decline Curves, suggests that many other factors may influence the observed results, such as changes in extraction methods and protocols or even changes in extraction technologies and equipment. The nature and distribution of results and other statistical assumptions must be considered and the appropriate methods for performing trend analyses used based on data set characteristics. Revise the Work Plan to provide the decision logic used for the use of R^2 as the preferred data assessment metric.

*Specific Comment # 8 : According to Section 6.2.3 (page 67 of report) – "*Reductions in the frequency of monitoring is anticipated (initially to annual) but this will not occur until after all LNAPL recovery activities has ceased at the site and sufficient time has elapsed since termination of recovery (anticipated to be 4 semi-annual events) that plume stability (post recovery termination) has been demonstrated. Ultimately all groundwater monitoring will cease when the Tier II SSTLs are achieved in all perimeter wells". Please note that additional semi-annual monitoring would be required for several years after the SSTLs are achieved to ensure that the goals have been met. The details regarding the extent of post-remedial monitoring warranted will be the subject of further discussion between EPA and the POC.

Specific Comment #9- Section 6.3, Natural Source Zone Depletion Assessment, Page 71: It is unclear which wells will be analyzed for groundwater geochemistry during the Phase 1 effort. LNAPL wells as well as dissolved phase monitoring wells need to be included in the Phase 1 sampling and analysis plan to support MNA evaluations. Revise the Work Plan to specify all wells to be sampled in support of this effort.

Specific Comment #10: Section 6.3, Natural Source Zone Depletion Assessment, Page 71: During Phase II, it is proposed that E-flux and an equivalent E-flux method for carbon dioxide measurements in the subsurface will be

performed using a grid approach. Flux methods depend on reliable estimates of flux through vadose zone media to obtain reliable estimates for expected concentrations of methane and carbon dioxide over time. As noted by ITRC (2018) guidance, it is also possible to use vapor probes properly positioned to emulate flux through differing geologic units at several depths above the LNAPL, but below the surface, to more accurately estimate carbon dioxide and methane concentrations in vadose zone media. This type of application may be more desirable based on the LNAPL CSM for this Site. Less permeable media, which could include limestones with only limited secondary porosity features, alluvium, reef overburden, fill, and evaporite deposits may enhance or drastically reduce the effectiveness of NSZD. Given the variability in the geology at the Site, flux type measurements may be unacceptable for use. It is also unclear why these analyses will not be performed during Phase I, as the collection of this data may be essential to the decision-making process and it will take some time to incorporate the results into the remedial process.

January 8, 2021

Carol A. Stein, PE
Environmental Engineer
Land and Resources Programs Branch

Re: Response to Technical Review, LNAPL CSM and Remedial Action Work Plan, St. Croix, U.S. Virgin Islands, St. Croix Alumina Site, Dated July 2020. EPA ID Number VID090302084

Dear Carol A. Stein,

EHS Support has reviewed the *Response to Technical Review, LNAPL CSM and Remedial Action Work Plan* for the St. Croix Alumina Site, St. Croix, U.S. Virgin Islands (hereafter 'Site'), and prepared the following responses to the comments. For ease of review the comment provided by United States Environmental Protection Agency (USEPA) has been provided and a response in Italics.

We look forward to discussion and resolution of these comments and moving forward with the supplemental assessments so that light non-aqueous phase liquid (LNAPL) mobility/recoverability can be better understood and a decision process (in accordance with Interstate Technology & Regulatory Council [ITRC] and USEPA) can be developed for management of LNAPL recovery and remedial actions with the ultimate goal of achieving restoration of groundwater quality.

General Comment 1*:* The *LNAPL CSM and Remedial Action Work Plan, St. Croix, U.S. Virgin Islands, St. Croix Alumina Site*, dated July 2020 (Work Plan), summarizes the Tier I and Tier II risk assessment reports that were prepared in 2002 and 2003 for the St. Croix Alumina Site. EPA is reviewing these risk assessments to determine whether updates are warranted to reflect both the current Conceptual Site Model (CSM) and the potential for vapor intrusion impacts for any projected or potential reuse of the property. EPA will be contacting you regarding the results of this review. Additionally, please ensure the references to the risk assessments are accurate. In at least one instance (page 45, last paragraph), the date of the Tier 1 risk assessment is incorrectly cited as ES&T 2012 which leads the reader to assume the risk assessment is more recent; However, the date of the reference needs to be corrected to read ES&T 2002.

Response to General Comment 1: *References to risk assessments have been double checked, and the noted error was corrected.*

General Comment 2*:* The Work Plan does not provide specific actionable remedial goals in Step 4 of Section 6.2 for the proposed transition from LNAPL recovery to natural source zone depletion (NSZD) that accounts for the anticipated uncertainty and variability in NSZD, including the variability of a calculated NSZD depletion rate on a well-by-well basis. Without this information, the adequacy of the Work Plan cannot be assessed, and a complete list of data gaps cannot be determined to transition from phase separated petroleum hydrocarbon (PSPH) recovery to NSZD. Please revise the Work Plan to incorporate more details on Step 4 and a cross-walk showing how the proposed NSZD will be evaluated against LNAPL recovery. Also, please note that the transmissivity and corresponding 1-gallon per day criteria (noted in Section 6.2 and elsewhere in the document) is a starting point for evaluating when sippers may no longer

be effective tools for removing LNAPL. However, this is dependent on the plume being stable, which has not yet been established at this site. The reason for the apparent instability of the plume may be related to the secondary porosity features present at the site and the buoyancy changes in the system created by LNAPL pumping activity. We anticipate that further information regarding NSZD and plume stability may be available after additional vapor probe investigations are conducted.

Response to General Comment 2: *Step 4 of Section 6.2 states, that the performance of ongoing recovery relative to natural mass losses will be evaluated. A chart on the following page illustrates that the proposed transition from phase separated petroleum hydrocarbon (PSPH) recovery to natural source zone depletion (NSZD) will occur when natural PSPH mass losses exceed engineered mass losses.*

As requested in the EPA review comment, the following details about how NSZD mass depletion rates will be compared to engineered recovery was included in Step 4 of Section 6.2:

The range of engineered mass losses (gallons per day) for site wells will be tabulated from site recovery operation data as described above. NSZD rates will be calculated at locations where PSPH is present using several approaches to account for potential variability in site conditions (as outlined in greater detail in a forthcoming NSZD Workplan):

- *Aqueous NSZD rates (gallons PSPH per day) will be estimated by comparing maximum, mean, and minimum differences of terminal electron acceptor (TEA) concentrations in groundwater and background wells to source zone (beneath PSPH) and downgradient wells, as outlined in CRC CARE (2018) and ITRC (2009). NSZD assimilative capacity (AC) values will be computed from the maximum, mean, and minimum differences to provide a range of NSZD rates at each location for comparison to engineered mass losses.*
- *Vapor phase and aqueous phase NSZD rates will be estimated using the differential temperature method, by measuring the temperature at specific points within the vadose zone and beneath water table. Heat flux will then be estimated using Fourier's first law of conduction and divided by the enthalpy of formation for a middle distillate fuel oil to yield an NSZD rate (corrected by the heat capacity of water for the aqueous portion of the rate calculation and converted to units of gallons per day).*
- *Based on the outcome of the above assessments, an additional line of evidence will be selected to determine NSZD rates, that may include one or a combination of passive CO_2 traps, use of a dynamic closed chamber, and/or the vadose gas gradient method.*

Given the variability of conditions at the Site, variability in NSZD rates are anticipated at different locations and will be integrated across the maximum extent of LNAPL using a Thiessen Polygon approach for direct comparison to the total engineered PSPH mass loss.

To demonstrate plume stability, figures depicting historical LNAPL thickness and plume extent estimates from previous consultants (Appendix B of the LNAPL CSM and Remedial Action Work Plan) have been updated to facilitate comparisons from the second half of 2002 through second half of 2019 (a 17-year period) – please note: this was also completed to fulfill the request presented in ***General Comment 3*** *(below).*

As is apparent in the revised time-series figures in Appendix B of the LNAPL CSM and Remedial Action Work Plan, and broadly apparent in time series charts of LNAPL thickness in Appendix D of the LNAPL

CSM and Remedial Action Work Plan, the extent of LNAPL has been constant to diminishing over 17 years, and LNAPL thicknesses have decreased overall. Note, apparent shifts in the LNAPL mass are inversely related to minor seasonal fluctuations in water level, where LNAPL drains into wells when the water level drops (i.e., an apparent thickness increase that does not reflect the true distribution of LNAPL in pore space).

General Comment 3: The Work Plan proposes to provide additional visual comparisons of the LNAPL plumes. To ensure the information is readily comparable, ensure the images provided include the following:

- Consistent presentation of information in sufficient size and scale to allow for direct comparison of historical and current LNAPL extent.
- Consistent labeling of LNAPL contour intervals for ease of understanding of the information presented.
- Development of current figures for all information presented.
- Revise the Work Plan to address this issue.

Response to General Comment 3: *As noted above, LNAPL thickness contours presented in Appendix B of the LNAPL CSM and Remedial Action Work Plan have been revised for consistent presentation of information. The revised contours clearly indicate the extent and thickness of LNAPL has remained stable to decreasing over the 17-year time frame.*

General Comment 4: Throughout the Work Plan, reference is made to the potential impacts of calcification and an apparent reduction in the inherent porosity of the limestone beneath the Site. However, boring logs are generally poor quality and there are no data provided which substantiate that porosity and permeability in the limestone is restricted to secondary porosity features. Evidence for the statements made regarding secondary porosity is not provided in the Work Plan. The presence of evaporites is only indicated on Figure 4-6 in wells outside the LNAPL treatment areas (specifically in wells VW-33, VW-37, VW-35, VW-3), yet the extent of mapped evaporites is shown near extraction well VW-13B. Based on the data shown on Figure 4-6, it is unclear how the extent of the potential infilling of reef carbonate porosity because of evaporite deposition and calcification was developed.

Also, large scale geologic cross-sections shown in Figure 4-3 do not cut through the majority of the LNAPL treatment area and do not show the juxtaposition or even the presence of any evaporite facies. Smaller scale treatment-area specific geologic cross-sections that show the relationship between the limestone and evaporite facies are needed. Cross-sections are needed along with the salient extraction well completions showing the LNAPL extent to support the project specific CSM for the Site.

Further, the cross-sections need to indicate the approximate location of the water table in critical extraction wells such that the thickness of LNAPL can be evaluated relative to changes in the relationships between geology and well completions and the apparent thicknesses of LNAPL. The relationship of geology to well screens and the water table can have major impacts on LNAPL removal efficiencies and apparent thicknesses of the LNAPL measured in the field. Please revise the Work Plan such that it incorporates site-specific data capable of supporting the LNAPL CSM as discussed above. In the event such data do not exist, then identify the necessary steps to fill the data gaps to ensure the presented CSM is substantiated by site-specific data.

Response to General Comment 4: *As this comment from EPA contains several elements, the response is parsed into the following categories for clarity:*

1. *Calcification and original porosity/permeability*
2. *The presence of evaporite minerals, particularly in relation to VW-13B*
3. *Cross section location*
4. *Relationship between limestone and evaporites*
5. *Water table on cross sections*

1. Evidence for reduction in primary porosity in limestone at the Site is provided by the Geraghty and Miller, Inc., (1982) study. In addition to their own observations, information from geological and geotechnical studies carried out at the plant site and surrounding area by U.S. Geological Survey (USGS) and researchers from various universities was incorporated.

During their investigation, Geraghty and Miller, Inc., (1982) documented the following, which has been introduced in Section 4.3. of the LNAPL CSM and Remedial Action Work Plan for clarity:

> *"Weathering and percolating subsurface waters have altered the original texture of the limestones in places. In many instances' porosity has been destroyed by the alteration of sand grains to micrite (carbonate clay) and by infilling of the interstices between grains with crystalline calcite. In other places, percolating water has increased the porosity by dissolving cement between grains, and by creating cavities and caverns."*

2. It is important to clarify that evaporites are not the same as calcification of primary (and potentially secondary) porosity. Calcite that reprecipitated in pore spaces identified at the Site by Geraghty and Miller, Inc., (1982) is (geologically speaking) a relatively recent process whereby groundwater supersaturated with respect to calcium carbonate precipitates calcite in cavities/porosity in the modern aquifer.

The deepest locations of evaporite minerals at the Site (calcite [$CaCO_3$], gypsum [$CaSO_4$], and chert [amorphous SiO_2]) are inferred to be depositional in origin (primary chemical sedimentary rocks) due to the occurrence of chert identified on some logs (e.g., VW-13B immediately above an interval of gypsum), which forms from diatom frustules and is indicative of shallow lagoon/strandline depositional environment where marine evaporites may form. Because this common evaporite sequence is identified on the log for VW-13B, an area of evaporites is drawn around VW-13B on Fig. 4-6. Lagoon evaporites are typically associated with low permeability and fine-grained siliciclastic (clay) and/or micrite (carbonate clay) associated with a relatively calm lagoonal/strandline depositional environment. However, the occurrence of an evaporite lagoonal facies does not preclude the presence of secondary porosity features.

The text has been revised to clarify this distinction.

3. A more detailed cross section across the treatment area was drafted (note, large-scale means more detailed and small-scale means less detailed). The new larger scale cross section passes through VW-6 and VW-13B; two wells with historically the thickest LNAPL. The scale here was modified from 1-inch = 50 feet to 1-inch = 25 feet vertically, and from 1-inch = 500 feet to 1-inch = 250 feet horizontally. The new

cross section passes through the treatment area, as indicated on the inset image on the figure that shows the cross-section location with respect to the extent of LNAPL in December 2019. Wells projected onto the section are indicated with dashed lines on this inset image to obviate coverage over the affected area.

4. On the cross sections (Fig 4-3A and 4-3B), locations of evaporite minerals are labeled "caliche" in keeping with the descriptions given on the original boring logs. The cross sections show the relationship of limestone lithologies and evaporite minerals.

5. The location of the water table and LNAPL thicknesses from December 2019 have been added to the new cross section, which incorporates most critical wells at the Site.

General Comment 5: Throughout the Work Plan the weathered nature of the LNAPL at the Site is noted as potentially impacting viscosity and the transmissivity of the LNAPL, but no viscosity data is provided. The authors imply that the effective solubility data for the LNAPL at the Site resembles a fresh diesel and No.2 fuel oil as provided in Tables 5-2 and 5-3. Please explain how the effective solubilities for the LNAPL at the Site can be similar to fresh diesel and No.2 fuel oil while the LNAPL can be described as highly weathered. Viscosity data for the LNAPL and other geochemical information is needed to substantiate that weathering has impacted the transmissivity of the LNAPL at the Site. Further, if the geochemical data substantiate that the hydrocarbons are weathered, additional lines of evidence regarding the appropriate effective solubility for the site hydrocarbon releases is needed.

Response to General Comment 5: *Weathered vs. fresh LNAPL transmissivity vs. effective solubility.*

LNAPL Viscosity data can be collected as part of the NSZD study. Based on the preferential depletion of low molecular weight compounds and in particular paraffins and iso-paraffins, which are the most easily degraded hydrocarbon compounds, LNAPL viscosity is expected to increase over time resulting in changes in further reductions in LNAPL transmissivity. Further detail on impacts of weathering on LNAPL viscosity and transmissivity are provided in ITRC (2018) which has been referenced extensively throughout the document.

In terms of effective solubility, we did not imply that the effective solubility is the same as fresh diesel and No.2 fuel oil. Effective solubility calculations using site specific data are provided in Table 5-1 and show the LNAPL to have low solubility with only naphthalene effective solubility exceeding relevant groundwater criteria. Tables 5-2 and 5-3 were only provided for comparative purposes and we consider that the effective solubility calculations based on LNAPL analytical testing data accurately reflects the properties of the weathered LNAPL at this Site. It is critical to note that effective solubility is the concentration in water in direct contact with oil and is not the concentrations that will be observed in groundwater. The absence of BTEX and naphthalene detections in recent groundwater monitoring data is consistent with the effective solubility of the LNAPL as documented in Table 5-1.

General Comment 6: In Section 5.5, LNAPL Mobility and Recoverability, reference is made to previous studies that indicate seepage rates at the Site for LNAPL are 0.1 foot/day. Reference to dissolved phase monitoring results as an indication of plume stability also is cited. Substantiation of the mobility of the LNAPL plume needs to be presented separately from any determination of the stability of the dissolved phase plume. LNAPL buoyancies and the orientation of main secondary fracture zones will control

LNAPL mobility and host rock storativity. Neither of these two factors are adequately defined for the Site. Without information regarding the orientation of the primary and secondary fracture zones or LNAPL buoyancy, the recoverability of the LNAPL and the stability of the LNAPL plume cannot be adequately established. Please revise the Work Plan to address these data gaps.

Additionally, in Appendix B, NAPL Thickness Maps, the extent of LNAPL is shown for 2002 and 2003, and then from 2006 through 2019. A review of the plume maps indicates the LNAPL thickness has varied over time. The shifting LNAPL thicknesses shown on these images do not support the interpretation that the plume is stable. Revise the discussion of plume stability to address the shifting configuration of the LNAPL plume.

Response to General Comment 6:

Consistent with the means and methods outlined in the ITRC guidance, a number of factors are used to define LNAPL plume stability. These include:

1. *The Interpreted extent of LNAPL. As is shown in the updated figures the extent of LNAPL has declined over time in response to a combination of LNAPL recovery efforts and NSZD.*
2. *The absence of appearance of LNAPL in new wells. There has been no LNAPL occurrence in new wells over more than 10 years. New wells have been installed in areas of known or suspected LNAPL impacts and LNAPL encountered, and LNAPL has been observed to appear and disappear in select wells with changes in groundwater elevation or in response to changes in recovery efforts.*
3. *In the context of sites where dissolved phase impacts are associated with LNAPL impacts it is generally accepted that a stable or decreasing dissolved phase plume extent is an indicator or a pre-requisite for LNAPL stability. Increasing extents of dissolved phase plumes (especially for BTEX constituents which degrade rapidly) is considered a potential indicator of plume expansion and therefore dissolved plume stability is a pre-requisite for stable LNAPL plume.*

A secondary line of evidence is the age of the release and as documented in the ITRC guidance (2018). As stated in the ITRC Guidance,

> *When an LNAPL release occurs, the LNAPL will move vertically downward under the influence of gravity through the permeable pathways (e.g., unconsolidated soil, fractures, and macropores) and, if sufficient LNAPL volume and head is generated by the release, the LNAPL will eventually encounter the water table. During the downward movement of LNAPL through the soil, the presence of confining layers, subsurface heterogeneities, or other preferential pathways may result in irregular and complex lateral spreading and/or perching of LNAPL before the water table is encountered. Once at the water table, the LNAPL will spread laterally in a radial fashion as well as penetrate vertically downward into the saturated zone, displacing water to some depth proportional to the driving force of the vertical LNAPL column (or LNAPL head). The vertical penetration of LNAPL into the saturated zone will continue to occur as long as the downward force produced by the LNAPL head or pressure from the LNAPL release exceeds the counteracting forces produced by the resistance of the soil matrix and the buoyancy resulting from the density difference between LNAPL and groundwater.* ***Once the release of LNAPL is terminated, the areal extent of the LNAPL body will continue to expand for a relatively short***

> ***time, and eventually stop once the resistive forces in the soil balance the driving force of the diminishing LNAPL head. When the LNAPL body reaches this state, the LNAPL body has stabilized in extent, and will not typically expand further unless additional releases or significant subsurface hydraulic changes occur.*** *(ITRC Guidance Section 3.2.1, emphasis added- 3. Key LNAPL Concepts – LNAPL Update (itrcweb.org))*

Consistent with the description above and given the considerable time that has elapsed since operations, it is reasonable to assume that the LNAPL plume has stabilized. There is no data to indicate that there have been new releases at the Site and/or that further migration of the LNAPL Plume has occurred.

LNAPL thickness changes in mature plumes are not an indicator of plume mobility. Rather they are simply indicators of changes in local scale conditions associated with water table elevation changes (drops in groundwater elevation resulting in vertical drainage of LNAPL in the formation into the well) and or changes in stressors such as recovery activities within the well or adjacent wells.

Commentary is provided by USEPA on the factors affecting LNAPL migration, notably, "LNAPL buoyancies and the orientation of main secondary fracture zones will control LNAPL mobility and host rock storativity". To clarify, the variability in the geology (including secondary porosity features and the degree of cementing) impacted on the historical migration of LNAPL at the Site. There is no ongoing migration of the plumes (consistent with the comments above) and so in the context of this site these features are important in understanding the variability in LNAPL transmissivity, total LNAPL recovery volumes and current LNAPL recovery rates.

In the context of the study moving forward, our near-term focus is on NAPL transmissivity and recovery across the plume and correlating this with subsurface conditions. In the context of the site, the POC considers that the primary goals of plume delineation and plume containment have been achieved and demonstrated through years of groundwater monitoring. The focus of our efforts moving forward are on recovery of LNAPL to the extent practical and ultimately (through NSZD processes after recovery becomes impractical) achieving restoration of the aquifer.

General Comment 7: The presence of reducing conditions capable of substantiating the potential for reductive MNA processes to act on the LNAPL were only measured in dissolved phase monitoring wells shown in Table 54. The results in monitoring wells are variable as shown in Table 1 of the *37th Groundwater Monitoring Event and 1st Semiannual 2020 Status Report for the St. Croix Alumina Groundwater Remediation Project, Geomonitoring Services (GMS), August 31, 2020.* Some data presented in this table suggest the presence of reductive conditions while other wells have values for oxygen reductive potential (ORP) and dissolved oxygen (DO) which are positive and higher respectively, which is indicative of more oxygenated conditions in the groundwater sampled. It is noted in the first sentence of the second paragraph on page 45 of the Work Plan that "Extensive assessment of natural attenuation processes has not been conducted at the site." Additional ORP and DO measurements are needed from wells and associated groundwater beneath the LNAPL plume to evaluate geochemical conditions in groundwater beneath the LNAPL plume and the potential for MNA processes to reduce LNAPL volumes over time. Currently, the lack of geochemical data represents a significant data gap in substantiation that transition to NSZD and MNA is warranted. Ensure the Work Plan adequately addresses this data gap.

Response to General Comment 7: *It is duly noted that further assessment of groundwater geochemistry is needed to document and confirm monitored natural attenuation (MNA) processes at the Site. As noted in the response to General Comment 2, an extensive assessment of groundwater geochemistry is outlined in greater detail in the recently submitted NSZD Workplan, including field parameter measurements and samples of groundwater from beneath LNAPL.*

Table 5-4 presents some field parameter data from dissolved phase wells outside and immediately downgradient of the LNAPL footprint. These wells are clearly suboxic to anoxic in terms of dissolved oxygen (DO) measurements, considering the resolution of most instruments is in the 0.2 to 0.5 mg/L range. Additionally, most DO results are below 0.5 milligrams per Liter (mg/L) in Table 1 of the 37th Groundwater Monitoring Event and 1st Semiannual 2020 Status Report for the St. Croix Alumina Groundwater Remediation Project, Geomonitoring Services (GMS), August 31, 2020.

Very generally speaking, oxidation-reduction potential (ORP) values less than +50 millivolts (mV) (relative to an Ag/AgCl electrode) suggest a reductive pathway is possible, and values less than -100 mV suggest a reductive pathway is likely (Wiedemeier et al, 1998[1]). Very generally, ORP values of +50 to -50 mV are indicative of NO_3^- reduction, -50 to -250 mV of SO_4^{2-} reduction, and -175 to -400 mV of CH_4 production. Stabilized ORP values of most wells are in a range suggestive of a reductive pathway in Table 1 of the 37th Groundwater Monitoring Event and 1st Semiannual 2020 Status Report for the St. Croix Alumina Groundwater Remediation Project, GMS, August 31, 2020.

Indeed, current data are strongly suggestive of reductive microbial respiration in the LNAPL affected area relative to background areas, and Table 5-4 and the associated text has been revised to capture this. The only wells with stabilized DO and ORP values that do not fall in a favorable range for reductive degradation are VW-25, VW-37, GM-14, and MMX.

- *VW-25 is at the westernmost edge of the LNAPL.*
- *VW-37 is over 2000 feet side-gradient from the LNAPL.*
- *GM-14 is located adjacent to the shipping canal and is affected by oxygenated seawater as is apparent from the elevated conductivity value.*
- *MMX is located about 800 feet upgradient of the LNAPL.*

General Comment 8: In section 5.5.1, Bail Down Tests Assessments of Transmissivity and Mobility, second to the last paragraph, in the last sentence on page 48, the Work Plan notes that additional bail down testing both spatially and temporally is required. Presumably, this is because current modeling results are only based on bail down tests from three out of approximately 21 wells inside the mapped LNAPL plume. The Work Plan calls for bail down tests at the extraction wells in the proposed network. It is unclear how many, where, and in what wells additional bail down tests will be performed. Please revise the Work Plan to present the locations of additional bail down testing and ensure the selection of those locations considers geologic setting, the presence or absence of fractures, LNAPL thickness, and water table elevation.

Response to General Comment 8:

[1] Wiedemeier, T.H., et al. 1998. Technical protocol for evaluating natural attenuation of chlorinated solvents in groundwater. EPA/600/R-98/128.

As documented in the work plan, a range of methods can be used to assess remedy performance relative to ITRC's LNAPL transmissivity limits. This includes baildown tests where LNAPL Transmissivity values are estimated and conversion of LNAPL recovery rates to LNAPL Transmissivity. The proposed approach is to opportunistically collect LNAPL transmissivity data over time in wells at the Site through a combination of the following:

1. *Measure LNAPL thickness rebound over time in wells during the process of solar sipper pump removal for routine maintenance and/or relocation to another well. Effectively this is considered opportunistic as LNAPL thicknesses will already be depressed in the well due to operation of the skimmer. LNAPL thickness will be allowed to rebound (and rate of increase of LNAPL thickness in well will be measured), and once equilibrated the accumulated LNAPL will be evacuated again and the rebound in LNAPL thicknesses measured over time.*
2. *Baildown testing in wells that are not part of the current LNAPL recovery program but may be incorporated into the program if LNAPL transmissivity in the wells is higher than that measured in other wells and above the ITRC practicality threshold.*

A minimum of one baildown test will be collected from the following wells (although multiple tests may be conducted on select wells over time). The wells proposed for baildown testing (assuming minimum LNAPL thickness threshold of 0.25 feet is present prior to bail-down test) are summarized in the table below.

PROPOSED WELLS FOR BAILDOWN TESTING

Well Id	*Operational Status of Well*	*Additional Comments*
VW6	*Continuous Solar Sipper Operation in high yielding wells*	*Opportunistic baildown test to be completed during removal of pump for routine inspection/maintenance. Solar sipper to be replaced in well after completion. Multiple baildown tests likely to be conducted over time.*
VW13		
VW13B		
VW14		
VW31		
VW5	*Continuous solar sipper operation in low to moderate LNAPL recovery rate wells*	*Baildown tests to be conducted at the end of a 6-month operational period and used to determine if solar sippers will be retained at these well locations.*
VW20		
VW20B		
VW24		
VW29		
VW32		
VW21B	*Periodic solar sipper operations in low LNAPL recovery wells. Solar sippers may be moved from these wells to other historic low yield wells (see list below)*	*Baildown test to be conducted upon removal of solar sipper*
VW23		
VW24		
VW2	*LNAPL wells with insufficient LNAPL for initial recovery*	*Baildown tests to be conducted on all wells which exceed the*
VW7		

Well Id	*Operational Status of Well*	*Additional Comments*
VW15	*actions by solar sippers. Solar sippers may be implemented in wells based on baildown test data.*	*minimum LNAPL thickness threshold*
VW18		
VW19		
VW21		
VW26		
VW28		
VW30		
VW35		

General Comment 9: LNAPL recoveries shown in Table 5-6 show inconsistent expected LNAPL transmissivity values that exceed the practicality limits provided in the ITRC (2018) guidance and calculated by the authors of greater than 1 gallon per day (gpd) based on an expected transmissivity value of 0.8 foot squared/day. Based on this data, it is unclear how long it might be before individual wells might consistently fall below this estimated practical recovery limit. Many more wells have consistent recovery values that exceed the 0.5 gallon per day recovery limit in this table. Optimization of the solar sipper systems followed by operation of the systems for an additional period of time is warranted before the system can be established as not providing additional value in terms of LNAPL removal rates and total volumes. Solar sippers that can be cycled more regularly allowing for recharge of LNAPL and the addition of additional fluid storage at each location may change the observed recoveries. EPA would be interested in further exploring with the ERT ways to optimize the solar sipper systems. Additionally, changes in the LNAPL removal methods may also change LNAPL recoveries shown in Table 5-6, which is attached at end of the draft Work Plan.

Response to General Comment 9: *We agree that the LNAPL recovery rates in Table 5-6 show variability over time associated with operation of the solar sippers (pumping being turned on and off and adjusted). To mitigate this variability and provide more consistent recovery rates (that can be used for reservoir decline curve analysis) we have proposed adjustments to the Operation and Maintenance (O&M) program including installation of ISO/Totes to provide longer operational times and instructing our field staff to not make adjustments to elevation and setting of the solar sippers.*

We consider that the capacity of the solar sippers is sufficient to keep LNAPL thicknesses at the desired minimum threshold of 0.1 to 0.25 feet in the recovery wells (some LNAPL is required in the well to provide continuity between the well and formation in order for LNAPL to enter the well). Use of the larger ISO containers will allow for prolonged operation of the high yield wells to demonstrate the effectiveness (sufficient pumping capacity) of the solar sippers.

General Comment 10*:* Section 6.2 discusses the proposed framework for LNAPL recovery well shutdown. Four steps are listed, but Step 4 indicates that Steps 2 and 3 would not have to be met when the POC concludes that the active remediation is no more effective than NSZD, or 'where NSZD processes are particularly robust'. Please note that any deviation to the listed steps would require EPA approval. Please revise the Work Plan to note that the POC is not authorized to discontinue active remediation of the system without prior approval from EPA.

Response to General Comment 10: *Comment is noted, any proposed permanent shutdown of recovery wells will only be conducted with USEPA approval.*

Specific Comment #1 *- Table 5-4, Groundwater Parameters, Page 45:* Data presented in Table 5-4 of the Work Plan indicates that reducing conditions are present in key wells. No basis is provided for how the wells were identified as key in terms of the potential for MNA to occur at the site. The Work Plan suggests that the reducing conditions in these key wells are capable of supporting nitrate and sulfate reduction and methanogenesis of LNAPL constituents. Section 5-4 (p. 45) also cites the GES/ES&T model results which indicate that there are 3,379 barrels of oil remaining in the ground, and that there has been a 91.1% decrease in estimated hydrocarbons. However, insufficient information is provided to substantiate that a 91.1% reduction has occurred as stated in the text. If the POC is interested in continuing to refer to the results of this model, the Work Plan would need to provide sufficient detail about how these modeled estimates were derived to allow for concurrence with the stated results. The oxidation reduction conductivity (ORP) and the dissolved oxygen (DO) data would need to be provided for all wells where LNAPL or dissolved phase contamination is present. Furthermore, the work plan would need to be revised to provide the requested information, to provide the decision logic for the selection of key wells, and to provide sufficient detail regarding the model used to determine the stated percent reduction to allow for an independent assessment of the information provided.

Response to Specific Comment 1:

The MNA data for key wells is discussed in the response for General Comment 7. Please note, Table 5-4 was updated with the most recent round of monitoring data and text was added to the LNAPL CSM document to clarify this issue.

Our approach does not rely on historic modelling as there are fundamental flaws with that type of modelling in this setting. The reference to 91.1% reduction reflects the conclusions of past reports which is supported by other lines of evidence include the declines in recovery rate over time, thicknesses in wells and the lateral extent of LNAPL impacts.

Our approach moving forward will be focused on collection of empirical data on LNAPL transmissivity and LNAPL recovery and natural source zone depletion rates. A NSZD Work Plan has been prepared and submitted to USEPA which documents the extent of this proposed program of work.

Specific Comment #2 *Table 5-7, Summary of Recovery August 2018 through to May 2020, Page 53:* Under Section 5.5.3, Table 5-7 provides LNAPL recovery rankings for different wells. However, the Work Plan needs to clarify how these rankings were established and whether these rankings are based on geological conditions and the resulting amount of PSPH recovered from these wells over time. Additionally, details regarding the calculations of "% of total LNAPL" and "oil/water cut (%)" need to be presented as well as the data used needs to be provided.

Response to Specific Comment 2: *The rankings provided in Table 5-7 were simply based on the total volume of LNAPL recovered over the trial period of August 2018 through to May 2020. Well VW13B with the largest LNAPL recovery volume over this period (1197.10 gallons) was ranked as number 1. The other calculations were:*

- *% of total LNAPL being the % from the well over the period relative to the total volume of LNAPL over the period (for example VW13B was 1191.10 gallons relative to a total volume recovered of 4566.37 gallons which is 26.22%).*

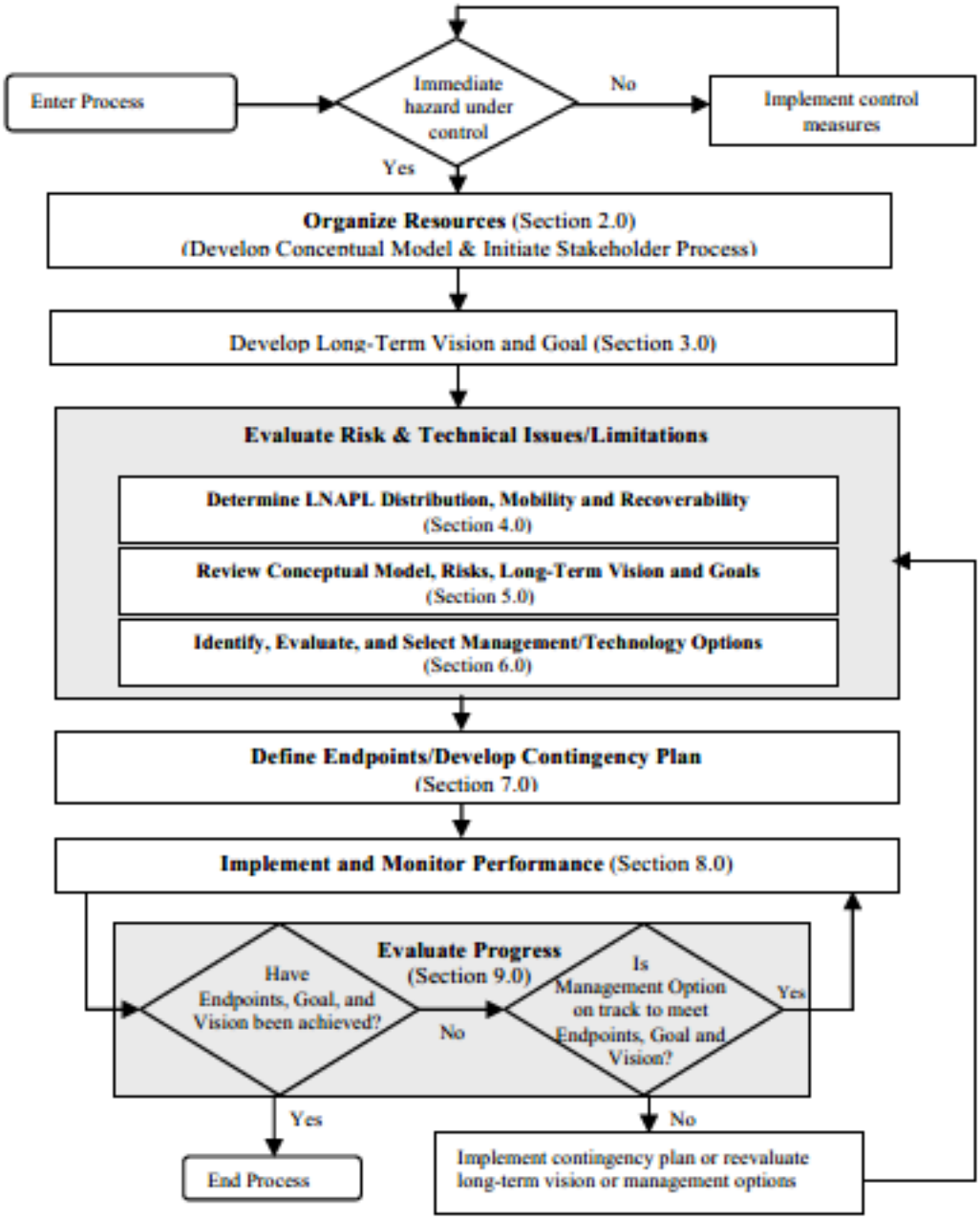
- *% oil/water cut was calculated as the volume of oil removed from the well relative to the volume of water. % oil/water cut is an indicator of efficiency and as LNAPL transmissivity declines over time the % oil/water cut is expected to decline (assume same technology and approach applied over the period).*

Footnotes will be added to the table to document how these calculations were made.

***Specific Comment #3**: Section 6, Updated Remedial Action Work Plan, Page 63:* Section 6 discusses the scope of the Work Plan, which is an updated version of the previously EPA approved July 23, 2001 document. One of the stated objectives of the Work Plan (a.k.a., the updated work plan) is the optimization of LNAPL recovery efforts in order to cease LNAPL recovery. How "optimization" will be determined, what lines of evidence will be used to perform the optimization, and how it will be determined that the system has been optimized to the degree possible is not defined. Site specific performance goals and decision thresholds need to be defined to achieve consensus for the proposed approach. A decision tree and a contingency plan are recommended for integration into the Work Plan, to help determine which decision criteria to use to move the site forward through the optimization process. A decision tree is outlined in *"A Decision-Making Framework for Cleanup of Sites Impacted with Light Non-Aqueous Phase Liquids (LNAPL), EPA 542-R-04-001, March 2005* [and a similar decision tree is outlined in LNAPL-3: LNAPL Site Management: LCSM Evolution, Decision Process, and Remedial Technologies, ITRC, March 2018).

***Response to Specific Comment #3**. We agree that a decision-making process can be developed for the benefit of USEPA but inherently the purpose of this work plan was to outline our approach, reach some consensus of practical endpoints, and collect data to validate and finalize the CSM. Consistent with the ITRC (2018) Guidance and USEPA (2006), (as shown below), a CSM must be developed prior to the endpoint determination. Given that NSZD is considered a critical component of the remedial approach moving forward, this assessment must be completed before we can define our final endpoint vision and*

The purpose of the document was to frame some endpoint considerations which can be assessed as part of the supplemental investigation scope of work. From review of USEPA comments we see that there is no objection to using the ITRC (2018) guidance framework and inherently then the mobility/recoverability practicality endpoints for LNAPL. Similarly, USEPA is in apparent agreement that NSZD is a component of the remedial approach for the Site. What is uncertain is whether we have reached a point at certain locations that NSZD should be considered as the approach moving forward, what will be the restoration time frame with NSZD, where hydraulic recovery of LNAPL will continue in the short term and what are the contingency plan and associated triggers.


Enter Process
Immediate hazard under control
No
Implement control measures
Yes
Organize Resources (Section 2.0)
(Develop Conceptual Model & Initiate Stakeholder Process)
Develop Long-Term Vision and Goal (Section 3.0)
Evaluate Risk & Technical Issues/Limitations
Determine LNAPL Distribution, Mobility and Recoverability
(Section 4.0)
Review Conceptual Model, Risks, Long-Term Vision and Goals
(Section 5.0)
Identify, Evaluate, and Select Management/Technology Options
(Section 6.0)
Define Endpoints/Develop Contingency Plan
(Section 7.0)
Implement and Monitor Performance (Section 8.0)
Evaluate Progress
(Section 9.0)
Have Endpoints, Goal, and Vision been achieved?
No
Is Management Option on track to meet Endpoints, Goal and Vision?
Yes
Yes
No
End Process
Implement contingency plan or reevaluate long-term vision or management options

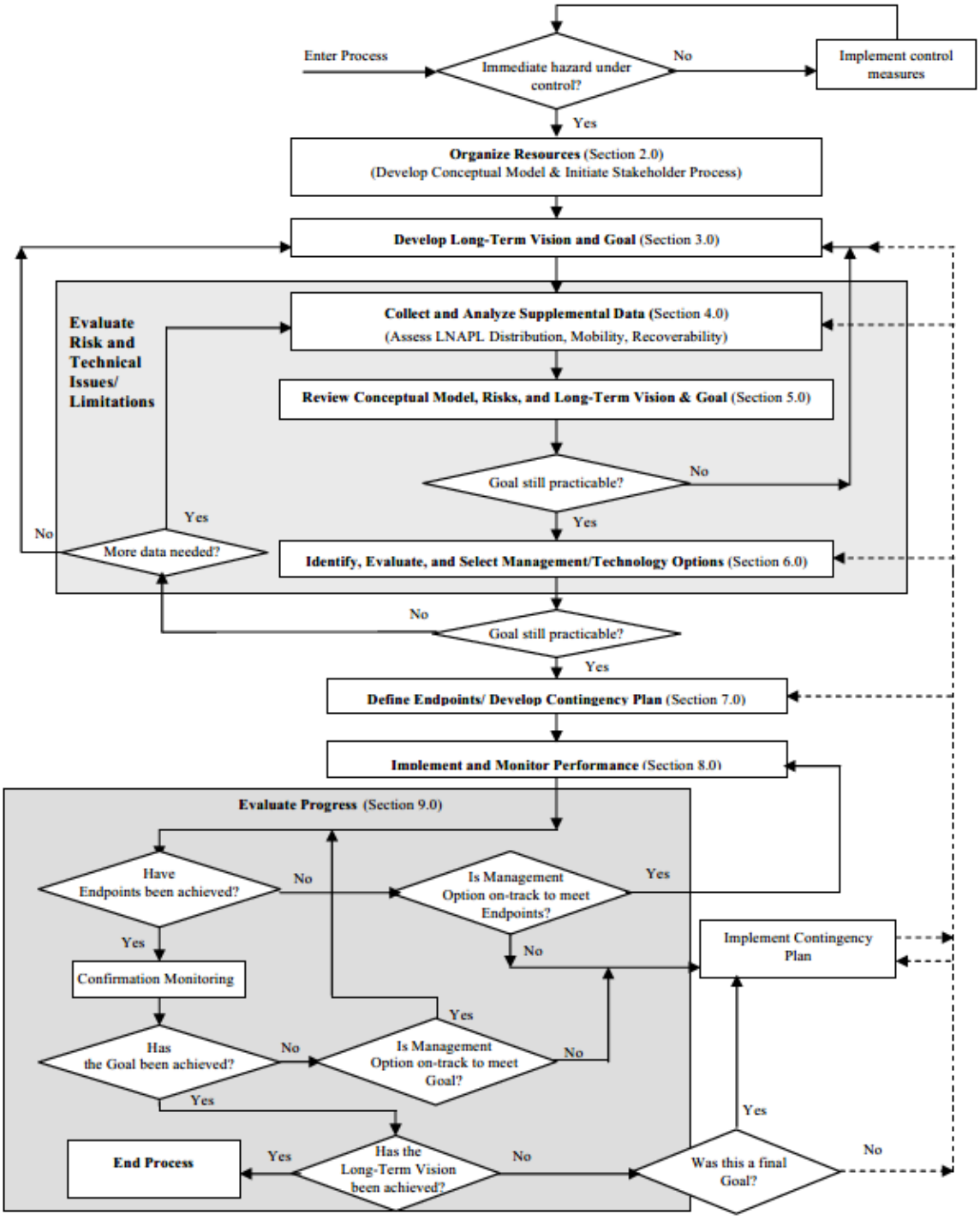


Figure 1. NAPL Management Decision-Making Framework Process

Specific Comment #4*: Section 6.1, LNAPL Recovery Activities, first paragraph, Page 63*: The Work Plan indicates that active measures to manage the LNAPL at the Site should only proceed until June 2021. No rationale is presented for this date. Revise the Work Plan such that the firm date of June 2021 is removed, and lines of evidence are presented that will be attained prior to the cessation of LNAPL recovery.

Response to Specific Comment #4*. As documented in this section, we propose to operate the system without interruption until June 2021 to enable collection of data for more detailed analysis of LNAPL transmissivity and LNAPL reservoir (recovery) decline curves. As stated in the document,*

> *"At this time, it is anticipated that sufficient data will be available to support systematic shutdown of recovery wells and a transition to MNA/NSZD processes in accordance with the framework described below. It should be noted that this assessment will be done on a well-by-well basis and the number of recovery wells that are shutdown after June 2021 will be informed by the data collected during this period and the process described below."*

What is being stated here is the data we have collected will determine if and what wells may not warrant further recovery actions and that any such decisions will be made on a well-by-well basis. Further and consistent with USEPA's comments, recommendations for shutdown will be provided to USEPA for approval.

It is anticipated that some wells will still be recovering sufficient LNAPL that LNAPL recovery actions will be continuing after June 2021. It should be noted that this date can be revised based on the approval date of this workplan and the NSZD work plan as it is critical that we have both LNAPL transmissivity and NSZD data in order to complete the assessments and provide recommendations for ongoing operations.

Specific Comment #5 *- Section 6.1, LNAPL Recovery Activities, Bullet 1 Page 64:* In the second to last paragraph, it is noted that solar sipper systems will be visited monthly. Because of the low transmissivities of wells at the site, sippers should be checked and cycled more often and on a regularly frequency during the optimization process to assure maximum recoveries are obtained. Weekly assessments, at least during start up, could potentially increase system efficiencies and be used to evaluate the viability of reducing the frequency of system checks and optimization activities. Revise the Work Plan to allow for more frequent initial visits for optimization related activities.

Response to Comment #5 – Routine inspections of the well will be conducted to confirm that the pumps are operational and functioning. However, no adjustments to the pump elevation and operation will be made during this test period. Constant tinkering and adjustments to the pump are the direct cause of the data variability that made data analysis challenging (as noted in USEPA's comments) and it is critical that we get constant operations.

The solar sipper is equipped with a floating intake, and as such water table elevation adjustments are not required. The pumping rate will be dialed in to minimize the amount of LNAPL in the well (target 0.1 to 0.25 feet in the well) but will not be adjusted once set. This may mean that the pump activates and pumps some air to surface. Consistency is key during this part of the evaluation.

Specific Comment #6: *Section 6.2, Proposed Framework for LNAPL Recovery Well Shutdown, Bullet 3, Page 65; and Section 6.2.1, Rationale and Methodology for Reservoir Decline Curve Analysis, Page 66:* In Section 6.2, a goal of 80 percent removal of the recoverable LNAPL is proposed. However, few details are provided regarding how this criterion will be applied to the Site. The Work Plan needs to be revised to include specifics regarding how this criterion would be developed and used for decision making purposes before it can be adopted for use at the Site. Additionally, EPA is not in concurrence that this should be the end goal for removal. We would be interested in exploring with the POC ways to increase the removal of recoverable LNAPL beyond 80% removal.

Response to Specific Comment #6: *Consistent with the discussion provided in Section 6.2.1, this is only one of the goals for the recovery systems. The primary determinant is an LNAPL transmissivity less than 0.8 ft^2/day (based on ITRC defined goals). Each Step in the process addresses key considerations and some of the comments provided by USEPA above.*

- ***Is the well being operated efficiently?*** *Step 1 of the process asks are LNAPL recovery operations being optimized to ensure that LNAPL is effectively removed from the well (LNAPL thicknesses measured in wells are maintained as much as possible below 0.25 feet during active recovery) thereby ensuring that the LNAPL recovery rates (on a well by well basis) continue to decrease over time.*
- ***Have we reached practical endpoint for hydraulic recovery?*** *Step 2 in the process uses ITRC (2018) recommended transmissivity value of 0.8 ft^2/day to define this decision point. Baildown tests (as discussed above) and LNAPL recovery rates will be used to determine if this end point has been reached. This is the primary metric to determine the practical endpoint for recovery, however Step 3 evaluates another.*
- ***Since LNAPL Transmissivity is Limiting Further Recovery can natural processes facilitate restoration of the aquifer in a reasonable period of time?*** *Whatever the endpoint for hydraulic recovery is at some point in time natural processes will be relied upon to facilitate restoration of the aquifer. Once the magnitude of these NSZD processes becomes known, the time period for restoration of the aquifer can be estimated.*

If the LNAPL transmissivity is > 0.8 ft^2/day then recovery will continue whether the reservoir decline curve analysis demonstrates that 80%, 90% or 95% of the potentially recoverable has been recovered.

Specific Comment #7 *Section 6.2.1, Rationale and Methodology for Reservoir Decline Curve Analysis, Page 66:* In Section 6.2.1, in the second to the last sentence, a criterion for R^2 squared of 0.1 is suggested for use when deciding to perform data analyses and estimating trends. The basis for suggesting this criterion is presented as being based on the inherent variability within geostatistical data sets. Provide a literature reference indicating that use of 0.1 is preferred for analyzing geostatistical data trends. A review of the current regression analyses, provided in Appendix C, Reservoir Decline Curves, suggests that many other factors may influence the observed results, such as changes in extraction methods and protocols or even changes in extraction technologies and equipment. The nature and distribution of results and other statistical assumptions must be considered and the appropriate methods for performing trend analyses used based on data set characteristics. Revise the Work Plan to provide the decision logic used for the use of R^2 as the preferred data assessment metric.

Response to Specific Comment #7*. The 0.1 R^2 coefficient is a minimum that is used to determine if there is some additional data processing required. The text will be revised accordingly. Consistent with the*

reservoir/recovery decline curve analysis methodology a best fit line needs to be established for the relationship between recovery rate and total recoverable volume. A discussion of this method is provided in the ITRC (2018) guidance. Regression coefficients are the accepted tool for assessing the quality of fit.

The scatter in the data was identified as a key constraint for analysis and recommendations for modifications to operations and monitoring for the solar sippers. As noted on the conference call with USEPA, the collection of recent data on a high frequency (relative to historical monitoring frequencies) creates an inherent bias (all data points are given the same weighting in correlation and regression coefficients) and impacts on the assessment and establishment of best fit lines. A range of methods exist for addressing these issues including outlier analysis (Cooks D Statistic or other outlier test) as well as time weighted averaging of recent data to ensure later time record data has the same periodicity of measurement as older data.

It is recommended that as more data are collected, a range of statistical tools will be used to determine how best to improve the fit of the best fit line.

***Specific Comment # 8**: According to Section 6.2.3 (page 67 of report)* – "Reductions in the frequency of monitoring is anticipated (initially to annual) but this will not occur until after all LNAPL recovery activities has ceased at the site and sufficient time has elapsed since termination of recovery (anticipated to be 4 semi-annual events) that plume stability (post recovery termination) has been demonstrated. Ultimately all groundwater monitoring will cease when the Tier II SSTLs are achieved in all perimeter wells". Please note that additional semi-annual monitoring would be required for several years after the SSTLs are achieved to ensure that the goals have been met. The details regarding the extent of post-remedial monitoring warranted will be the subject of further discussion between EPA and the POC.

***Response to Specific Comment #8**. Comment is noted. It is anticipated that an LNAPL Management Plan will be developed after completion of both the supplemental assessments and NSZD study. This LNAPL management plan will provide a decision-making framework for LNAPL consistent with the referenced ITRC and USEPA guidance and will be supported by a monitoring plan. This monitoring plan will consider the monitoring requirements associated with ongoing LNAPL recovery (if occurring) and natural source zone depletion and will demonstrate stability of the LNAPL and dissolved phase plumes. It is recognized monitoring and management will be required until Tier II site specific target levels (SSTL's) have been demonstrated to have been achieved.*

***Specific Comment #9**- Section 6.3, Natural Source Zone Depletion Assessment, Page 71:* It is unclear which wells will be analyzed for groundwater geochemistry during the Phase 1 effort. LNAPL wells as well as dissolved phase monitoring wells need to be included in the Phase 1 sampling and analysis plan to support MNA evaluations. Revise the Work Plan to specify all wells to be sampled in support of this effort.

***Response to Specific Comment # 9:** The text in Section 6.3 has been updated to list wells to be analyzed for geochemical parameters during the Phase 1 NSZD effort. An NSZD workplan with additional details has been provided to USEPA for review and does include this information.*

Specific Comment #10: *Section 6.3, Natural Source Zone Depletion Assessment, Page 71:* During Phase II, it is proposed that E-flux and an equivalent E-flux method for carbon dioxide measurements in the subsurface will be performed using a grid approach. Flux methods depend on reliable estimates of flux through vadose zone media to obtain reliable estimates for expected concentrations of methane and carbon dioxide over time. As noted by ITRC (2018) guidance, it is also possible to use vapor probes properly positioned to emulate flux through differing geologic units at several depths above the LNAPL, but below the surface, to more accurately estimate carbon dioxide and methane concentrations in vadose zone media. This type of application may be more desirable based on the LNAPL CSM for this Site. Less permeable media, which could include limestones with only limited secondary porosity features, alluvium, reef overburden, fill, and evaporite deposits may enhance or drastically reduce the effectiveness of NSZD. Given the variability in the geology at the Site, flux type measurements may be unacceptable for use. It is also unclear why these analyses will not be performed during Phase I, as the collection of this data may be essential to the decision-making process and it will take some time to incorporate the results into the remedial process.

Response to Specific Comment 10: *Given the effort and expense for implementing E-flux traps and need to quantify the spatial variability in NSZD processes occurring at the Site, it is proposed to first assess geochemical indicators (among other factors), subsurface soil gases and temperature profiles in existing wells to better understand NSZD variability across the site. A NSZD workplan with additional details on the proposed Phase 1 and II work has been submitted to USEPA for review.*

The process of NSZD assessments is complex and all methods have limitations. There are numerous questions that need to be answered first as part of the assessment to define the preferred approach. E-Flux (if all methane is converted to carbon dioxide) is a good methane measurement as it provides temporal averaging and captures advective (for example diurnal temperature and pressure movements of subsurface soil gases) and diffusive processes. Equally vertical transects of soil gas probes using Ficks First Law of Diffusion can look at a broad range of soil gases but only involves snap shots of soil gas concentration. Before we finalize our means and method and consistent with the NSZD Work Plan submitted to USEPA which involves a multiple lines of evidence approach, we are proposing to conduct a Phase 1 program of works to assess the following:

1. *Are the geochemical conditions supportive of sulfate reduction and methanogenesis (note these windows of degradation overlap)?*
2. *In terms of methane is complete degradation to carbon dioxide occurring or anticipated to occur in the unsaturated zone?*
3. *Do other data sets indicate variability in NSZD rates across the site and how should the sampling program be modified to reflect this variability?*
4. *Are there background methane and carbon dioxide sources that need to be considered?*

Based on the Phase 1 program, recommendations for the Phase 2 NSZD Studies will be provided to USEPA for approval.

Sincerely,
EHS Support Corporation

Respectfully,

Nigel Goulding
Senior Vice President

Dr. Andrew Fowler
Senior Hydrogeologist

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 2
290 BROADWAY
NEW YORK, NY 10007-1866

January 29, 2021

Mr. Brian Epperson,
Director, Environmental Health & Safety
HOVIC
1501 McKinney Street
Houston, Texas 77010

Re: Review of the draft LNAPL Natural Source Zone Depletion Work Plan, St. Croix Alumina Groundwater Plume, U.S. Virgin Islands; EPA ID Number: VID090302084

Dear Mr Epperson:

EPA has reviewed the *LNAPL Natural Source Zone Depletion Work Plan,* dated November 2020, for the St. Croix Alumina groundwater plume, located in St. Croix, U.S. Virgin Islands. The enclosed comments specify the additional information needed. They include input from EPA Region 2's Laboratory Services & Applied Science Division, as well as from our RCRA contractor, Toeroek. If you have any questions regarding these comments, please feel free to contact me via telephone at 212-637-4181, or via email at stein.carol@epa.gov

Sincerely,

Carol A. Stein

Carol A. Stein, PE
Environmental Engineer
Base Program Management Section
Land and Resources Programs Branch

Enclosure

cc: Austin Callwood, Director, USVI-DPNR-DEP (electronic copy w/enclosure)
Syed Syedali, USVI-DPNR-DEP (electronic copy w/enclosure)
Brad Martin, Toeroek (electronic copy w/enclosure)

ENCLOSURE

COMMENTS ON DRAFT LNAPL NATURAL SOURCE ZONE DEPLETION WORK PLAN ST CROIX ALUMINA GROUNDWATER PLUME, NOVEMBER 2020 ST CROIX, USVI

I. QUALITY ASSURANCE PROJECT PLAN (QAPP)

Comment #1 - QAPPs normally have a lifecycle of 5 years. The QAPP included as Appendix C to the Work Plan is outdated and needs to be resubmitted. Any new scopes of work will also require the submission of a new QAPP. Please also note that the submitted QAPP was used for the work associated with the dissolved phase petroleum hydrocarbon. Whereas the work proposed under the draft LNAPL NSZD work plan is for assessing the LNAPL source zone depletion. Hence, a separate QAPP would be needed for LNAPL sampling and analysis. In addition, please note that EPA Region 2 has adopted the Uniform Federal Policy for Quality Assurance Project Plans (UFP-QAPP) format for QAPP documentation. Additional information can be found at the following EPA webpage: https://www.epa.gov/fedfac/assuring-quality-federal-cleanups. The UFP-QAPP Manual and the accompanying Optimized Worksheets are available for reference in the same webpage. The UFP-QAPP, which contains 37 worksheets, is designed to be a standalone document for project personnel to carry out their responsibilities. After the work plan is updated in accordance with the comments noted in this letter, it would be sufficient to cite in each of the QAPP worksheets where each of the requested items are located (section, page) within the revised work plan.

Comment #2 - For the Key Study Questions in Section 3.3 and Data Quality Objectives (DQO's), please use the EPA's 7-step DQO process in order capture the decisions that will be made and the required level of data quality with corresponding acceptance criteria. With the UFP-QAPP, the Optimized Worksheet #11 should be used to document this information.

Comment #3 - Key investigation questions are provided in Table 3-1 (included in the body of the Work Plan), but the questions lack specificity. The questions need to be expanded to present the specific logic and decisions that will be made regarding the NSZD monitoring effort. Table 1 (included in the Table section) provides some clarification in terms of how data will be used, but does not provide adequate cross-references to appropriate sections of the Work Plan for ease in understanding and identification of decision criteria that might be considered during decision making. As noted above, please revise the Work Plan to ensure the DQO development is consistent with the approach outlined in the UFP-QAPP.

II. General Questions

a. Section 3.2 - The rationale for selection of monitoring wells to be used in the Phase I monitoring program are not adequately discussed in the text and associated tables, specifically Table 3. The Phase I program is noted as being conducted in conjunction with the semiannual monitoring event, but the omission of certain wells historically inside the light non-aqueous phase liquid (LNAPL) plume (i.e., wells VW-15, VW-17, VW-18, VW-19, VW-26, VW-28 and VW-38) are excluded from the proposed well network. The rationale for excluding these wells but including others needs to be provided in the Work Plan. Please revise Table 3 of the Work Plan to include, as part of the data quality objectives (DQOs), the intended informational purpose for each well location selected.
b. Please specify where the temperature profiling and well head space soil gas measurements will be collected.
c. (Section 2) - Important elements of the Natural Source Zone Depletion (NSZD) conceptual site model (CSM) including the depth of the groundwater table relative to well screens, location and thickness of LNAPL, and geology across well screen intervals are not provided in the associated maps and cross-sections. Data is available to define these features in the LNAPL NSZD CSM. The NSZD CSM serves an important role in evaluating the reliability of proposed data to be collected during the Phase I and II programs. Please revise the Work Plan to include a more detailed site NSZD CSM for critical wells and portions of the NSZD study area.
d. Section 4.2.1 – The first paragraph of this section indicates that the presence of methane and carbon dioxide above baseline concentration in the vadose zone provide a strong line of evidence that hydrocarbon degradation and mass loss are occurring. Please clarify when the baseline concentration was determined. In addition, please explain what the basis is for the selecting which efflux gas measurement methods (passive flux trap or dynamic closed chamber method) will be used.
e. Decision Criteria: The decision criteria that will be used to decide how grids for surface samples collected using either E-flux passive samples (E-flux) or dynamic closed chamber (DCC) samplers is not presented. The decision logic for establishment of the sampling point grids needs to be presented in a flow chart/decision tree that can be used to understand how decisions will be made to select one method and establish the associated grid to be used during Phase II of the NSZD evaluation program. Please revise the Work Plan to include this information.
f. Groundwater Flow Direction*:* As noted in the Work Plan, the cause for the anomalous groundwater elevation at well GM-22 is currently unknown. Arrows showing estimated flow directions on the piezometric surface map provided in the Work Plan appear to be erroneous at key locations. Groundwater flow beneath the plume is not always south to southeast as suggested in the CSM and the map

arrows. The piezometric surface high surrounding VW-30 and VW-35 as mapped beneath the LNAPL plume suggests that although groundwater gradients in this area are low, groundwater flow could be radially outward to the northwest and southeast of these groundwater highs or mounds and could very well explain, in part, the historical geometry of the LNAPL plume (See Figure 4). The CSM that focuses on the areas where NSZD is to be further evaluated, needs to be revised to include a more detailed and corrected piezometric surface map and a discussion of possible localized flow directions for groundwater beneath the historic LNAPL plume.

g. Because a multiple lines of evidence approach will be used during decision making after completion of Phases I and II, it is essential that a formal weight of evidence approach be described including a flow chart that supports the proposed decision-making process in the Work Plan. The decision logic needs to identify the benefits and limitations of decision criteria used at critical points of the program. This decision process needs to also indicate what parameters have the greatest potential for introducing errors to the decision process for estimating NSZD rates identified in the Work Plan and in subsequent deliverables. Please revise the Work Plan to include the decision logic to be used.

h. The Work Plan calls for the use of a gradient method that combines soil gas readings from inside wells near the water table with shallow one-foot below ground surface (bgs) soil gas measurements adjacent to the paired wells. Because of the complexity of the geology at the site it may not be adequate to use only two points to verify changing conditions in the vadose zone, particularly where secondary porosity features may influence advective flow in the subsurface. American Petroleum Institute (API) NSZD Guide (2017) suggests that multiple levels of soil gas probes may be needed when water tables are greater than five feet below ground surface (bgs) to better define the limits of vapor phase diffusion coefficients and NSZD rates using a gradient method. The depth to groundwater at the site appears to range up to 40 feet bgs. The Work Plan needs to describe how the proposed gradient method can be considered representative of site conditions.

i. Also, gradient methods assume that diffusion is the only soil gas distribution mechanism above an LNAPL plume. Given that secondary diagenetic features such as calcification and bedding planes are potentially controlling mechanisms for advection (i.e., flow) beneath the site, it is not clear how these potential influences will be overcome using the simple two point gradient test proposed in the LNAPL NSZD Work Plan. The Cooperative Centre for Contamination Assessment and Remediation of the Environment (CRCCARE) in Technical Report No. 44, Technical measurement guidance for LNAPL NSZD (CRCCARE Guide), suggests in Figure 9 of this report that gradient methods in limestone sites should be carefully considered prior to use. Table 6 of the CRCCARE guidance indicates gradient methods should include soil gas probes installed below 1.5 meters bgs to avoid root zones. Moisture content in the subsurface may also have

a substantial influence on any calculated NSZD rates calculated using gradient and other soil gas measurement methods. The Work Plan needs to address how the current designs can be reliably used given site conditions. How and when moisture content issues related to NSZD activities will be addressed needs to be integrated more specifically into the site decision logic and sampling plan discussed in the Work Plan. Please revise the Work Plan to address these issues.

j. The decision whether to use DCC as opposed to passive E-flux meters during Phase II will depend on whether methane is completely digested at a specific location and across the site. Given the flux of soil gas through the E-flux sampler can only be estimated, it is essential that flux rates are estimated as closely as is possible under site conditions during NSZD testing. Please revise the Work Plan to include sufficient information on how flux rates will be estimated should E-flux be proposed for use at the site during Phase II. Further, the Work Plan should also discuss how the potential for excessive winds to over-estimate NSZD rates when using E-flux will be addressed.

k. Section 4.3.9.2 – For the dynamic closed chamber method, it is not clear how the CO_2 detection limit is determined and the process/method that will be used for data validation. Since weather condition is a factor in efflux measurements calculations, it is not clear what type of weather-related information will be collected and/or instrumentation used.

III. LABORATORY QA/QC

a. Section 4.3.9.1 – Please provide the name of the laboratory that will be analyzing the traps for CO_2, as well as the method to be used and the laboratory's reporting limit. In addition, information regarding acceptance criteria for the duplicates should also be included.

b. Section 5.7 – It is not clear what will be the acceptance criteria to evaluate the specified QA/QC samples. In addition, the collection frequency for the QA/QC samples was not included. Please provide.

c. Section 5.8 – For the specified laboratory analysis, it is not clear what are the project's required reporting limits and whether there are there any criteria that are being used for comparing the results. Please also provide the laboratory's accreditation information for these analyses (type of accreditation and expiration date).

   In addition, please provide the method specifications that will be used for the dissolved gases. Please also include the filter size that will be used to collect the sample for dissolved metals; please note that a consistent filter size is needed for consistent results, and that 0.45 microns is a typical filter size for dissolved metals.

d. Section 6.0 – Please clarify which procedures will be used for validating the data generated and the process for assessing the data usability. Also, please include any SOPs that will be used. The type of decision that will be made with the data will typically dictate the level of validation.

IV. SPECIFIC COMMENTS

Specific Comment 1: Section 1.1 last paragraph, Figure 2: As noted in the last sentence, potential source areas are located on the west side of the site. The location of these potential source areas needs to be shown on Figure 2 as they could impact where samplers are placed and the geochemistry of the soil gas near these impacted surface materials. Please revise Figure 2 accordingly.

Specific Comment 2: Section 1.2 Paragraph 4, Figure 3: In this paragraph it is noted that the groundwater table is broadly consistent with the Kingston Limestone. However, Figure 3 does not support this statement. The depth to the water table and relationship of well screens in the LNAPL NSZD study area needs to be described more accurately in this section and on Figure 3 of the Work Plan. Careful inspection of Figure 3 also shows that boring logs from some wells such as VW-14 and projected well VW-18 were not honored on the cross-section. Some explanation, perhaps as a footnote to Figure 3, of why these well logs were not included in the cross-section is needed. An updated set of cross-sections, specifically for the LNAPL plume study area, are needed in the Work Plan to demonstrate the spatial relationships between well screened intervals, LNAPL, geologic, and hydrogeologic features. Also, the cross-sections shown on Figure 3 need to be updated to include detailed LNAPL study-specific well diagrams that support verification of the LNAPL transmissivity bail down tests.

Specific Comment 3: Section 1.3, first paragraph, Figure 4: In this paragraph groundwater flow is noted as generally to the south-southwest and south towards the sea. Inspection of Figure 4 indicates that localized flow beneath the plume may occur radially to the northwest and southeast away from several groundwater highs in the vicinity of wells VW30 and VW35. These features suggest a very flat gradient beneath the LNAPL plume and potentially variable flow directions that could explain, in part, the geometry of the historical LNAPL plume. A more detailed piezometric surface map underlain by the most extensive historical plume map, such as those provided in Appendix A of the Work Plan is needed. The extent of historical subsurface contamination needs to be presented along with the interpreted localized groundwater elevations beneath the LNAPL plume. The locations of potential source areas also needs to be identified on Figure 4 or another more detailed piezometric surface map prepared for the LNAPL NSZD plume study area.

Specific Comment 4: Section 3.2.2: The scope of the Phase 2 program is poorly defined. This section of the Work Plan needs to be more detailed to allow for a better idea of the number of

samplers of various types which may be used along with dimensions of any proposed study areas. Other information that needs to be included in this section includes whether geochemistry parameters collected during Phase 1 will be repeated in subsequent phases or monitoring events, and whether temperature monitoring will be included in Phase 1 and subsequent well sampling events as a means for long term monitoring of NSZD.

Specific Comment 5: ***Section 3.2.2, Last Bullet:*** In the last Bullet, it is suggested that during Phase 2, analysis of wells for carbon fractionation using compound specific isotopic methods for carbon will be performed to determine if a background correction can be applied successfully to remove the impacts of carbon signatures from native carbonate rocks from signatures from NSZD of the LNAPL. It would be beneficial to perform these analyses as soon as possible to assure that passive Flux or DCC soil gas sampling data will be representative of NSZD of the LNAPL and not biased high because of contributions from native carbonate contributions to carbon dioxide values. Ensure the Work Plan allows for the collection of this data at the earliest step.

Specific Comment 6: ***Section 3.2.3***: This section does not provide a specific time frame for reporting Phase 1 results to EPA. Please modify the Work Plan to provide more specific timing for the Phase 1 report.

Specific Comment 7: Table 3-1 includes general data quality objectives. These DQOs are based on the content in Appendix B of the Technical Measurement Guidance for LNAPL Natural Source Zone Depletion (CRC-CARE Technical Report No. 44) (CRCCARE). The checklists included in Appendix B of the CRCCARE report are intended to be used as place holders to prompt the development of site-specific DQOs. However, the Work Plan needs to develop site specific DQO's that define how the data from Phase 1 and 2 will be used to bound decision making concerning the evaluation of NZSD at the site. Development of the specific DQOs can occur in Table 1 of the Work Plan and should be consistent with those presented in Worksheet #11 of the associated UFP-QAPP.

Further, the information included in Table 1 of the Work Plan includes site specific principal study questions in a format that is more in tune with EPA's DQO approach, but Table 1 does not provide an adequate cross-walk between applicable sections of the Work Plan and the Table contents for the column heading "Data Use Objective". Information in Table 1 should be consistent with UFP-QAPP, Optimized Worksheet #17 which supports the information included in Worksheet #11. Please revise Table 1 to include references to the supporting information within the Work Plan as well as UFP-QAPP Worksheet#17 or its equivalent. Additionally, please ensure that the Work Plan includes a diagram or flow chart indicating the intended decision logic to be used during data assessment. As cited in the reference section at the end of the Work Plan, the Interstate Technology & Regulatory Council (ITRC) updated its LNAPL guidance: ITRC 2018. *Light Non-Aqueous Phase Liquid (LNAPL)* Site *Management: LCSM*

Evolution, Decision Process, and Remedial Technologies, LNAPL-3. Washington, D.C. https://lnapl-3.itrcweb.org (LNAPL-3). Hence the list of references cited at the bottom of Table 1 needs to include the ITRC's LNAPL-3. Appendix B of LNAPL-3 includes examples of site-specific decision logic diagrams to guide the decision-making process. Please ensure that the Work Plan includes a site-specific decision logic diagram or flow chart consistent with the ITRC LNAPL-3 guidance.

Specific Comment 8: ***Table 3:*** This table identifies the wells in the proposed LNAPL plume monitoring network, as well as those wells selected as being indicative of background and down gradient. No rationale is provided for how and why the background wells were selected. Presumably, their selection is based on location and proximity to the study area and past monitoring and sample analyses performed at these locations. Additional detail is needed in the Work Plan concerning how the background wells were selected. A review of down gradient well locations given the current piezometric surface provided in Figure 4 indicates that many of these wells are upgradient or cross-gradient of the study area. Understanding there may be a significant data error/anomaly in the reported groundwater value for GM22, Table 3 will need to be reevaluated before the wells listed in it can be considered representative for LNAPL NZSD study purposes as either down-gradient or upgradient.

Additionally, the work on the redetermination of the casing elevation of GM22 and other wells should be considered during Phase 1 to better inform the CSM.

Specific Comment 9: ***Figure 7:*** The Figure shows potential locations for E-flux samplers. However, it is unclear how the configuration shown in the figure was developed and why there is not a figure which also shows potential locations for DCC samplers should they be selected for use. Please include this information. It also would be useful to include a presentation of where gradient evaluations may be performed.

EVALUATION OF RESPONSE TO USEPA COMMENTS

DATED DECEMBER 14, 2020

ON THE

LNAPL CSM AND REDEDIAL ACTION WORK PLAN

ST. CROIX, U.S. VIRGIN ISLANDS

DATED JULY 2020

In general, the Response to Comments (RTCs) addressed EPA's comments and are acceptable with the following considerations. The following evaluation includes only responses where additional information or clarification is required.

A revised version of the Light Non-Aqueous Phase Liquid (LNAPL) Conceptual Site Model (CSM) and Remedial Action Work Plan (Work Plan) was not provided, and as such an evaluation of the whether the RTCs were incorporated into the Work Plan was not able to be completed. A revised Work Plan incorporating the proposed revisions is needed.

EVALUATION OF RESPONSES TO GENERAL COMMENTS:

***Evaluation of the Response to General Comment 1 (Risk Evaluation)*:** As noted in our conference call of February 3, 2021, the risk assessment will need to be updated to address current conditions. Additionally, an evaluation currently is being conducted to provide input to help determine if the Site Specific Target Levels (SSTLs) need to be updated for the SCA plume site.

Evaluation of the Response to General Comment 2 (Remedial Goals): The response partially addresses the concerns expressed. The interpretation of transmissivity sits at the crux of the assessment of LNAPL recovery. Transmissivity assessment is made on a well-by-well basis. Assurances that each well used to determine transmissivity is appropriately screened to support such an assessment needs to be demonstrated. As such, the cross-section presented in Figure 4-3B omits the presentation of the screen interval with respect to the water table, the historical high-water level, the historical low-water level, and the currently known LNAPL thickness in the well screen. Any well included as part of the transmissivity assessment needs to have a well screen which straddles all of the high, low, and LNAPL levels. Also, changes in apparent product thickness may change the LNAPL transmissivities measurements planned for collection during Phase 1 activities. Any significant changes in groundwater levels and associated apparent product thicknesses may necessitate additional transmissivity measurements. Please revise the Work Plan to ensure it presents well logs showing the following for each well: the historical high-water level, the historical low-water level, and the currently known LNAPL thickness in the well screen. Also, include a contingency for additional transmissivity measurements based on observed changes to LNAPL thicknesses.

EVALUATION OF RESPONSES TO SPECIFIC COMMENTS

Evaluation of the Response to Specific Comment 3 (*Section 6, Updated Remedial Action Work Plan, Page 63)* **:** The last sentence in the first paragraph of this response is incomplete and needs to be revised. The purpose of providing a non site-specific decision logic diagram in the response is unclear.. A Site-specific decision logic diagram needs to be prepared and discussed with the EPA prior to moving

forward, even if some of the steps are contingent upon the finalization of the CSM. CSM contingent decision steps could be uniquely noted as such in the site-specific decision tree configuration.

Evaluation of the Response to Specific Comment 6 (*Section 6.2, Proposed Framework for LNAPL Recovery Well Shutdown, Bullet 3, Page 65; and Section 6.2.1, Rationale and Methodology for Reservoir Decline Curve Analysis, Page 66)****:***

The following rules-of-thumb are noted in Appendix C of the Interstate Technology Regulatory Council 2018 LNAPL guidance (ITRC-3), Section 1.1:

- *LNAPL transmissivity between the range of 0.1 to 0.8 ft^2/day may be used as a decision point for remedial system operation or technology transitions. While LNAPL transmissivity is useful for evaluating LNAPL hydraulic recovery potential, it should not be used as a sole means to determine whether an LNAPL remedy for a site is necessary or unnecessary.*
- *A threshold LNAPL transmissivity value, typically representative of an LNAPL saturation that is nominally above the residual LNAPL saturation for the formation, may be established at the outset of the LNAPL recovery action and used as a trigger for stopping LNAPL recovery. The decision on whether to implement an LNAPL remedial action should be based on the broader site LNAPL CSM rather than LNAPL transmissivity alone.*
- *It should be noted that LNAPL transmissivity measurements often vary in both space and time. For example, groundwater fluctuations can occur such that the LNAPL fluctuates from unconfined to confined conditions. In that situation, it may be necessary to measure LNAPL transmissivity values under both conditions.*

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EPA recognizes that your response to comments indicates that additional goals will be evaluated. However, more details are needed to justify these goals. Appendix C, Section 1.2 of ITRC-3 notes the following:

There are a number of methods that can be used individually or in combination to demonstrate that free product has been removed to the maximum extent possible. According to Appendix C, Section 1.2 of the LNAPL-3 document, these include:

- *comparing mobile LNAPL mass to the mass of LNAPL in the smear zone,*
- *analyzing LNAPL recovery data and determining that future recovery will not be meaningful,*
- *showing that LNAPL thicknesses are small and/or intermittently observed,*
- *modeling future potential LNAPL recovery using a multiphase model,*
- *demonstrating that the LNAPL body is stable and that stability will not change in the future, and*
- *presenting information that shows an unreasonable cost per gallon or pound of LNAPL recovered.*

The current plan does not clearly define what multiple lines of evidence have been or will be used in the future to support a decision to turn existing wells off in terms of performing continued product removal. At present insufficient data and conclusions have been presented to EPA to support the proposed decision criteria and decision logic. Specifically, more information is needed in terms of explaining the basis for why a transmissivity criterion of 0.8 foot squared/day or 1 gallon per day LNAPL recovery criteria should be agreed upon for use at the site. Please ensure that the Work Plan outlines how these issues will be addressed going forward.

Memo

To: Brian Epperson, Hess Corporation

From: Nigel Goulding EHS Support LLC
Dr. Andrew Fowler EHS Support LLC

CC: Brad Freeman, Geo Monitoring Services

Date: February 19, 2021

Re: Response to January 29, 2021 United States Environmental Protection Agency (USEPA) Review of the draft light non-aqueous phase liquid (LNAPL) Natural Source Zone Depletion (NSZD) Work Plan, St. Croix Alumina Groundwater Plume, U.S. Virgin Islands, EPA ID Number: VID090302084

EHS Support LLC ("EHS Support") has prepared this response to the United States Environmental Protection Agency (USEPA) review of the draft light non-aqueous phase liquid (LNAPL) Natural Source Zone Depletion (NSZD) Work Plan (Work Plan) for St. Croix Alumina U.S. Virgin Islands site (Site), dated January 29, 2021.

From our review of USEPA comments, we recognize that there is general alignment that multiple lines of evidence are needed to assess NSZD at the Site. We also note that that there are no comments on the calculations and technical aspects of the methodology that we proposed as these align with Interstate Technology and Resource Council (ITRC) and Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE) guidance.

In development of the NSZD Work Plan, it was evident that the work needed to be phased so that preliminary information could be used to better define the work scope and address potential concerns associated with: (a) background carbon dioxide; (b) heterogeneity of NSZD process and geology across the LNAPL affected area, which would impact the study design, and (c) the potential that all methane was not being converted to carbon dioxide prior to fluxing to atmosphere. This was explicitly discussed in the Work Plan and the strengths and weaknesses of various quantification methods was explored in the context of those uncertainties. The lack of definition for the Phase II program of works simply reflected the group's desire to collect preliminary data (as Phase I) and provide a more informed study design for the more expensive flux-based methods (E-flux or dynamic closed chamber using a LI-COR meter).

During the routine January 2021 monitoring and sampling event at the Site, we obtained some supplemental field measurements. The intention for the work was to, coupled with the comments provided by USEPA, help refine work proposed for Phase I and Phase II in a revised NSZD Work Plan. As described below, the supplemental measurements provide strong qualitative evidence for ongoing NSZD

occurring in the LNAPL source area at the Site and indicate that the proposed assessment is a critical component in development of the remedial strategy for this Site. In addition, the supplemental measurements indicate there is relatively low spatial heterogeneity in the manifestations of NSZD at the Site, despite the observed geologic and hydrogeologic heterogeneity. Based on these results, we propose to modify our approach to include additional wells for temperature profiling and head space measurements. Wells VW4, VW7, VW15, and VW18 will be added to the Phase I temperature profiling program, and Phase I well headspace gas measurements will be made at all wells where temperature profiles are to be measured. Additionally, the density of temperature measurements will be increased from three measurements per well to five per well to better capture vertical heterogeneity.

This letter is divided into two sections: **Section 1** a brief summary of the supplemental measurement methodology and results, and **Section 2** direct responses to USEPA comments on the draft NSZD Work Plan. To facilitate review of our direct responses in '2)', USEPA comments are shown in black text and our responses are shown in blue text.

1 Supplemental Measurements

Supplemental measurements were collected on January 26, 2021 during the routine monitoring event. Vadose and saturated zone temperature profiles along with monitoring well headspace gas concentrations were measured. Vadose zone temperatures were measured 2 feet below ground surface (bgs), half-way to the water table, and 1-foot above groundwater. Saturated zone temperatures were measured 1 foot below groundwater, 5 feet below groundwater, and 10 feet below groundwater. Headspace gases were measured 2 feet below top of casing and 1-foot above groundwater.

Supplemental measurements were collected from the following locations:

- Source area wells where LNAPL was present (VW2, VW5, VW6, VW13, VW13B, VW14, VW15, VW23, VW31, and VW32).
- One downgradient well where LNAPL was absent (VW17)

Groundwater temperature data collected from background monitoring wells MMX and VW37 as part of the routine field parameter suite were used to compare with those obtained from the supplemental measurements.

The following observations were made from the supplemental data:

1. Vadose zone temperatures qualitatively indicate NSZD. Vadose temperatures are elevated above the maximum daily air temperature (28.9 degrees Celsius [^{o}C]) on the sampling date (in-text **Figure 1A**).
2. Groundwater temperatures qualitatively indicate NSZD. Groundwater temperatures are elevated beneath the LNAPL by up to 3.1 ^{o}C compared to background groundwater at wells MMX and VW37 (27.6 ^{o}C) (in-text **Figure 1A**).
3. Temperature distributions qualitatively indicate NSZD. Groundwater temperatures increase in the downgradient direction beneath LNAPL, indicating progressive addition of heat as groundwater passes beneath the source zone (in-text **Figure 1B**).

4. Well headspace gas concentrations 1 foot above the liquid level qualitatively indicate NSZD processes. Gases indicative of NSZD processes (methane [CH_4], hydrogen sulfide [H_2S] and carbon dioxide [CO_2]) are present at notable concentrations (in-text **Figures 2A** and **2B**).
5. As shown on the in-text Figures, virtually all locations in the LNAPL affected area show temperature changes and gas concentrations in the same direction (i.e., elevated), except possibly in the vadose zone at VW-6. Additionally, the CO_2 and CH_4 concentrations are all largely within the same order of magnitude. This observation suggests that variations in geology and hydrogeology at the site may not have a particularly large effect on the NSZD processes that are occurring at the Site, and a Thiessen polygon approach to calculate cumulative NZSD processes will likely be adequate.

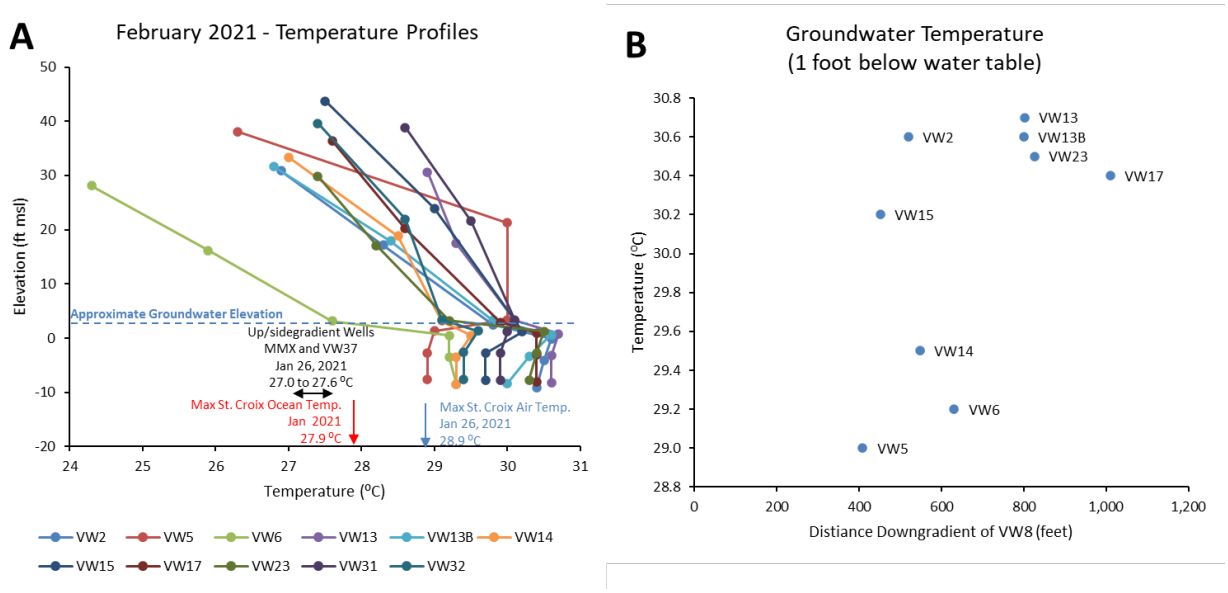

Figure 1 Results for the supplemental temperature survey. A) Down hole temperature survey results compared to background and ambient values. B) Temperatures beneath the western LNAPL lobe as a function of downgradient distance from upgradient well VW8.

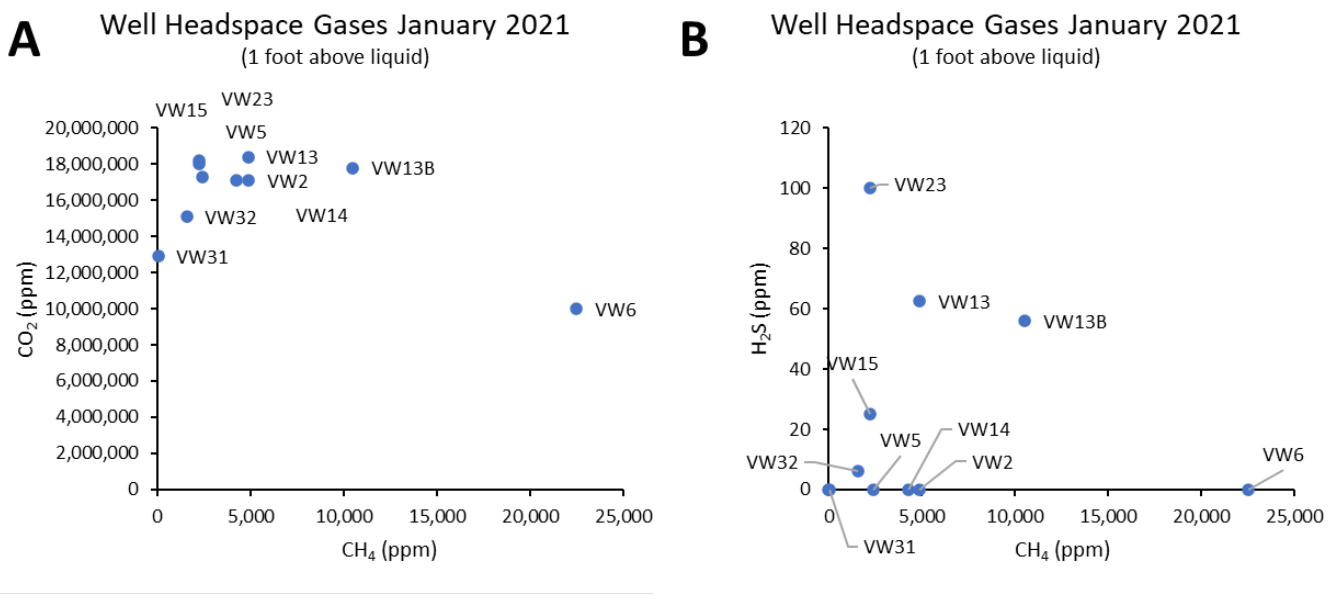

Figure 2 Results for well head space readings taken 1 foot above the liquid level in the well. A) CO2 and CH4 are elevated in wells where LNAPL is present, but absent in VW17 where LNAPL is absent. This supports that background concentrations of these gases are low and that appreciable volumes are produced by NSZD processes. B) The presence of H2S and methane provides evidence of sulfate reduction and methanogenesis may also contribute to NSZD. This contention is also supported by historic dissolved oxygen and ORP measurements of groundwater in wells downgradient of the LNAPL plume.

2 Responses to USEPA Comments on the Draft NSZD Work Plan

I. QUALITY ASSURANCE PROJECT PLAN (QAPP)

Comment #1 - QAPPs normally have a lifecycle of 5 years. The QAPP included as Appendix C to the Work Plan is outdated and needs to be resubmitted. Any new scopes of work will also require the submission of a new QAPP. Please also note that the submitted QAPP was used for the work associated with the dissolved phase petroleum hydrocarbon. Whereas the work proposed under the draft LNAPL NSZD work plan is for assessing the LNAPL source zone depletion. Hence, a separate QAPP would be needed for LNAPL sampling and analysis. In addition, please note that EPA Region 2 has adopted the Uniform Federal Policy for Quality Assurance Project Plans (UFP-QAPP) format for QAPP documentation. Additional information can be found at the following EPA webpage: https://www.epa.gov/fedfac/assuring-quality-federal-cleanups. The UFP-QAPP Manual and the accompanying Optimized Worksheets are available for reference in the same webpage. The UFP-QAPP, which contains 37 worksheets, is designed to be a standalone document for project personnel to carry out their responsibilities. After the work plan is updated in accordance with the comments noted in this letter, it would be sufficient to cite in each of the QAPP worksheets where each of the requested items are located (section, page) within the revised work plan.

2.1 Response to Comment #1

We acknowledge that a revised QAPP based on the Uniform Federal Policy for Quality Assurance Project Plans (UFP-QAPP) format is required. As stated above, the QAPP will only be required for the LNAPL sampling and analysis. We propose to update the QAPP for both LNAPL, dissolved phase, and other groundwater geochemistry testing that will be required to implement this scope of work and long-term groundwater monitoring (including monitored natural attenuation [MNA] and NSZD performance monitoring). As we understand, field-based methods such as field screening of soil gas concentrations, downhole soil gas monitoring and the E-flux and Flux Chamber LI-COR monitoring will not be included in the QAPP.

Once agreement is reached on the means and methods proposed in the draft NSZD Work Plan, a revised QAPP will be submitted to USEPA for review.

Comment #2 - For the Key Study Questions in Section 3.3 and Data Quality Objectives (DQO's), please use the EPA's 7-step DQO process in order capture the decisions that will be made and the required level of data quality with corresponding acceptance criteria. With the UFP-QAPP, the Optimized Worksheet #11 should be used to document this information.

2.2 Response to Comment #2

USEPA's 7-step DQO process has been incorporated into attached **Table 1** of the Work Plan and the key study questions in Section 3.3 of the Work Plan have been updated and provided for your review.

Comment #3 - Key investigation questions are provided in Table 3-1 (included in the body of the Work Plan), but the questions lack specificity. The questions need to be expanded to present the specific logic and decisions that will be made regarding the NSZD monitoring effort. Table 1 (included in the Table section) provides some clarification in terms of how data will be used, but does not provide adequate

cross-references to appropriate sections of the Work Plan for ease in understanding and identification of decision criteria that might be considered during decision making. As noted above, please revise the Work Plan to ensure the DQO development is consistent with the approach outlined in the UFP-QAPP.

2.3 Response to Comment #3

Attached **Table 1** has been updated by adding reference to the relevant sections of the work plan. In-text **Table 3-1** of the Work Plan (Key Questions) has been updated to include specific statements and has been provided as an attachment for review.

II. General Questions

a. Section 3.2 - The rationale for selection of monitoring wells to be used in the Phase I monitoring program are not adequately discussed in the text and associated tables, specifically Table 3. The Phase I program is noted as being conducted in conjunction with the semiannual monitoring event, but the omission of certain wells historically inside the light non-aqueous phase liquid (LNAPL) plume (i.e., wells VW-15, VW-17, VW-18, VW-19, VW-26, VW-28 and VW-38) are excluded from the proposed well network. The rationale for excluding these wells but including others needs to be provided in the Work Plan. Please revise Table 3 of the Work Plan to include, as part of the data quality objectives (DQOs), the intended informational purpose for each well location selected.

2.4 Response to General Question II.a.

Source area wells were selected as those that most recently had LNAPL present. Upgradient and downgradient wells were selected to be representative geology/hydrogeology variations, historical chemistry data, and provide geographical coverage without committing to sampling all Site wells. **Table 3** (attached) has been revised to include a column that specifies the rationale behind each location and has been provided for review.

b. Please specify where the temperature profiling and well head space soil gas measurements will be collected.

2.5 Response to General Question II.b.

Well headspace measurement and temperature profiling intervals are provided in Section 3.2.1 of the Work Plan, specifically:

- Vadose zone temperatures will be measured 2 feet bgs, half-way to the 1-foot above groundwater, and three equally spaced intervals in between.
- Saturated zone temperatures will be measured 1 foot below groundwater, 5 feet below groundwater, and 10 feet below groundwater.
- Headspace gases will be measured 1-foot above groundwater.

c. (Section 2) - Important elements of the Natural Source Zone Depletion (NSZD) conceptual site model (CSM) including the depth of the groundwater table relative to well screens, location and thickness of LNAPL, and geology across well screen intervals are not provided in the associated maps and cross-sections. Data is available to define these features in the LNAPL NSZD CSM. The NSZD CSM serves an

important role in evaluating the reliability of proposed data to be collected during the Phase I and II programs. Please revise the Work Plan to include a more detailed site NSZD CSM for critical wells and portions of the NSZD study area.

2.6 Response to General Question II.c.

We propose to update the NSZD Work Plan by incorporating the following elements from the LNAPL Conceptual Site Model (CSM) provided to in response to USEPA comments on the LNAPL CSM dated January 8, 2021:

- Revised cross sections have been developed and submitted to USEPA in response to comments on the Site LNAPL CSM. The revised cross sections indicate location and thickness of LNAPL and will be included in a revised NSZD Work Plan. The revised cross sections (new **Figure 3A** and **Figure 3B** in the revised Work Plan) are attached.
- Figure 5 (Geology across well screens) was included in the draft Work Plan that was submitted. Coupled with the revised cross sections, this is expected to adequately address the request for information about geology across well screens.

d. Section 4.2.1 – The first paragraph of this section indicates that the presence of methane and carbon dioxide above baseline concentration in the vadose zone provide a strong line of evidence that hydrocarbon degradation and mass loss are occurring. Please clarify when the baseline concentration was determined. In addition, please explain what the basis is for the selecting which efflux gas measurement methods (passive flux trap or dynamic closed chamber method) will be used.

2.7 Response to General Question II.d.

The statement here is not intended to be site specific and is a general statement that the presence of carbon dioxide and methane indicate NSZD is occurring. A reference to the ITRC guidance where this information was sourced will be inserted for clarification.

Consistent with USEPA's comments on the LNAPL CSM and Remedial Action Plan, decision logic diagrams have been prepared to support the assessment of the NSZD data collection and analysis (**Figure A4** and **Figure A5** of the package of LNAPL and NSZD decision logic diagrams included with the latest response to comments on the LNAPL CSM). This decision logic considers that the NSZD process may not be uniform across the Site and that the various methods (as described by ITRC and CRC Care have limitations). Criteria that will be evaluated to identify if passive trap or dynamic closed chamber (DCC) methods will be used include:

- If methane is detected at ground surface, the dynamic closed chamber will be favored as latest instruments are capable of measuring methane for incorporation into an NSZD rate calculation, whereas passive traps do not measure methane.
- Text will be added to state that weather will be a consideration of the utility of the passive trap method. Specifically, data for wind speed and duration downloaded from the National Oceanic and Atmospheric Administration (NOAA) data bases (or equivalent) from the region will be assessed in context of manufacturer recommendations as to the utility of the method. Note that a NOAA weather station is located less than 1.5 miles from the Site. Also please note that background and source area locations will be equally affected by wind, assuming the traps have

equivalent exposure. Therefore, the effect of wind will be minimized during the background correction.

- The passive trap method will be utilized if there are indications that high and/or variable concentrations of carbon dioxide are identified in background locations. In this situation, passive traps will be employed to obtain stable and radiogenic carbon isotope data to quantify background carbon dioxide concentrations that are not attributable to NSZD processes.
- Based on the outcome of supplemental measurements taken in January 2021, we recognize that geological variability may preclude use of either passive trap or DCC methods if gases produced by NSZD are not representative at the ground surface where these methods are employed.

Therefore, to assess the bulleted points above, we revised the NSZD Work Plan to propose installing three soil vapor monitoring locations in the source areas and one at a background well location during Phase 1. Specific locations will be determined based on access considerations during site reconnaissance but will generally target the center of each of the three main lobes of the LNAPL plume. The clusters will be adjacent to an existing monitoring well so that a well can be used to collect a deep soil gas measurement immediately above the liquid level in the well (as performed during collection of supplemental measurements described in this letter). The generalized construction of each soil vapor monitoring location will consist of sampling points installed 5 feet above the groundwater table (targeting the sand unit present at or above most screened intervals), midway between the ground surface and top of well screen (approximately 20 feet below ground surface [bgs] in most locations) and one 5 feet bgs.

e. Decision Criteria: The decision criteria that will be used to decide how grids for surface samples collected using either E-flux passive samples (E-flux) or dynamic closed chamber (DCC) samplers is not presented. The decision logic for establishment of the sampling point grids needs to be presented in a flow chart/decision tree that can be used to understand how decisions will be made to select one method and establish the associated grid to be used during Phase II of the NSZD evaluation program. Please revise the Work Plan to include this information.

2.8 Response to General Question II.e.

The decision logic to be used in defining the grid spacing and placement is provided in **Figure A4** and **Figure A5**. The variability in NSZD rates estimated via the temperature methodology as well as differences in groundwater geochemistry and soil gas concentrations down well will inform the grid spacing and locations which best capture the subsurface processes contributing to NSZD at the Site. It is understood that additional sampling and monitoring points may be required following field reconnaissance at the site and evaluation of Phase I results. A preliminary layout of Phase II E-Flux or LI-COR sampling locations has been provided but updates to this are anticipated.

The following potential outcomes from the evaluation of Phase I data could indicate:

- A uniform grid is appropriate for application at the Site.
- The grid spacing as provided in the preliminary layout is appropriate.
- The grid spacing should be smaller than that proposed layout provided on the figure.
- The grid spacing and locations should be modified to reflect key subsurface features/conditions contributing to NSZD rates.
- Locations should be avoided where surface cover or soil water saturation could result in a high or low bias and/or an inability to collect data.

f. Groundwater Flow Direction: As noted in the Work Plan, the cause for the anomalous groundwater elevation at well GM-22 is currently unknown. Arrows showing estimated flow directions on the piezometric surface map provided in the Work Plan appear to be erroneous at key locations. Groundwater flow beneath the plume is not always south to southeast as suggested in the CSM and the map arrows. The piezometric surface high surrounding VW-30 and VW-35 as mapped beneath the LNAPL plume suggests that although groundwater gradients in this area are low, groundwater flow could be radially outward to the northwest and southeast of these groundwater highs or mounds and could very well explain, in part, the historical geometry of the LNAPL plume (See Figure 4). The CSM that focuses on the areas where NSZD is to be further evaluated, needs to be revised to include a more detailed and corrected piezometric surface map and a discussion of possible localized flow directions for groundwater beneath the historic LNAPL plume.

2.9 Response to General Question II.f.

We concur that groundwater flow at GM-22 is a data gap and is identified as such in the NSZD Work Plan. We have subsequently verified that the survey data at this location is accurate and the mound is likely real. We note the following:

- We identified that GM-22 is within the footprint of the former red mud pond (see **Figure 3**below).
- Nearby and former well GM-10 (see **Figure 3** below) historically had anomalously high groundwater elevations, which was attributed to artificial recharge from a former cooling pond that was 10 feet above sea level and filled with seawater for cooling a power plant and residual brine from a desalinization plant (Geraghty and Miller, 1982)[1].
- Well GM-7 (see **Figure 3** below) was shown to be dry on Figure 4 of the draft NSZD Work Plan. The top of casing at GM-7 is 26.04 feet above sea level, and the well is 35 feet deep. Therefore, the groundwater mound is not present in this location.
- We identified a complex wastewater treatment system that recharges the groundwater system with reclaimed water is located to the west of wells GM-10 and GM-22. The system contains a network of subsurface pipes that may also potentially leak.

We expect that groundwater at GM-22 (and GM-10) is perched due the buried features and/or abundant clay in these locations from the historic Krause Lagoon that was present where these wells are sited. The source of the water is conceivably from the groundwater recharge system or leaking infrastructure, which has been in place for decades. We intend to sample GM-22 for cations, anions, and alkalinity, to verify if the water type at this location is geochemically distinct to verify this.

Once the cause of the mound has been identified, future groundwater contour maps will be revised accordingly.

FIGURE 3 REVIEW OF GERAGHTY AND MILLER (1982)[1] SHOWS THAT GM-22 IS WITHIN THE FORMER RED MUD POND AREA.

g. Because a multiple lines of evidence approach will be used during decision making after completion of Phases I and II, it is essential that a formal weight of evidence approach be described including a flow chart that supports the proposed decision-making process in the Work Plan. The decision logic needs to identify the benefits and limitations of decision criteria used at critical points of the program. This decision process needs to also indicate what parameters have the greatest potential for introducing errors to the decision process for estimating NSZD rates identified in the Work Plan and in subsequent deliverables. Please revise the Work Plan to include the decision logic to be used.

2.10 Response to General Question II.g.

Decision logic diagrams have been provided as **Figure A4** and **Figure A5**. In the context of the ITRC and CRC Care guidance, highest weight will be assigned to the Phase II assessment methods (unless key limitations to the application of these methods are identified in Phase 1).

The key decisions that need to be determined as part of this process include:

[1] Geraghty and Miller, Inc., 1982. Installation of a ground-water monitoring network for Martin Marietta Alumina, St. Croix, U.S. Virgin Islands. June.

1. Do the background (upgradient) CO_2 concentrations indicate that naturally occurring CO_2 could impact the analysis of the data? If background $CO_2$is 10 percent of the concentrations observed in the source area, then this impact is significant, and a correction will need to be applied to the calculations. Where detectable concentrations are observed to be less than this threshold, a correction may not be required, and the presence of background sources of carbon dioxide will be discussed in the uncertainty section of the data analysis.
2. Is CH_4 elevated in shallow soil gas sampling locations such that use of the E-Flux approach would result in a low bias in NSZD rate estimates? If CH_4in shallow soil gas (at 5 feet bgs) is greater than 10 percent of the CO_2 concentration (normalized for molecular weight of carbon in both molecules) then the potential bias is considered significant and either an alternative method (flux chamber and LI-COR meter or additional vertical soil gas profiles) will need to be utilized.
3. Identify the areas where hard sand is present that may lead to the accumulation of soil gases. These areas will have to be avoided for Phase II testing methods and sampling grids and locations modified accordingly.
4. Identify the areas where water ponding or water-logged soils may exist that could act to impede the vertical migration of gases. These areas will have to be avoided for Phase II testing methods and sampling grids and locations will be modified accordingly.

h. The Work Plan calls for the use of a gradient method that combines soil gas readings from inside wells near the water table with shallow one-foot below ground surface (bgs) soil gas measurements adjacent to the paired wells. Because of the complexity of the geology at the site it may not be adequate to use only two points to verify changing conditions in the vadose zone, particularly where secondary porosity features may influence advective flow in the subsurface. American Petroleum Institute (API) NSZD Guide (2017) suggests that multiple levels of soil gas probes may be needed when water tables are greater than five feet below ground surface (bgs) to better define the limits of vapor phase diffusion coefficients and NSZD rates using a gradient method. The depth to groundwater at the site appears to range up to 40 feet bgs. The Work Plan needs to describe how the proposed gradient method can be considered representative of site conditions.

2.11 Response to General Question II.h.

Please see our proposed revisions to the gas gradient method in our Response to General Question II.d (**Section 2.7**).

i. Also, gradient methods assume that diffusion is the only soil gas distribution mechanism above an LNAPL plume. Given that secondary diagenetic features such as calcification and bedding planes are potentially controlling mechanisms for advection (i.e., flow) beneath the site, it is not clear how these potential influences will be overcome using the simple two point gradient test proposed in the LNAPL NSZD Work Plan. The Cooperative Centre for Contamination Assessment and Remediation of the Environment (CRCCARE) in Technical Report No. 44, Technical measurement guidance for LNAPL NSZD (CRCCARE Guide), suggests in Figure 9 of this report that gradient methods in limestone sites should be carefully considered prior to use. Table 6 of the CRCCARE guidance indicates gradient methods should include soil gas probes installed below 1.5 meters bgs to avoid root zones. Moisture content in the subsurface may also have a substantial influence on any calculated NSZD rates calculated using gradient and other soil gas measurement methods. The Work Plan needs to address how the current designs can

be reliably used given site conditions. How and when moisture content issues related to NSZD activities will be addressed needs to be integrated more specifically into the site decision logic and sampling plan discussed in the Work Plan. Please revise the Work Plan to address these issues.

2.12 Response to General Question II.i.

Consistent with the framework provided in the work plan, the NSZD Work Plan uses an extensive range of methods to determine what methods can best quantify NSZD rates at this Site and ultimately be included into a long-term monitoring program. The limitations of the various methods were recognized in the development of the program and as such a range of methods were employed. Every method has limitations and short comings; consequently, our program of works attempted to facilitate early data collection with higher resolution lower quality methods to inform the sampling design for the Phase II high quality testing methods. The approach proposed by the group is consistent with the Triad approach and is designed to aid the group and USEPA in making informed decisions on modifications to the Phase II program of works. In the context of limestone geology, the surface-based flux measurement methods (E-Flux and LI-COR) involve sampling in the upper 6 inches of the subsurface which in all cases is unconsolidated media (and in many cases fill). In this context these methods will be not affected by the presence of secondary diagenetic features. In the event that site heterogeneity (including secondary diagenetic features) results in major differences in subsurface soil gas and temperature profiles, (work completed as part of Phase I) revisions to sampling density and locations will be made in accordance with the decision logic diagrams referenced above.

Further, our proposed revisions to the gas gradient method in our Response to General Question II.d. go part way to addressing this issue; through the installation of nested soil vapor probes we hope to better constrain the spatial and vertical distribution of gases in the subsurface. We are aware of issues related to elevated moisture and surface cover exist and as part of the Phase I activities (refer decision logic diagram), therefore, detailed site reconnaissance will be completed and revisions to the Phase II scope of work will be required. To support the further understanding of soil vapor diffusivity (including moisture effects), the tracer method will be used to quantify soil vapor diffusivity at vadose gas monitoring points. This proposed additional testing is included in the work plan.

j. The decision whether to use DCC as opposed to passive E-flux meters during Phase II will depend on whether methane is completely digested at a specific location and across the site. Given the flux of soil gas through the E-flux sampler can only be estimated, it is essential that flux rates are estimated as closely as is possible under site conditions during NSZD testing. Please revise the Work Plan to include sufficient information on how flux rates will be estimated should E-flux be proposed for use at the site during Phase II. Further, the Work Plan should also discuss how the potential for excessive winds to over-estimate NSZD rates when using E-flux will be addressed.

2.13 Response to General Question II.j.

The work plan has been revised to include more information on how passive E-flux rates are estimated by the vendor. Please note that a detailed description of the calculation method and equations are already provided in Section 4.3.9.1 of the work plan . By quantifying the mass of CO_2 on the sorbent media and knowing the time over which the trap was deployed flux rate is estimate (mass/time – for example grams per day/grams per hour etc.). Specifically, the vendor (E-Flux; www.soilgasflux.com) analyzes traps and

provides a rate estimate. The specific method is outlined in McCoy et al. (2014)[2], which is properly referenced in the Work Plan but will be expanded upon in the revised submission. Additionally, a Standard Operating Procedure (SOP) that describes the method is included in the appendices of the work plan. Consideration of excessive winds were addressed as described in our Response to General Question II.d (**Section 2.7**) and will be a factor in the decision to use E-flux technology.

k. Section 4.3.9.2 – For the dynamic closed chamber method, it is not clear how the CO2 detection limit is determined and the process/method that will be used for data validation. Since weather condition is a factor in efflux measurements calculations, it is not clear what type of weather-related information will be collected and/or instrumentation used.

2.14 Response to General Question II.i.

Text is provided on attached **Table 1** to clarify how detection limits are verified using the DCC method. The detection limit is measured on a chamber that is sealed off. 60 measurements are made on the sealed chamber. The detection limit is simply the mean value of the measurements plus three times the standard deviation, a typical method commonly used to quantify detection limits.

Text will be updated to specify that weather-related information will be obtained from the nearby NOAA station "LTBV3 - 9751401 - Lime Tree Bay, St. Croix, VI", which is located approximately 1.5 miles southeast of the site.

III. LABORATORY QA/QC

a. Section 4.3.9.1 – Please provide the name of the laboratory that will be analyzing the traps for CO2, as well as the method to be used and the laboratory's reporting limit. In addition, information regarding acceptance criteria for the duplicates should also be included.

2.15 Response to III.a.

If passive traps are selected for use, they will be obtained from E-Flux (www.soilgasflux.com). E-Flux uses industry-accepted practices and methodologies, including quality assurance and quality control protocols. In combination with their proprietary technology, the carbonate and ^{14}C analyses are based on two ASTM methods:

- D4373-14, Standard Test Method for Rapid Determination of Carbonate Content of Soils.
- D6866-18, Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis (includes stable carbon isotope analysis).

This information has been included in the revised attached **Table 1**. E-Flux completes their own quality assurance/quality control (QA/QC) checks in accordance with these standard methods and will provide statements about data quality and useability in their reports (**Appendix E**).

[2] McCoy, K., Zimbron, J., Sale, T. and Lyverse, M., 2015. Measurement of natural losses of LNAPL using CO2 traps. Groundwater, 53(4), pp.658-667.

b. Section 5.7 – It is not clear what will be the acceptance criteria to evaluate the specified QA/QC samples. In addition, the collection frequency for the QA/QC samples was not included. Please provide.

2.16 Response to III.b.

Attached **Table 1** has been updated to include quality control procedures. The following QA/QC strategies are utilized in the technique:

- A travel blank that accompanies the samples during shipping to and from the Site. CO_2 detected in the travel blank is subtracted from the primary samples.
- Radiocarbon/stable carbon isotope corrections for non-NSZD gases inputs.
- Deployment of an upgradient/background trap to account for contributions from wind/weather or background sources not captured in the isotope analysis.
- One duplicate trap per 10 deployments. For the duplicate trap, the results will be compared and a target of +/- 30 percent will be established as a preliminary goal. No formal quality control metrics have been proposed in the guidance or by the vendor.

c. Section 5.8 – For the specified laboratory analysis, it is not clear what are the project's required reporting limits and whether there are there any criteria that are being used for comparing the results. Please also provide the laboratory's accreditation information for these analyses (type of accreditation and expiration date). In addition, please provide the method specifications that will be used for the dissolved gases. Please also include the filter size that will be used to collect the sample for dissolved metals; please note that a consistent filter size is needed for consistent results, and that 0.45 microns is a typical filter size for dissolved metals.

2.17 Response to III.c.

We have requested this information from E-Flux and will include the requested documentation in the revised Work Plan as (**Appendix E**). We will specify that a 0.45 micron filter will be used.

d. Section 6.0 – Please clarify which procedures will be used for validating the data generated and the process for assessing the data usability. Also, please include any SOPs that will be used. The type of decision that will be made with the data will typically dictate the level of validation.

2.18 Response to III.d.

An updated QAPP is being developed for the routine groundwater sampling and the targeted LNAPL and groundwater sampling proposed as part of the NSZD Assessment. In terms of the Phase II E-Flux assessment, it is assumed that reference to the literature (McCoy et al., 2014[3] & CRC CARE, 2018[4])

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[3] McCoy, K., Zimbron, J., Sale, T. and Lyverse, M., 2015. Measurement of natural losses of LNAPL using CO2 traps. Groundwater, 53(4), pp.658-667.

[4] CRC CARE. 2018. Technical measurement guidance for LNAPL natural source zone depletion. CRC CARE Technical Report 44. Adelaide, Australia: CRC for Contamination Assessment and Remediation of the Environment.

would be adequate. We will extract the relevant information and provide it in the revised text (Section 4.3.9.1.1). Specifically, (from CRC CARE):

"*QA/QC procedures are important in evaluating the accuracy and precision of the data collected. One duplicate trap location every 10 locations is recommended to evaluate consistency between installation procedures and replication of results. Place the duplicate trap approximately 0.3 m from the parent location and install it in an area of similar ground cover. Statistics such as the calculation of a relative percent difference (RPD) from the parent and duplicate sample data can be performed to assess data quality. An elevated RPD of greater than 30% is typically used as a criterion to re-evaluate the soil receiver pipe installation procedures to ensure a good seal with the subsurface was attained. However, heterogeneities in the subsurface impact the ability to achieve an RPD of less than 30% at many sites, therefore the 30% criterion may not be achieved in all cases.*

As discussed above, a TB must be provided by the passive flux trap supplier and analyzed along with the samples for each field event. The TB accounts for CO2 not associated with flux from the subsurface that either came from manufacturing or sorbed from atmosphere (through the caps) during the shipment.

*The detection limit of a passive CO2 trap is dictated by the detection limit of the analytical method. The detection limit of the analytical method is found by multiplying a typical coefficient of variation of 3% on trap CO2 analyses, and a typical blank trap CO2 content of 1% by weight by five (i.e., 3% cv * 1% CO2 by weight * 5). The detection limit of the analytical method of CO2 trap is approximately 0.15% CO2 by weight of the sorbent (API 2017). Then using deployment time, the area exposed to efflux, and the quantity of sorbent material the detection limit of the CO2 trap can be determined. The detection limit is typically 0.1 µmol/m2/s for a 15-day deployment time, a cross-sectional diameter of 10.16 cm of the Schedule 40 polyvinyl chloride (PVC) receiver pipe, and 40 g of sorbent material A decrease in deployment time of 4 days would result in approximately a 5-fold increase in the detection limit (0.5 µmol/m2/s). Note that if laboratory results are less than the specified analytical detection limit, the resulting detection limit of the CO2 traps must be considered non-detect."*

For the LI-COR and soil gas vertical profile methods, field-based meters will be utilized. QA/QC will be achieved through calibration of the instrument against calibration standards in the field. It is proposed that consistent with the E-Flux methodology described above duplicate testing will be conducted at 10% of the locations. This will comprise completion of a duplicate sampling location with 2 feet of the primary sample location. As no laboratory testing will be conducted no other QA/QC processes are proposed.

IV. SPECIFIC COMMENTS

Specific Comment 1: Section 1.1 last paragraph, Figure 2: As noted in the last sentence, potential source areas are located on the west side of the site. The location of these potential source areas needs to be shown on Figure 2 as they could impact where samplers are placed and the geochemistry of the soil gas near these impacted surface materials. Please revise Figure 2 accordingly.

2.19 Response to Specific Comment 1.

Figure 2 has been revised and provided for review.

Specific Comment 2: Section 1.2 Paragraph 4, Figure 3: In this paragraph it is noted that the groundwater table is broadly consistent with the Kingston Limestone. However, Figure 3 does not support this statement. The depth to the water table and relationship of well screens in the LNAPL NSZD study area needs to be described more accurately in this section and on Figure 3 of the Work Plan. Careful inspection of Figure 3 also shows that boring logs from some wells such as VW-14 and projected well VW-18 were not honored on the cross-section. Some explanation, perhaps as a footnote to Figure 3, of why these well logs were not included in the cross-section is needed. An updated set of cross-sections, specifically for the LNAPL plume study area, are needed in the Work Plan to demonstrate the spatial relationships between well screened intervals, LNAPL, geologic, and hydrogeologic features. Also, the cross-sections shown on Figure 3 need to be updated to include detailed LNAPL study-specific well diagrams that support verification of the LNAPL transmissivity bail down tests.

2.20 Response to Specific Comment 2.

The Work Plan states "*An interval of gravels, sands, silt, and clay within the Kingshill Limestone is identified beneath the central portion of the Site that is broadly coincident with the location of the water table and intervals over which most Site wells are screened*."

Revised cross sections (Work Plan Figures 3A and 3B) showing the location of the water table relative to various lithology features has been provided to support our statement.

Specific Comment 3: Section 1.3, first paragraph, Figure 4: In this paragraph groundwater flow is noted as generally to the south-southwest and south towards the sea. Inspection of Figure 4 indicates that localized flow beneath the plume may occur radially to the northwest and southeast away from several groundwater highs in the vicinity of wells VW30 and VW35. These features suggest a very flat gradient beneath the LNAPL plume and potentially variable flow directions that could explain, in part, the geometry of the historical LNAPL plume. A more detailed piezometric surface map underlain by the most extensive historical plume map, such as those provided in Appendix A of the Work Plan is needed. The extent of historical subsurface contamination needs to be presented along with the interpreted localized groundwater elevations beneath the LNAPL plume. The locations of potential source areas also needs to be identified on Figure 4 or another more detailed piezometric surface map prepared for the LNAPL NSZD plume study area.

2.21 Response to Specific Comment 3.

We have partly addressed this comment in our Response to General Question II.f (**Section 2.9**). We intend to revise contour maps once geochemical fingerprinting of groundwater at GM-22 is available, a task that will be implemented in Phase 1 of the proposed work. We will include the footprint of historical LNAPL distributions on the revised groundwater contour map as requested.

Specific Comment 4: Section 3.2.2: The scope of the Phase 2 program is poorly defined. This section of the Work Plan needs to be more detailed to allow for a better idea of the number of samplers of various types which may be used along with dimensions of any proposed study areas. Other information that needs to be included in this section includes whether geochemistry parameters collected during Phase 1 will be repeated in subsequent phases or monitoring events, and whether temperature monitoring will be included in Phase 1 and subsequent well sampling events as a means for long term monitoring of NSZD.

2.22 Response to Specific Comment 4.

The scope of work proposed for Phase II is necessarily vague due to the need for information from Phase 1 to inform the program. However, we expect that our response to Comment #2 (**Section 2.2**, revising DQOs) provides the additional detail that is requested. As noted above, the decision logic diagrams describe how information from the Phase 1 scope of works will inform scoping and implementation of Phase II.

Specific Comment 5: Section 3.2.2, Last Bullet: In the last Bullet, it is suggested that during Phase 2, analysis of wells for carbon fractionation using compound specific isotopic methods for carbon will be performed to determine if a background correction can be applied successfully to remove the impacts of carbon signatures from native carbonate rocks from signatures from NSZD of the LNAPL. It would be beneficial to perform these analyses as soon as possible to assure that passive Flux or DCC soil gas sampling data will be representative of NSZD of the LNAPL and not biased high because of contributions from native carbonate contributions to carbon dioxide values. Ensure the Work Plan allows for the collection of this data at the earliest step.

2.23 Response to Specific Comment 5.

We propose collecting well headspace readings from upgradient locations (where NSZD is not expected to be occurring) during Phase 1 to identify if gases are present in the subsurface at concentrations that warrant the expense of employing compound specific carbon isotope analysis. If no gases are present in the subsurface at upgradient and side gradient locations, we believe the urgency for employing this technique will be reduced or eliminated.

Specific Comment 6: Section 3.2.3: This section does not provide a specific time frame for reporting Phase 1 results to EPA. Please modify the Work Plan to provide more specific timing for the Phase 1 report.

2.24 Response to Specific Comment 6.

Timing for implementation of Phase 1 will be provided once agreement is reached on the proposed scope of work. We anticipate completing a report within 90 days of completion of the Phase 1 field work.

Specific Comment 7: Table 3-1 includes general data quality objectives. These DQOs are based on the content in Appendix B of the Technical Measurement Guidance for LNAPL Natural Source Zone Depletion (CRC-CARE Technical Report No. 44) (CRCCARE). The checklists included in Appendix B of the CRCCARE report are intended to be used as place holders to prompt the development of site-specific DQOs. However, the Work Plan needs to develop site specific DQO's that define how the data from Phase 1 and 2 will be used to bound decision making concerning the evaluation of NZSD at the site. Development of the specific DQOs can occur in Table 1 of the Work Plan and should be consistent with those presented in Worksheet #11 of the associated UFP-QAPP. Further, the information included in Table 1 of the Work Plan includes site specific principal study questions in a format that is more in tune with EPA's DQO approach, but Table 1 does not provide an adequate cross-walk between applicable sections of the Work Plan and the Table contents for the column heading "Data Use Objective". Information in Table 1 should be consistent with UFP-QAPP, Optimized Worksheet #17 which supports the information included in Worksheet #11. Please revise Table 1 to include references to the supporting information within the Work

Plan as well as UFP-QAPP Worksheet#17 or its equivalent. Additionally, please ensure that the Work Plan includes a diagram or flow chart indicating the intended decision logic to be used during data assessment. As cited in the reference section at the end of the Work Plan, the Interstate Technology & Regulatory Council (ITRC) updated its LNAPL guidance: ITRC 2018. Light Non-Aqueous Phase Liquid (LNAPL) Site Management: LCSM Evolution, Decision Process, and Remedial Technologies, LNAPL-3. Washington, D.C. https://lnapl-3.itrcweb.org (LNAPL-3). Hence the list of references cited at the bottom of Table 1 needs to include the ITRC's LNAPL-3. Appendix B of LNAPL-3 includes examples of site-specific decision logic diagrams to guide the decision-making process. Please ensure that the Work Plan includes a site-specific decision logic diagram or flow chart consistent with the ITRC LNAPL-3 guidance.

2.25 Response to Specific Comment 7.

We have partly addressed this comment in our response to Comment #2 (**Section 2.2**) and Comment #3 (**Section 2.3**), and **Table 3-1** has been updated and provided for review. USEPA has recommended that decision-logic diagrams be included in both the LNAPL CSM and NSZD Assessment. In review of the ITRC guidance no specific decision logic diagram is provided for assessment and analysis of NSZD data.

A site-specific decision logic diagram based on NSZD 14 has been developed and is included with the response to comments on the LNAPL CSM (this response was provided at the same time as this response) as **Figure A1**and decision logic diagrams for the evaluation of Phase I and Phase II NSZD data is provided as **Figure A4** and **Figure A5** (and duplicated in this response to comment).

Specific Comment 8: Table 3: This table identifies the wells in the proposed LNAPL plume monitoring network, as well as those wells selected as being indicative of background and down gradient. No rationale is provided for how and why the background wells were selected. Presumably, their selection is based on location and proximity to the study area and past monitoring and sample analyses performed at these locations. Additional detail is needed in the Work Plan concerning how the background wells were selected. A review of down gradient well locations given the current piezometric surface provided in Figure 4 indicates that many of these wells are upgradient or cross-gradient of the study area. Understanding there may be a significant data error/anomaly in the reported groundwater value for GM22, Table 3 will need to be reevaluated before the wells listed in it can be considered representative for LNAPL NZSD study purposes as either down-gradient or upgradient.

Additionally, the work on the redetermination of the casing elevation of GM22 and other wells should be considered during Phase 1 to better inform the CSM.

2.26 Response to Specific Comment 8.

This comment is addressed in our Response to General Question II.a (**Section 2.4**). **Table 3** (attached) has been revised to include rationale for selecting wells.

Specific Comment 9: Figure 7: The Figure shows potential locations for E-flux samplers. However, it is unclear how the configuration shown in the figure was developed and why there is not a figure which also shows potential locations for DCC samplers should they be selected for use. Please include this

information. It also would be useful to include a presentation of where gradient evaluations may be performed.

2.27 Response to Specific Comment 9.

Rational for selecting E-flux sampling locations will be added to the text in Section 4.2 of the Work Plan, as requested. However, as noted in Response to General Question II.e (**Section 2.8**), grid spacing will ultimately be dependent on the Phase 1 sampling results. Specific data points that will be used are provided in the revised **Table 1** (attached), and revised **Table 3-1** (attached). The preliminary concept for sampling locations for the DCC locations will be identical to the E-Flux sampling locations. E-flux is the favored method as it provides time weighted averages. However, if methane is not being fully degraded before discharging to the atmosphere, and the mass balance of carbon equivalent concentrations indicates the error could be larger than 10 percent, then DCC may have to be used. It is recognized that the soil gas vertical gradient methods and temperature methods will provide a line of evidence and that data evaluation that must address this concern and E-Flux measurements still could be used as the primary high quality evaluation method.

The ITRC document does consider an iterative approach as proposed by the group as stated in ITRC-3 Appendix B.

> *"The required data density depends on multiple variable: site heterogeneity (including ground cover, soil type and stratigraphy, depth to groundwater/LNAPL) across the LNAPL footprint, LNAPL distribution as well as the data use objectives and costs. The practitioner might consider an iterative process in which the LCSM is informed in earlier stages with high data density of lower data quality, and lower data density of higher quality at the later stages. This is common practice in environmental remediation, as exemplified by the EPA Triad Approach (for example, see (Johnson 2010)).*"

We have completed a preliminary assessment using temperature profiles and head space readings in wells and propose to complete the Phase 1 testing program using the wells specified to understand the Site heterogeneity using lower data quality analysis methods. Based on the results from this testing, a method of high-resolution testing will be selected, and sampling density determined for application to the Site.

The decision process that will guide the analysis of data is provided in **Figure A4** and **Figure A5** and an updated sampling program for the Phase II will be prepared after completion of Phase I. As described above, this will involve changes in sample grid density and sampling locations based on data collected from the Phase I program. Phase II of the testing program will not commence until USEPA review of the Phase I data and approval of the proposed Phase II sampling program.

Memo

To: Brian Epperson, Hess Corporation

From: Nigel Goulding EHS Support LLC
Dr. Andrew Fowler EHS Support LLC

CC: Brad Freeman, Geo Monitoring Services

Date: February 18, 2021

Re: Response to February 08, 2021 US EPA Review of POCs Response to December 14, 2020 Comments on the LNAPL CSM and Remedial Action Work Plan, St. Croix Alumina Site, U.S. Virgin Islands, EPA ID Number: VID090302084

EHS Support LLC ("EHS Support") has prepared this response to the February 8, 2021 United States Environmental Protection Agency (USEPA) Review of Point of Contacts (POCs) Response to the December 14, 2020 comments on the Light Non-Aqueous Phase Liquid (LNAPL) Conceptual Site Model (CSM) and Remedial Action Work Plan ("LNAPL CSM and Work Plan") for the St. Croix Alumina U.S. Virgin Islands site ("site").

From our review of USEPA comments, we understand that USEPA is in general acceptance of the LNAPL CSM and Work Plan following EHS Support's responses, provided some additional information for clarification is made.

To facilitate review of our responses, USEPA comments are shown in black text and our responses are shown in blue text.

Responses to USEPA Comments on the LNAPL CSM and Work Plan:

EVALUATION OF RESPONSE TO USEPA COMMENTS

DATED DECEMBER 14, 2020

ON THE

LNAPL CSM AND REMEDIAL ACTION WORK PLAN

ST. CROIX, U.S. VIRGIN ISLANDS

DATED JULY 2020

In general, the Response to Comments (RTCs) addressed EPA's comments and are acceptable with the following considerations. The following evaluation includes only responses where additional information or clarification is required.

A revised version of the Light Non-Aqueous Phase Liquid (LNAPL) Conceptual Site Model (CSM) and Remedial Action Work Plan (Work Plan) was not provided, and as such an evaluation of the whether the RTCs were incorporated into the Work Plan was not able to be completed. A revised Work Plan incorporating the proposed revisions is needed.

EVALUATION OF RESPONSES TO GENERAL COMMENTS:

***Evaluation of the Response to General Comment 1 (Risk Evaluation)*:** As noted in our conference call of February 3, 2021, the risk assessment will need to be updated to address current conditions. Additionally, an evaluation currently is being conducted to provide input to help determine if the Site Specific Target Levels (SSTLs) need to be updated for the SCA plume site.

Response to Evaluation of the Response to General Comment 1

We understand that the risk assessment will need to be updated to reflect current conditions. Given that the plume extent has retracted and further weathering of the LNAPL has occurred over time, we do not consider major changes to the findings and conclusions of the risk assessment. We await receipt of USEPA's review and comments on the need to update the Site Specific Target Levels (SSTLs).

Evaluation of the Response to General Comment 2 (Remedial Goals): The response partially addresses the concerns expressed. The interpretation of transmissivity sits at the crux of the assessment of LNAPL recovery. Transmissivity assessment is made on a well-by-well basis. Assurances that each well used to determine transmissivity is appropriately screened to support such an assessment needs to be demonstrated. As such, the cross-section presented in Figure 4-3B omits the presentation of the screen interval with respect to the water table, the historical high-water level, the historical low-water level, and the currently known LNAPL thickness in the well screen. Any well included as part of the transmissivity assessment needs to have a well screen which straddles all of the high, low, and LNAPL levels. Also, changes in apparent product thickness may change the LNAPL transmissivities measurements planned for collection during Phase 1 activities. Any significant changes in groundwater levels and associated apparent product thicknesses may necessitate additional transmissivity measurements. Please revise the Work Plan to ensure it presents well logs showing the following for each well: the historical high-water level, the historical low-water level, and the currently known LNAPL thickness in the well screen. Also, include a contingency for additional transmissivity measurements based on observed changes to LNAPL thicknesses.

Response to Evaluation of the Response to General Comment 2

We have prepared **Table 1** (**Enclosure A**) to demonstrate well screen elevations vs. historic water and LNAPL levels from October 2002 through December 2019. Please note the following regarding wells where LNAPL has historically been detected:

- Five wells where LNAPL was historically present have had screens submerged at some point in the past (VW2, VW6, VW15, VW18, VW29, and VW30).
- Of these wells, only VW2 and VW30 screens have consistently been submerged below the LNAPL.
- Of these wells, only VW-2 had a filter pack submerged below the LNAPL. This occurred on one occasion at which time the LNAPL elevation was equal to the filter pack elevation.

- Of these wells, only VW2 and VW30 had screens submerged below the LNAPL during the last three quarters.

Please note the following regarding wells where LNAPL has *not* historically been detected:

- Three wells (VW3, VW11, and VW12) screens are submerged by groundwater during most monitoring events. These three wells are co-located at the upgradient site boundary where LNAPL is not expected. Additionally, wells VW7, VW8, VW9R, and VW10 are located between the LNAPL source area and the location of these wells. These wells delineate the extent of LNAPL impacts upgradient of the LNAPL plume.
- The screen for VW37 is consistently submerged. This well is up/side-gradient from the LNAPL source area and near VW-36, which has only had a submerged screen three times.
- GM11, GM14, GM7, and GM13D consistently have groundwater submerged screens. These wells monitor the dissolved-phase plume in deeper groundwater intervals beyond the network of shallower monitoring wells that do not have submerged screens.

We note that ASTM E2856-13 "Standard Guide for Estimation of LNAPL Transmissivity" does not exclude wells that historically had well screens submerged by LNAPL, only those with submerged screens at the time of testing. Consequently, VW2 and VW30 are the only wells that should be excluded from transmissivity testing based on the analysis above.

EVALUATION OF RESPONSES TO SPECIFIC COMMENTS

Evaluation of the Response to Specific Comment 3 (*Section 6, Updated Remedial Action Work Plan, Page 63)* ***:*** The last sentence in the first paragraph of this response is incomplete and needs to be revised. The purpose of providing a non site-specific decision logic diagram in the response is unclear. A Site-specific decision logic diagram needs to be prepared and discussed with the EPA prior to moving forward, even if some of the steps are contingent upon the finalization of the CSM. CSM contingent decision steps could be uniquely noted as such in the site-specific decision tree configuration.

Response to Evaluation of the Response to Specific Comment 3

Based on the interlinkages between Response to Specific Comment 3 and 6, a detailed response is incorporated below in the Response to Specific Comment 6. This response includes a site-specific decision logic diagram for monitoring wells in which LNAPL has been observed and active recovery wells where the decision to transition to natural source zone depletion (NSZD) is being evaluated.

Evaluation of the Response to Specific Comment 6 (*Section 6.2, Proposed Framework for LNAPL Recovery Well Shutdown, Bullet 3, Page 65; and Section 6.2.1, Rationale and Methodology for Reservoir Decline Curve Analysis, Page 66)****:***

The following rules-of-thumb are noted in Appendix C of the Interstate Technology Regulatory Council 2018 LNAPL guidance (ITRC-3), Section 1.1:

- *LNAPL transmissivity between the range of 0.1 to 0.8 ft^2/day may be used as a decision point for remedial system operation or technology transitions. While LNAPL*

transmissivity is useful for evaluating LNAPL hydraulic recovery potential, it should not be used as a sole means to determine whether an LNAPL remedy for a site is necessary or unnecessary.

- *A threshold LNAPL transmissivity value, typically representative of an LNAPL saturation that is nominally above the residual LNAPL saturation for the formation, may be established at the outset of the LNAPL recovery action and used as a trigger for stopping LNAPL recovery. The decision on whether to implement an LNAPL remedial action should be based on the broader site LNAPL CSM rather than LNAPL transmissivity alone.*

- *It should be noted that LNAPL transmissivity measurements often vary in both space and time. For example, groundwater fluctuations can occur such that the LNAPL fluctuates from unconfined to confined conditions. In that situation, it may be necessary to measure LNAPL transmissivity values under both conditions.*

EPA recognizes that your response to comments indicates that additional goals will be evaluated. However, more details are needed to justify these goals. Appendix C, Section 1.2 of ITRC-3 notes the following:

There are a number of methods that can be used individually or in combination to demonstrate that free product has been removed to the maximum extent possible. According to Appendix C, Section 1.2 of the LNAPL-3 document, these include:

- *comparing mobile LNAPL mass to the mass of LNAPL in the smear zone,*
- *analyzing LNAPL recovery data and determining that future recovery will not be meaningful,*
- *showing that LNAPL thicknesses are small and/or intermittently observed,*
- *modeling future potential LNAPL recovery using a multiphase model,*
- *demonstrating that the LNAPL body is stable and that stability will not change in the future, and*
- *presenting information that shows an unreasonable cost per gallon or pound of LNAPL recovered.*

The current plan does not clearly define what multiple lines of evidence have been or will be used in the future to support a decision to turn existing wells off in terms of performing continued product removal. At present insufficient data and conclusions have been presented to EPA to support the proposed decision criteria and decision logic. Specifically, more information is needed in terms of explaining the basis for why a transmissivity criterion of 0.8 foot squared/day or 1 gallon per day LNAPL recovery criteria should be agreed upon for use at the site. Please ensure that the Work Plan outlines how these issues will be addressed going forward.

Response to Evaluation of the Response to Specific Comment 6

USEPA has noted that the Group needs to complete an evaluation relative to the decision logic process outlined in the ITRC (2018) Guidance. For purposes of advancing the discussion and to address USEPA comments on both the LNAPL CSM and Work Plan and the NSZD Work Plan, the following document systematically uses the information contained in Appendix B of the ITRC guidance to evaluate metrics of success and provide a decision logic process for consideration.

The flowcharts from the NSZD guidance are provided below and the LNAPL CSM and NSZD Work Plans are discussed in the context of this guidance document. A number of data gaps and uncertainties were identified in the LNAPL CSM for which supplemental assessment and monitoring were proposed. Issues identified by EHS Support and USEPA included the temporal variability of solar sipper recovery rates (during the trial), which impacted the regression coefficients for the recovery decline curve analysis as well as potential operational issues (larger LNAPL thicknesses in the recovery wells than anticipated during operation of the pumps). This variability was attributed to the program of operation and maintenance activities being implemented during this period and revisions to the approach were proposed in the report, discussed with USEPA, and have been implemented in the field.

In addition, it was noted in discussions with USEPA that data smoothing/averaging (reflective of the high frequency of recent data relative to the older data sets) was required to more accurately complete trend analysis and improve the regression coefficients. This is proposed to be completed after completion of the optimization activities using the additional recovery data which will be collected from the recovery wells.

In the context of the decision logic diagram that USEPA has requested we develop, there are numerous decision logic diagrams provided in the ITRC guidance. A number of diagrams are associated with development of the initial LNAPL CSM and selection of technologies while others have been specifically developed for mature sites (such as St. Croix) where decisions associated with the possible transition to NSZD are being considered. Given the maturity of this site (i.e., where large volumes of LNAPL have been recovered, LNAPL plume extent and thicknesses have declined over time, and the limited risk [either based on the chemistry of the LNAPL or incomplete exposure pathways]), the focus has increasingly been on demonstrating recovery to the extent practical and achieving the long- term goal of groundwater restoration. Decision logic flowchart Figure NSZD-14 (**Enclosure B**) is considered the most appropriate starting framework for development of a site- specific "interim" decision logic diagram. It is understood that based on the findings from the supplemental LNAPL mobility/recoverability evaluations and NSZD evaluation, modifications to this process may be required.

A range of potential metrics were identified in the LNAPL CSM and were also provided in USEPA's most recent comments; they are listed below with additional clarification and discussion provided. USEPA has also specifically referenced the rules of thumb provided in Appendix C of ITRC-3 (2018) guidance. In review of these rules of thumb there is alignment between the group and USEPA on the use of the LNAPL transmissivity thresholds (upper bound of 0.8 ft^2/day). The other rules of thumb provided USEPAs evaluation of the groups response to comments are more challenging to apply or are a key qualitative/semi-quantitative consideration. For example, the rule of thumb listed below is not quantitative using terms like "nominally above" and inherently does not provide a quantitative link between laboratory saturation data and LNAPL transmissivity:

> *"A threshold LNAPL transmissivity value, typically representative of an LNAPL saturation that is nominally above the residual LNAPL saturation of the formation, may be established at the outset of the LNAPL recovery action and used as a trigger for stopping LNAPL recovery".*

In application of criteria such as this, terminology and test methods need to be considered. Permeability to oil can be estimated in petrophysical testing but transmissivity is not. Further, air displacing oil and water displacing oil imbibition tests can evaluate pore fluid drainage relative to applied stress but do not

provide LNAPL transmissivity. In this context most practitioners have reverted to using petrophysical tests to define in porous media LNAPL saturations at which "drainage can occur" and relying on field measurements to assess LNAPL transmissivity, mobility and recovery.

Commonly, practitioners have relied on the ITRC transmissivity value referenced above, LNAPL recovery rates from wells (as noted above 1 gallon per day [gpd] has been used at numerous refineries), reservoir decline curve analysis (recovery relative to total theoretical recoverable volume) and recovery efficiency (oil/water cuts and using this ratio to estimate LNAPL transmissivity from groundwater transmissivity).

In addition to these rules of thumb, USEPA also lists a number of methods that can be used individually or in combination to demonstrate that free product has been removed to the maximum extent possible (Section 1.2 of the LNAPL-3 document). Commentary on the application of these criteria to the site is provided after each item

- *Comparing mobile LNAPL mass to the mass of LNAPL in the smear zone*. This assessment method usually involves coring and petrophysical testing. Pore fluid saturations (oil and water phase) and water displacing oil imbibition tests (for LNAPL in saturated zone) are conducted to define the potentially mobile and immobile fractions. The methods are typically applied to porous media but can be modified to consolidated materials (if LNAPL is in secondary porosity of limestone).
- *Analyzing the LNAPL recovery data and determining that future recovery will not be meaningful*. This was proposed in our approach with the use of reservoir/recovery decline curve analysis. Typical application of this criteria has included percent recovery relative to the maximum theoretical recovery, a recovery rate metric aligned with LNAPL Transmissivity and oil/water percentages for total fluid recovery systems. As described further in **Table 2** (**Enclosure A**) the table below 80 percent and 90 percent of the maximum theoretical recovery has been used as a metric aligned with industry experience in upstream oil and gas. The proposed 1 gpd metric included in our report has been calculated based on the ITRC transmissivity threshold, and oil/water percentages are not applicable metrics for skimming.
- *Showing that LNAPL thicknesses are small and/or intermittently observed.* Routine gauging and groundwater sampling activities are conducted at the site. This data has demonstrated reductions in LNAPL thicknesses over time and a number of wells were LNAPL is only intermittently observed. As discussed extensively in the ITRC guidance, LNAPL thickness is not the primary determinant of LNAPL recoverability. LNAPL saturation and site geology are the critical controls on LNAPL transmissivity and in homogeneous geology LNAPL thickness is correlated with LNAPL transmissivity. Based on the complexity of the site geology (as described in the LNAPL CSM) LNAPL transmissivity at this site is more controlled by geology than thickness. Use of an LNAPL thickness metric is not recommended for this site and LNAPL baildown testing is considered a more reliable tool for assessing LNAPL transmissivity and recoverability.
- *Modeling future potential LNAPL recovery using a multi-phase model.* The American Petroleum Institute's (API) LNAPL Distribution and Recovery Model (LDRM) can be used to model the recoverability of LNAPL and provide future predictions. The model relies on the physical properties of soil, literature input values (potentially sourced from the API database), LNAPL saturation inputs or estimates, and estimates of LNAPL transmissivity. The models should be calibrated to current LNAPL recovery rates.

- *Demonstrating that the LNAPL body is stable and that stability will not change in the future.* Routine groundwater gauging and sampling is being conducted at the site and demonstrates that the plume is stable. Based on the hydraulic gradients at the site and that recovery efforts are focused on skimming, significant changes in groundwater conditions are not anticipated to occur. Long-term monitoring will be implemented when recovery activities are terminated at the site.
- *Presenting information that shows an unreasonable cost per gallon or pound of LNAPL recovered.* The cost of recovery at the site has significantly increased over time in response to the reduction in LNAPL recovery volumes. Early recovery efforts removed large volumes of LNAPL providing a low cost of removal. A graph of expenditures over time in dollars/gallon is provided (**Enclosure C**).

Decision Flowcharts

Detail decision *logic diagrams* using a hierarchy of decisions for both monitoring wells and recovery wells are provided (**Figure A1** through **Figure A5** in **Enclosure D**). The general decision process for a combined LNAPL and NSZD remedial approach is provided as **Figure A1**. Specific decision logic diagrams for LNAPL recovery wells (which should be incorporated into the process shown on **Figure A1**) are provided as **Figure A2** and the decision logic diagram for monitoring wells is provided as **Figure A3**.

For the decision logic diagram provided for monitoring wells (**Figure A3**), note that this flowchart is not applicable to recovery wells which are part of the permanent or temporary recovery program (see **Figure A2**). Once recovery and bail down tests have been completed and it has been determined that LNAPL has been recovered to the extent practical, recovery wells will be converted to long-term monitoring wells. The focus of the long-term monitoring program will be on demonstrating a *stable* LNAPL plume and that NSZD processes are continuing. As part of the process, changes in LNAPL thickness and extent will be evaluated to determine if recovery activities need to be reinstated in select wells.

For the active recovery wells at the site, **Figure A2** has been prepared and integrated into the decision logic provided by ITRC Figure NSZD-14 (**Enclosure B**). We consider this decision flowchart to best reflect the life stage of this project and the desired outcome of integrating NSZD processes into the existing LNAPL recovery program. The following key information (which is required to complete a site specific flowchart) is provided below:

<u>Remedial Action Objectives and Goals</u>

The cleanup criteria for LNAPL was described in the USEPA-approved Phase Separated Petroleum Hydrocarbon Plume Remediation Work Plan.[1]

> *The clean-up criteria for PSPH are based on two independent factors: risk and mobility. Corrective measures for PSPH will be complete when it is determined that PSPH:*

[1] Hess. 2001. Phase Separated Petroleum Hydrocarbon Plume Remediation Work Plan.

- *Poses no unacceptable risk to human health and the environment, or*
- *Is below the Practical Limits of Mobility (PLM) and is not likely to impact a receptor in the future."*

Define Performance Metrics, End Points and Transition Criteria

A range of metrics have been tracked over the years but no formal endpoints and transition criteria have been contextualized in documents. Proposed Criteria include:

- ***End Point – Restoration of Groundwater Quality.*** *As we understand the desired outcome is "restoration of groundwater" which will require no mobile/observable LNAPL in wells and achievement of water quality standards suitable for the future beneficial use of groundwater.*
- ***Performance Metrics –*** *A range of performance metrics are inherent with USEPA comments and EHS Supports LNAPL CSM these include:*
  - ***Ensure that the LNAPL plume is stable and not migrating.*** *Associated metrics would include:*
    - *No measurement of LNAPL in new wells (wells that have not historically had LNAPL)*
    - *LNAPL thicknesses measured in wells consistent with historic observations (and considering the potential effects of groundwater elevation fluctuations)*
  - ***Are the skimming pumps being effectively operated:***
    - *Are the intakes of the pumps within the LNAPL layer?*
    - *Are routine operational and maintenance activities being conducted to ensure high operational uptimes?*
    - *Do oil/water cuts (> 25%) support effective operation of the skimmer pump.*
    - *Are the LNAPL thicknesses in wells maintained below 0.33 feet (4 inches) – effective operational thickness.*
  - ***Recovery to the Maximum Extent Practicable (Practical Limits of Mobility) in individual wells (recovery will be terminated on a well by well basis) as defined by (in order of priority):***
    - *Baildown test LNAPL Thresholds in individual wells below the upper bound of ITRC Thresholds and not inconsistent with the observed LNAPL thickness in the well and geology/hydrogeology at that location. USEPA has requested a justification for use of the ITRC transmissivity value but has also asked us to use the ITRC guideline. The use of this guideline value is predicated on these values being the only defined quantitative guideline included in the guidance and its extensive use on other sites to define a point at which LNAPL recovery may be impractical.*
    - *LNAPL recovery rates less than 1 gpd (to be validated by baildown tests immediately conducted on suspension of recovery). This value as demonstrated in the LNAPL CSM equates to the LNAPL transmissivity threshold provided above. The use of an LNAPL recovery rate (as a surrogate for LNAPL Transmissivity) provides for ease of application but is metric which guides actions such as*

completing a baildown test or reservoir decline curve analysis (see decision logic diagram)

- *Reservoir decline curve analysis demonstrating that a minimum of 90% of the maximum theoretical LNAPL recovery volume has been achieved. It should be noted in the application of this criteria even if > 90% of the theoretical recoverable volume has been removed termination of recovery will be determined based on the measured transmissivity.*
- *In the event that the reservoir decline curve analysis does not yield a strong regression coefficient after application of common data filtering methods (spline functions, time weighted averages to standardize the temporal records over time or other smoothing algorithms) then other methods such as comparison on mobile and residual mass (using petrophysical testing) may be required.*

- ***Further recovery of LNAPL is uneconomic.*** *If USEPA wants to utilize the ITRC recommendations we can also include a metric around cost effectiveness and leverage a metric of $/gallon. Typically costs that have been utilized at other sites have included (a) costs in excess of the value of the product (b) costs a factor of 10 fold more than the value of the product. These metrics in many cases are arbitrary and we consider that they should be a consideration, not a formal metric.*

- ***Transition Criteria – In addition to achievement of recovery to the extent practicable. Transition criteria will be linked to the key concepts:***
  - ***Natural Mass Losses are greater than engineered mass losses.*** *This is focused on the concept that the natural processes must be sufficiently robust that the incremental gains of continued recovery (once the maximum extent practicable metrics are achieved) are limited*
  - ***Natural source zone depletion can facilitate restoration of the aquifer within a "reasonable" period of time.*** *This would require quantification of NSZD mass loss rates and quantification of mass in place to support calculation.*

The approach proposed by the group is also aligned with other guidance contained within ITRC **Figure NSZD-15** (**Enclosure B**) which includes the considerations discussed in the context of the site in **Table 2** (**Enclosure A**). We request that USEPA consider that the group is still seeking to collect and collate data for this site. Consistent with **Figure A2**, the magnitude of NSZD rates and assessment of risk are important considerations in the context of defining recovery to the extent practical. The group does understand that the metrics and goals provided will have to be refined and if reservoir/recovery decline curve analysis is constrained in its application then alternative methods may have to be incorporated into the approach.

Enclosures:

Enclosure A	Tables
Enclosure B	NSZD Figures
Enclosure C	Expenditures Figure
Enclosure D	Decision Logic Diagram Figures

TOEROEK
ASSOCIATES, INC.

April 8, 2021

Ms. Carol Stein, PE, MBA
U.S. Environmental Protection Agency, Region 2
290 Broadway
New York, NY 10007-1866

Re: **Contract #68HERH19D0018, TO 68HE0220F0069; Corrective Action and Permit Support for Hovensa and St. Croix Alumina Plume;: Draft Technical Evaluation of the Response to February 8, 2021 USEPA Review of POC's Response to December 14, 2020 Comments, dated March 24, 2021, on the LNAPL CSM and Remedial Action Work Plan, St. Croix, U.S. Virgin Islands, St. Croix Alumina Site, dated July 2020**

Dear Ms. Stein:

Toeroek Associates, Inc. (Toeroek) is pleased to present this draft technical evaluation of the Response to February 8, 2021 USEPA Review of POC's Response to December 14, 2020 Comments, dated March 24, 2021 (RTCs) on the *LNAPL CSM and Remedial Action Work Plan, St. Croix, U.S. Virgin Islands, St. Croix Alumina Site*, dated July 2020 (Work Plan). A revised version of the Work Plan was not provided, and as such an evaluation of the whether the RTCs were incorporated into the Work Plan was not able to be completed. This deliverable was reviewed as part of our quality assurance program under our Quality Management Plan for the REPA 6 Zone 3 contract. The letter serves as the deliverable and is attached in both MS Word and portable document format (PDF) files for your convenience.

The RTCs addressed EPA's comments and are acceptable. Please note, Toeroek did not review the Response General Comment 1 as this was prepared by EPA. Also of note, for the Response to Specific Comment 6, the financial comparison information to justify a process for mechanical removal of light non-aqueous phase liquid (LNAPL) in Attachment C are still under development and could not be reviewed. Further, Toeroek did have comments on the decision logic diagrams provided; however, as we already provided these comments to EPA on the evaluation of the PTPLLC Responses to EPA's January 29, 2021 Review, dated March 10, 2021 (Response to Comments [RTCs]) of the Light Non-Aqueous Phase Liquid (LNAPL) Natural Source Zone Depletion (NSZD) Work Plan, St. Croix, U.S. Virgin Islands, St. Croix Alumina Site, dated November 4, 2020, we have therefore not repeated the comments herein.

Finally, the Response to Specific Comment 6, provided an adequate process to evaluate the mass of LNAPL present in the vadose zone as compared to that immediately above and in the saturated zone. However, this issue remains unresolved until data is provided.

205 West Wacker Drive, Suite 1810
Chicago, IL 60606
Phone: 312-212-0934

Please contact Brad Martin, Toeroek Project Manager, directly at 312•212-0934 should you have any questions.

Sincerely,

Paul Kieler
REPA 6 Program Manager

cc: B. Martin, Toeroek
C. Dare, Toeroek
R. Howe, Toeroek
P. Rosa, EPA Region 2
Toeroek Project Files

EVALUATION OF THE

PTPLLC RESPONSES TO EPA'S JANUARY 29, 2021 REVIEW

DATED MARCH 10, 2021

OF THE

DRAFT LIGHT NON-AQUEOUS PHASE LIQUID (LNAPL)

NATURAL SOURCE ZONE DEPLETION (NSZD) WORK PLAN

ST. CROIX ALUMINA GROUNDWATER PLUME, U.S. VIRGIN ISLANDS

DATED NOVEMBER 4, 2020

In general, the Response to Comments (RTCs) addressed EPA's comments and are acceptable with the following considerations. The following evaluation includes only responses where additional information or clarification is required.

A revised version of the Light Non-Aqueous Phase Liquid (LNAPL) Natural Source Zone Depletion Work Plan (Work Plan) was not provided, and as such an evaluation of the whether the RTCs were incorporated into the Work Plan was not able to be completed. A revised Work Plan incorporating the proposed revisions is needed.

Additional data was collected and presented as part of these RTCs. No additional comments concerning the additional data presented were noted in this evaluation.

Evaluation of the Response to Comment 1: The response is partially acceptable. Field-based measurement technology manufacturer instruction and other measurement quality evaluations to be performed in the field should be provided as part of the revised quality assurance project plan (QAPP) in accordance with the Unified Federal Policy (UFP) format. Typically, Worksheets #20, #21, and #22 address field measurements. Field-based measurements will be an essential portion of the field program and as such additional duplicate measurements may be needed to ensure data quality over the guidelines suggested in a manufacturer's direction on how test kits and field measurement are evaluated prior to use in directing additional field efforts. Please ensure these worksheets are completed to address collection of field measurements.

Evaluation of the Response to Comment 2: The response is partially acceptable. The proposed changes to Table 1 are generally acceptable but should reference the appropriate sections of the revised UFP-QAPP once it is completed. It is noted that the Optimized UFP-QAPP Worksheet #11 includes text that cross references, at a minimum, content from Worksheet #17 as well as Worksheets #19, 20, 24, 25, 26, 27, 28, and 30. Field-based measurement requirements for both precision and accuracy and not just precision should be addressed in the UFP-QAPP and Table 1. The need for additional calibration checks is anticipated and should be included in the event the suggested manufactures guidelines are inadequate for supporting decision making in the field.

Evaluation of the Response to Comment 3: The response is acceptable; however, the table should be amended and included appropriate reference to specific sections of the UFP-QAPP as noted in the Evaluation of the Response to Comment 2 above.

Evaluation of the Response to General Question II.c.: Revised Table 1 is acceptable, but the figures are missing information. Although the Legend for Cross Section 3A includes a thin blue line noted as approximate groundwater elevation, no blue line could be identified on the cross section. Cross Section 3B shows well specific elevations, but still does not provide an interpreted groundwater elevation within the cross section that clearly shows the water levels in the wells. Further, cross-section 3B provided as Figure 5 does provide the needed water levels, but still does not properly indicate that wells like MW-13B and others are projected onto the cross-section line. Appropriate symbology that alerts the reviewer that some of the wells are projected onto the cross-section and are not "in-line" with the cross-section cut needs to be developed and applied to the image. Please review the cross-sections to identify any additional errors and omissions as this list is not inclusive.

Evaluation of the Response to General Question II.g.: The response is partially acceptable. It is assumed that the reference in "key decision 3" to "hard sand" should instead say "caliche cemented sands." Please revise this terminology as noted for clarity where needed in associated text and tables. These substances differ in several properties, including transmission of gases.

Evaluation of the Response to General Question II.k.: The response is acceptable. Please note that the comment response is mislabeled as response to General Question II.i. instead of II.k. This typographical error needs to be corrected, but response is acceptable for General Question II.k.

Evaluation of the Response to Laboratory QA/QC Question III.a.: The response is acceptable. Please ensure that some level of secondary review/data validation of the lab data/results will be performed when data is used to make critical decisions along with the results of any secondary/data usability reviews provided in the associated results reports.

Evaluation of the Response to Laboratory QA/QC Question III.b.: The response is acceptable.

Evaluation of the Response to Laboratory QA/QC Question III.c.: The response is acceptable contingent on verifying that the revised Appendix E of the revised Work Plan provides the information as stated in this comment response.

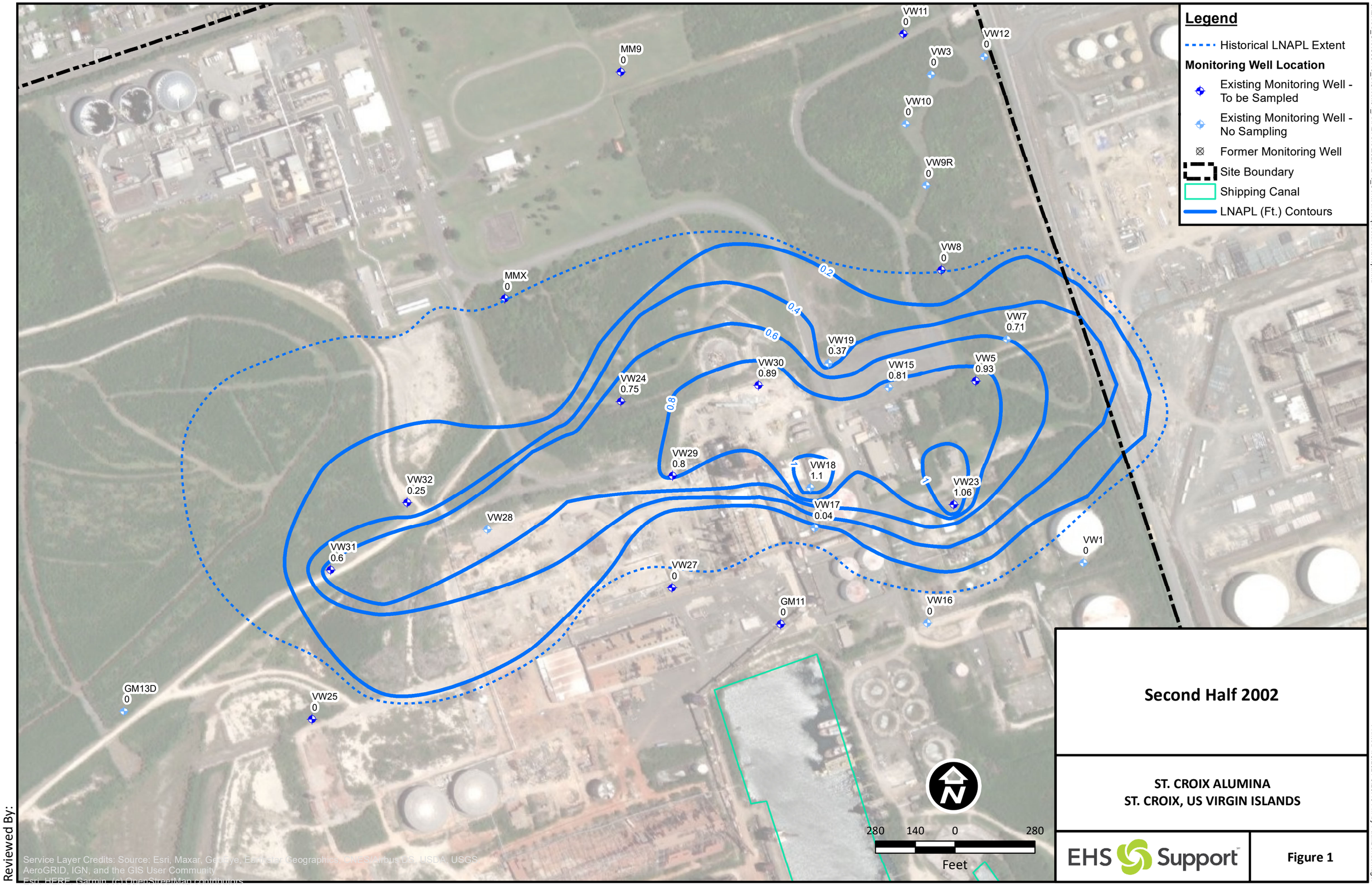
Evaluation of the Response to Laboratory QA/QC Question III.d.: The response is partially acceptable. The response indicates the performance of field duplicate QC samples at a rate of 10 percent and duplicate performance criteria of 30 percent. It does not however, address the primary question, which was how much of the data from field efforts will be validated and by whom and how the results of any validation will be used (i.e., at a minimum to assess training needs or the need for a secondary review of results) to assure the usability of the results. This type of information is still needed and should be provided in the revised UFP-QAPP and summarized in the Work Plan.

Evaluation of the Response to Specific Comment 2: The response is partially acceptable. Figure 3A still needs to be modified to clearly show the groundwater elevations and geology from projected wells as previously indicated. Also numerous projected wells are not identified on Figure 3B as noted previously in General Question Response II.c.

Evaluation of the Response to Specific Comment 7: The response is partially acceptable. The decision logic diagrams provided in Appendix A-are a good-start, but they do not clearly define the decision steps. Simplifying the diagrams and condensing them would make their use of critical decision points more

readily performed. The flowcharts need to be more clearly defined and simplified in order to clearly show what the decision steps are. Figure A1 (in Attachment D of your response) follows most closely the typical flow-charting symbology protocols with some notable issues. Other flowcharts are less clear. As a general rule of thumb, please note that ovals are normally used for start and stop points, rectangles are used for actions, and diamonds are used to indicate decision statements. For more information on formats when creating decision logic diagrams the following simple reference might be helpful (Flowchart Basics: How to Create Flowcharts like a Process Analysis Expert (creately.com). None of the other proposed decision logic diagrams follow the standard conventions used in decision logic diagrams and need to be modified before a careful review can be performed of the logic process outlined in each diagram.

Appendix B Historical NAPL Extent Maps



Second Half 2002

ST. CROIX ALUMINA
ST. CROIX, US VIRGIN ISLANDS

EHS Support

Figure 1

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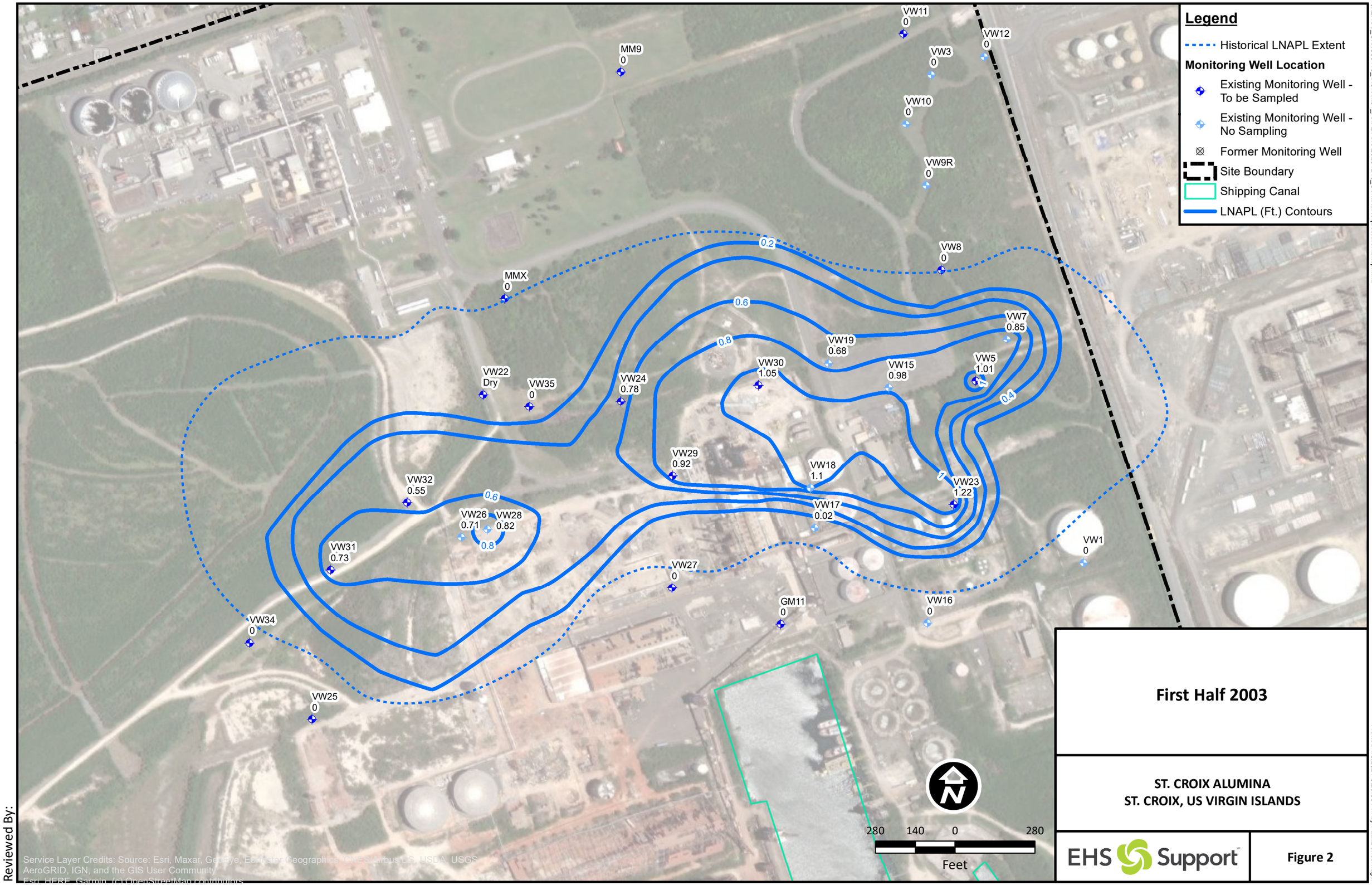

First Half 2003

ST. CROIX ALUMINA
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Figure 2

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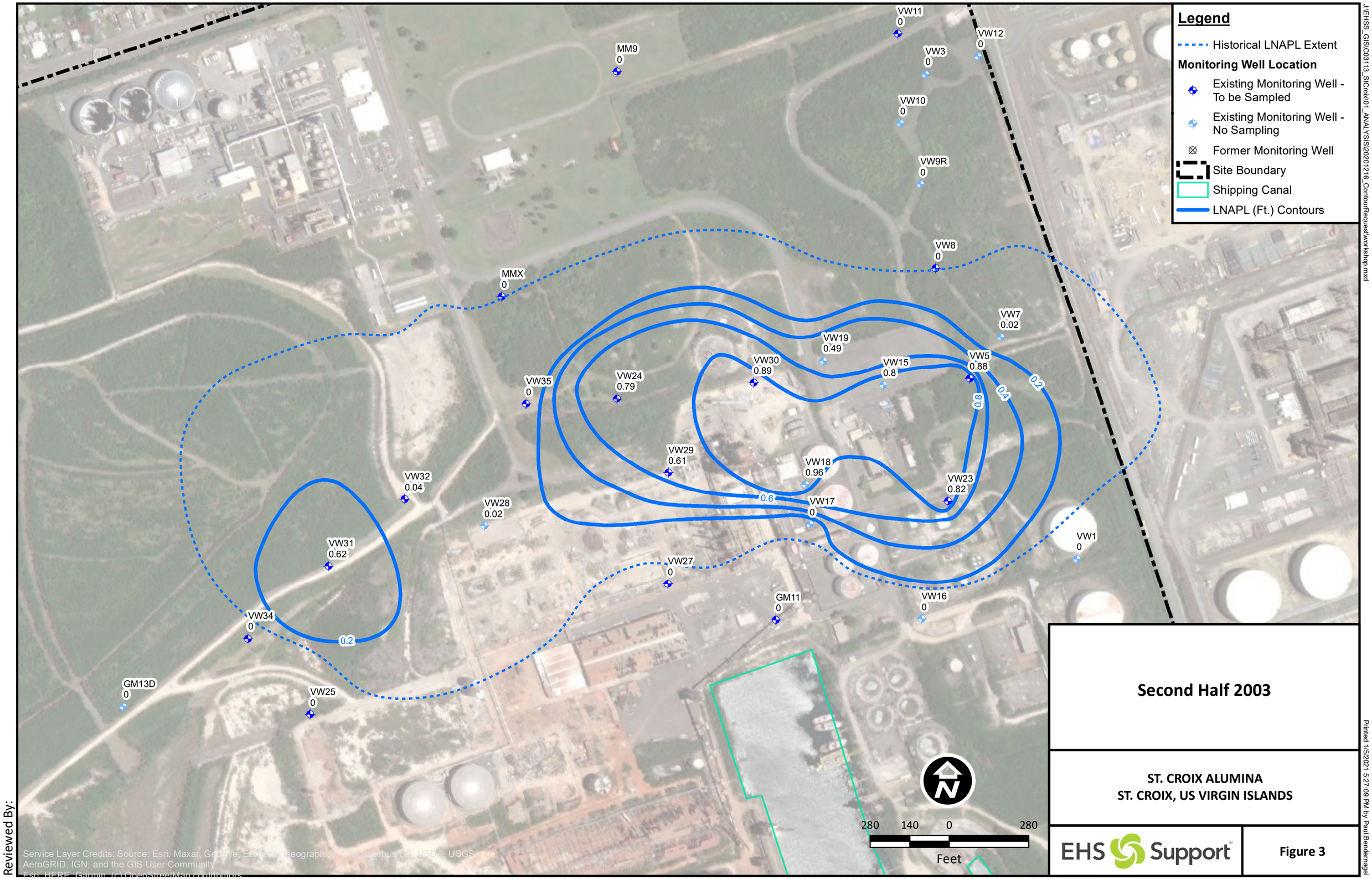

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Second Half 2003

ST. CROIX ALUMINA
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Figure 3

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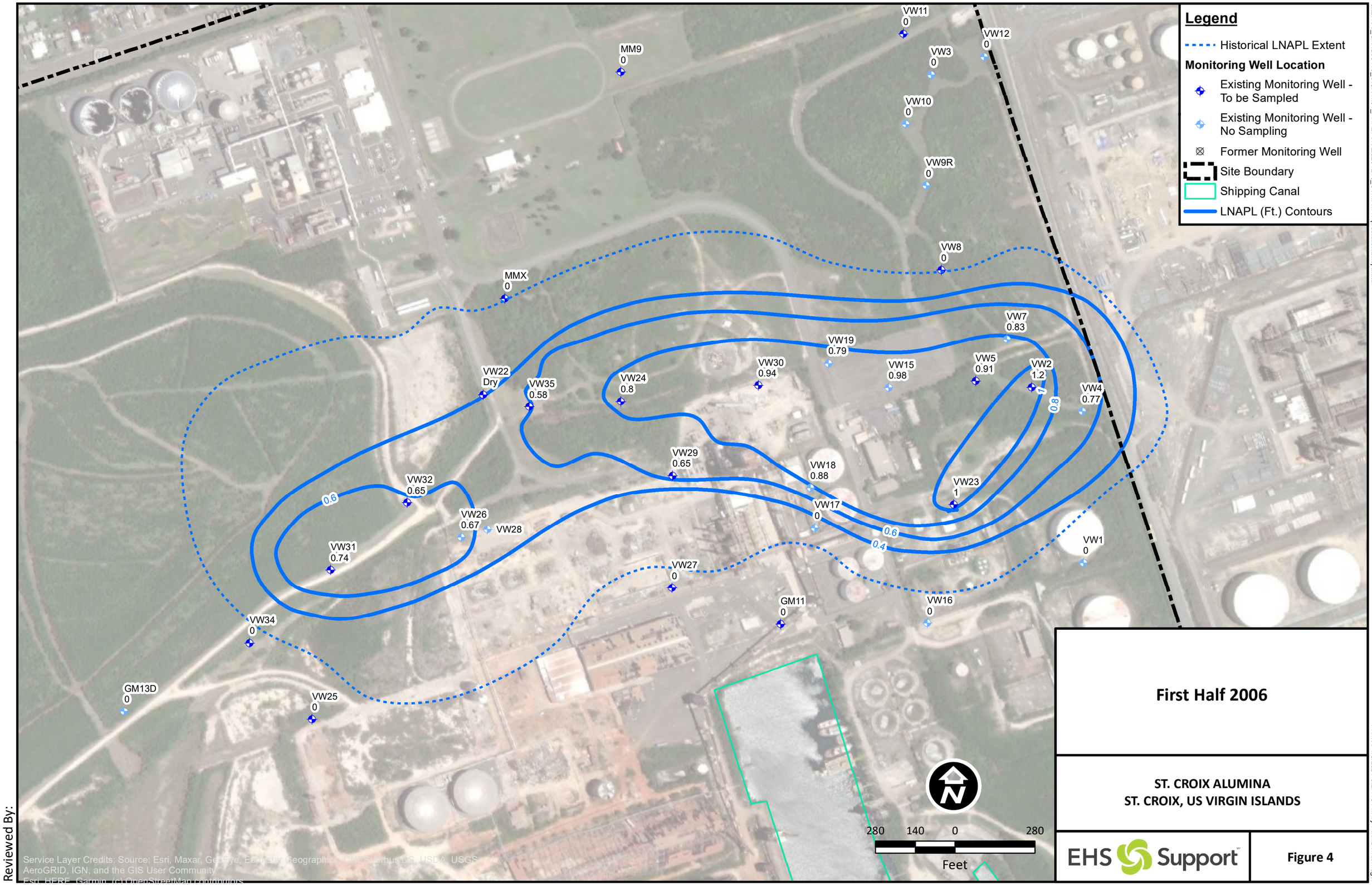

First Half 2006

ST. CROIX ALUMINA
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Figure 4

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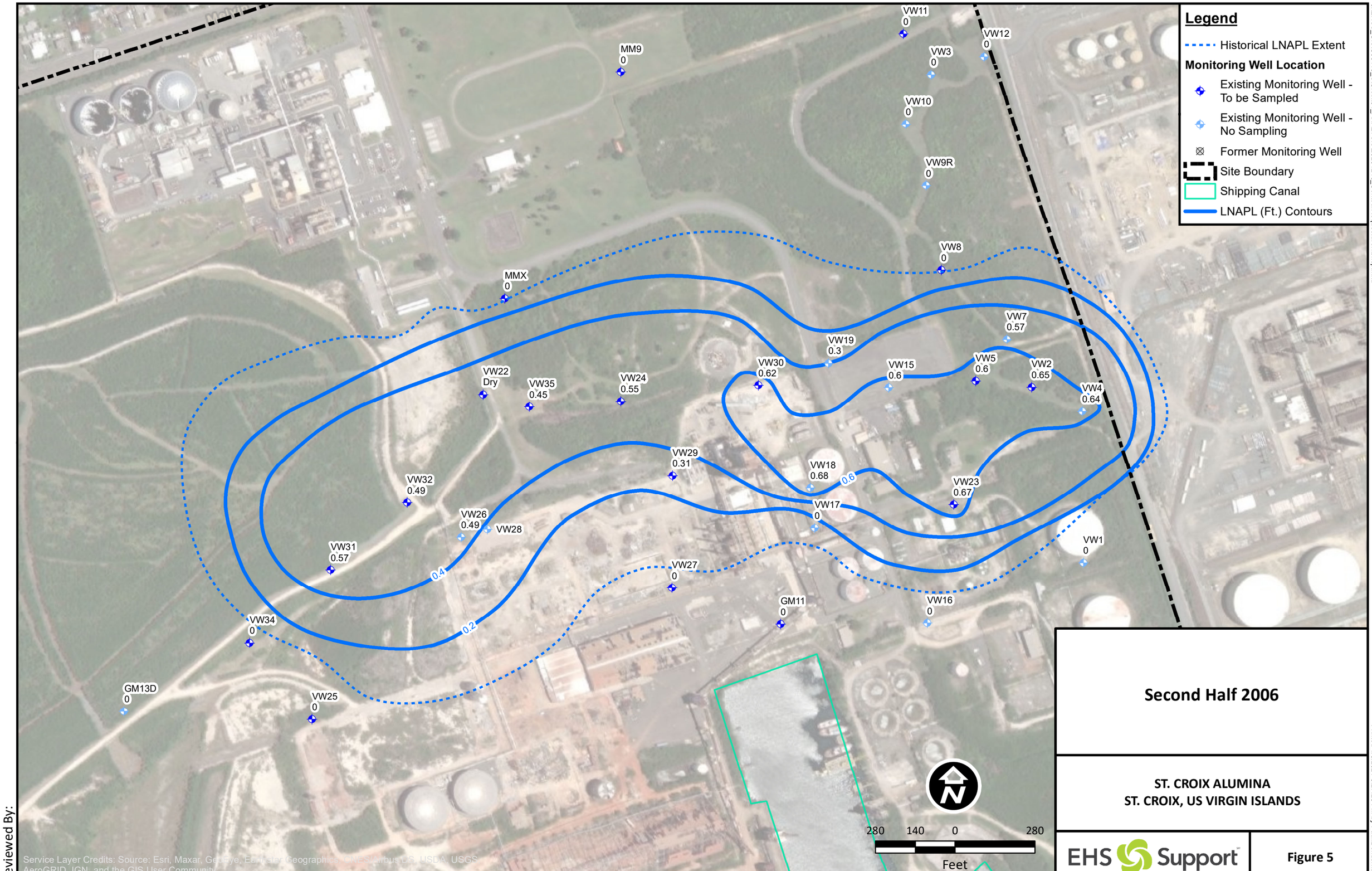

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Second Half 2006

ST. CROIX ALUMINA
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Figure 5

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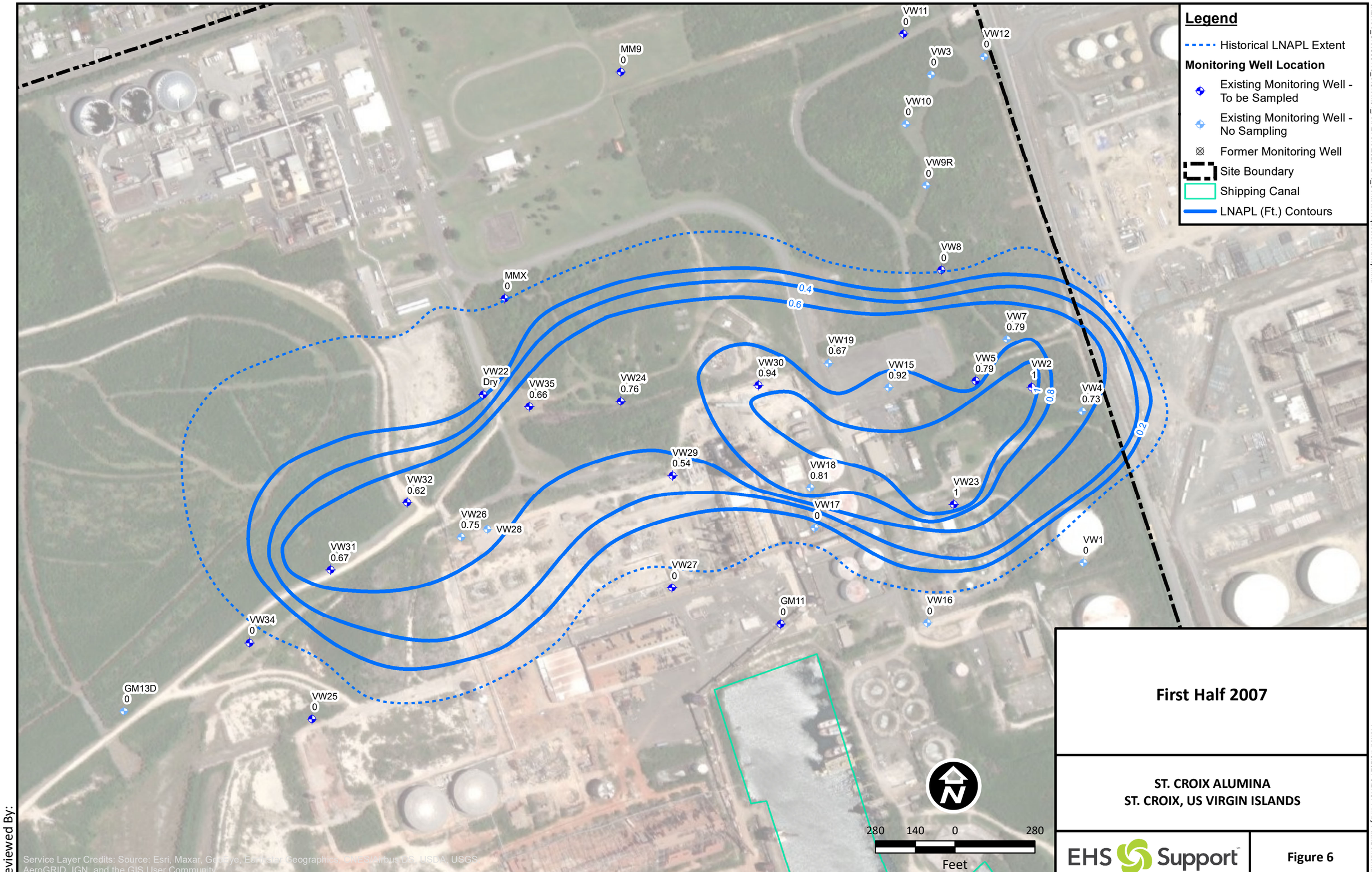

First Half 2007

ST. CROIX ALUMINA
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Figure 6

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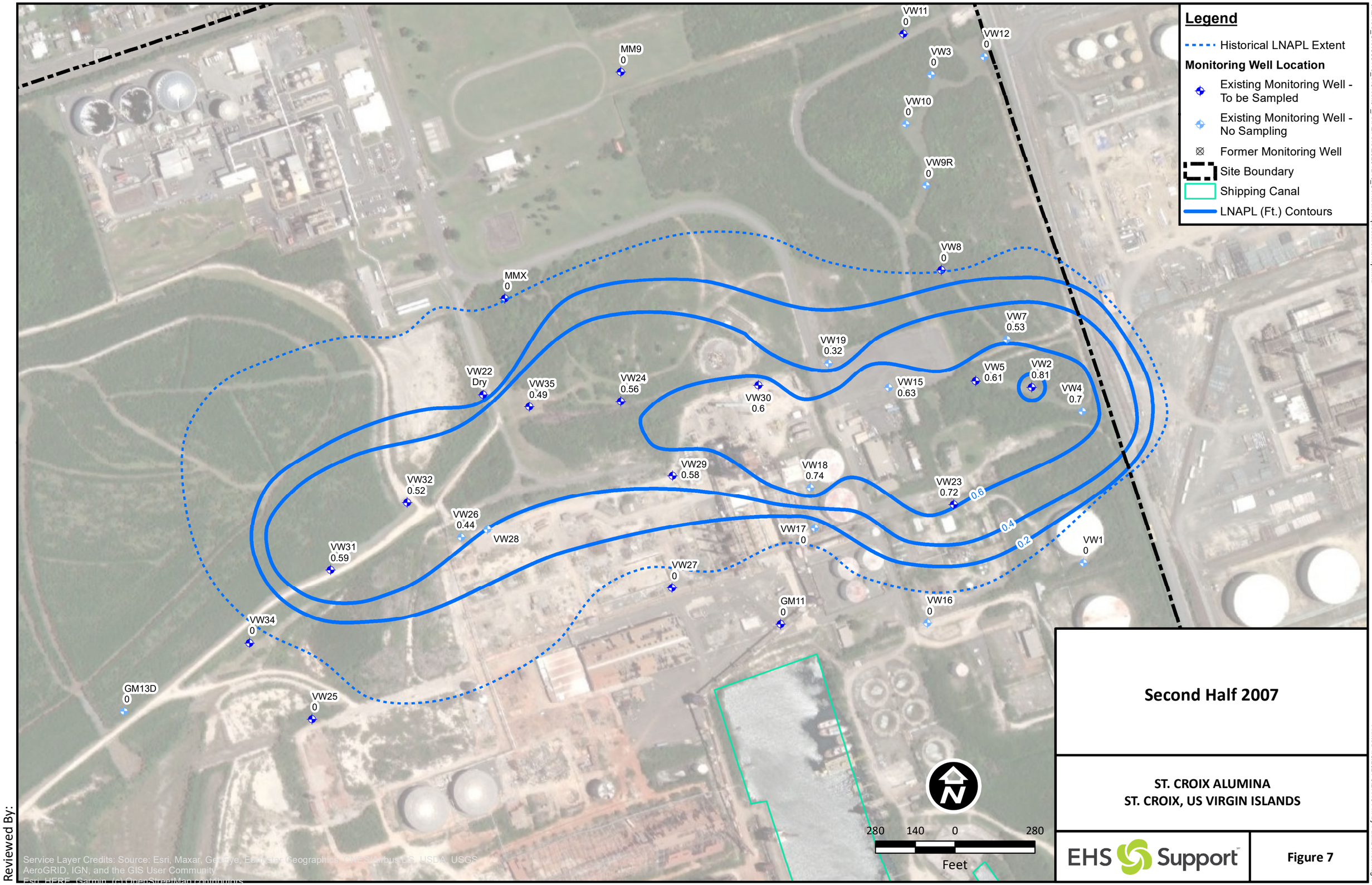

Second Half 2007

ST. CROIX ALUMINA
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Figure 7

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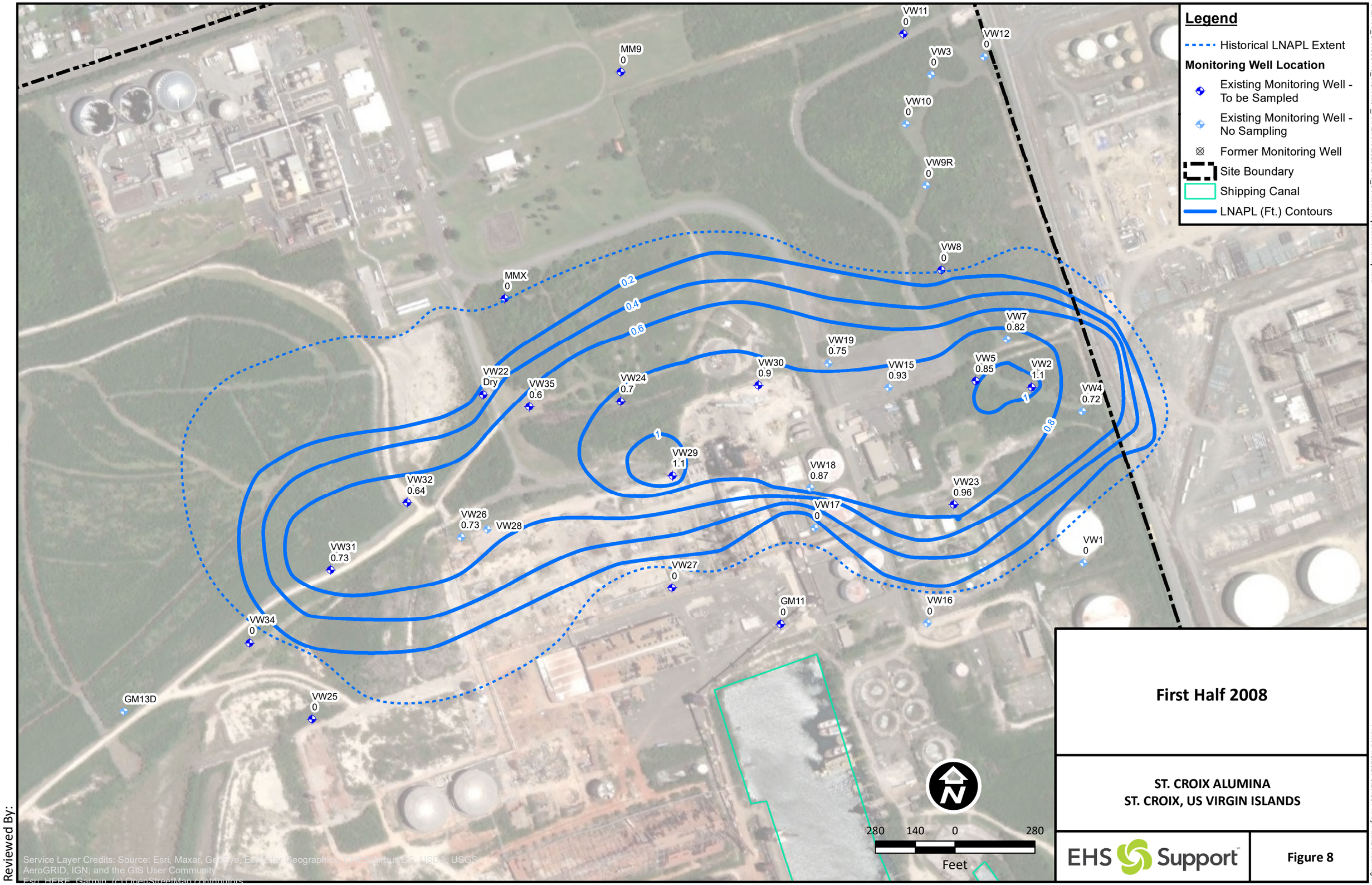

First Half 2008

ST. CROIX ALUMINA
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Figure 8

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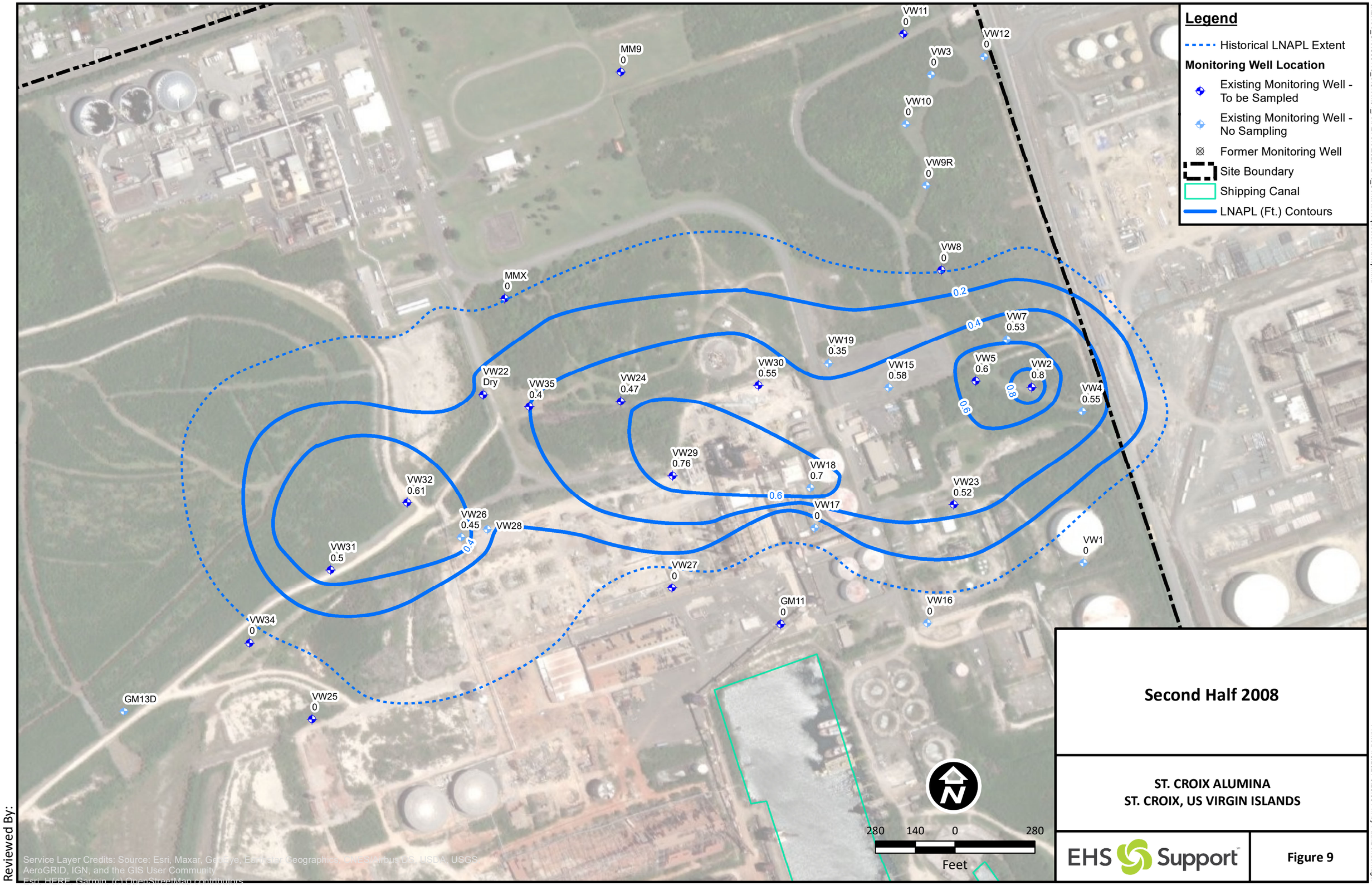

Second Half 2008

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Figure 9

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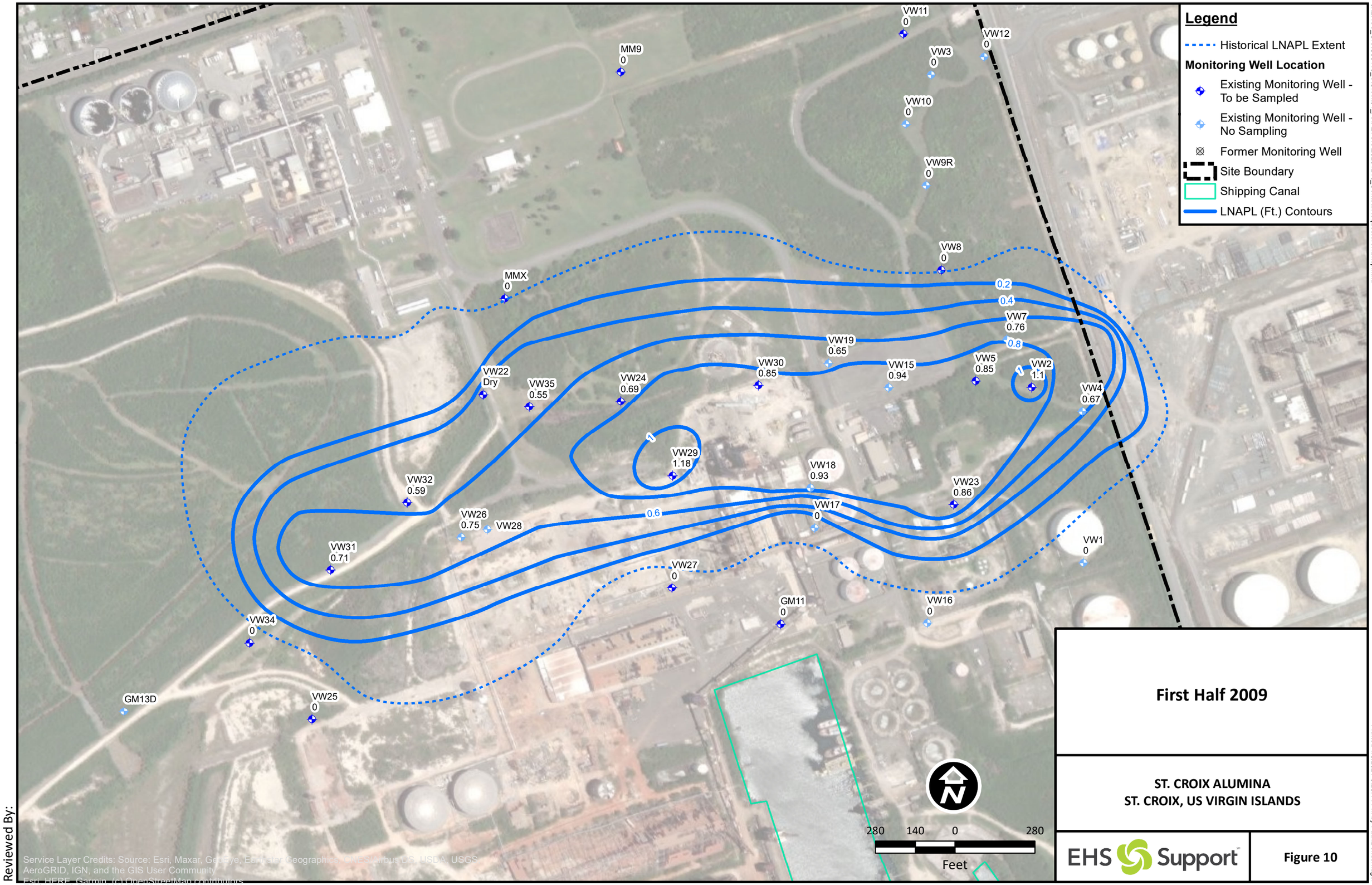

First Half 2009

ST. CROIX ALUMINA
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Figure 10

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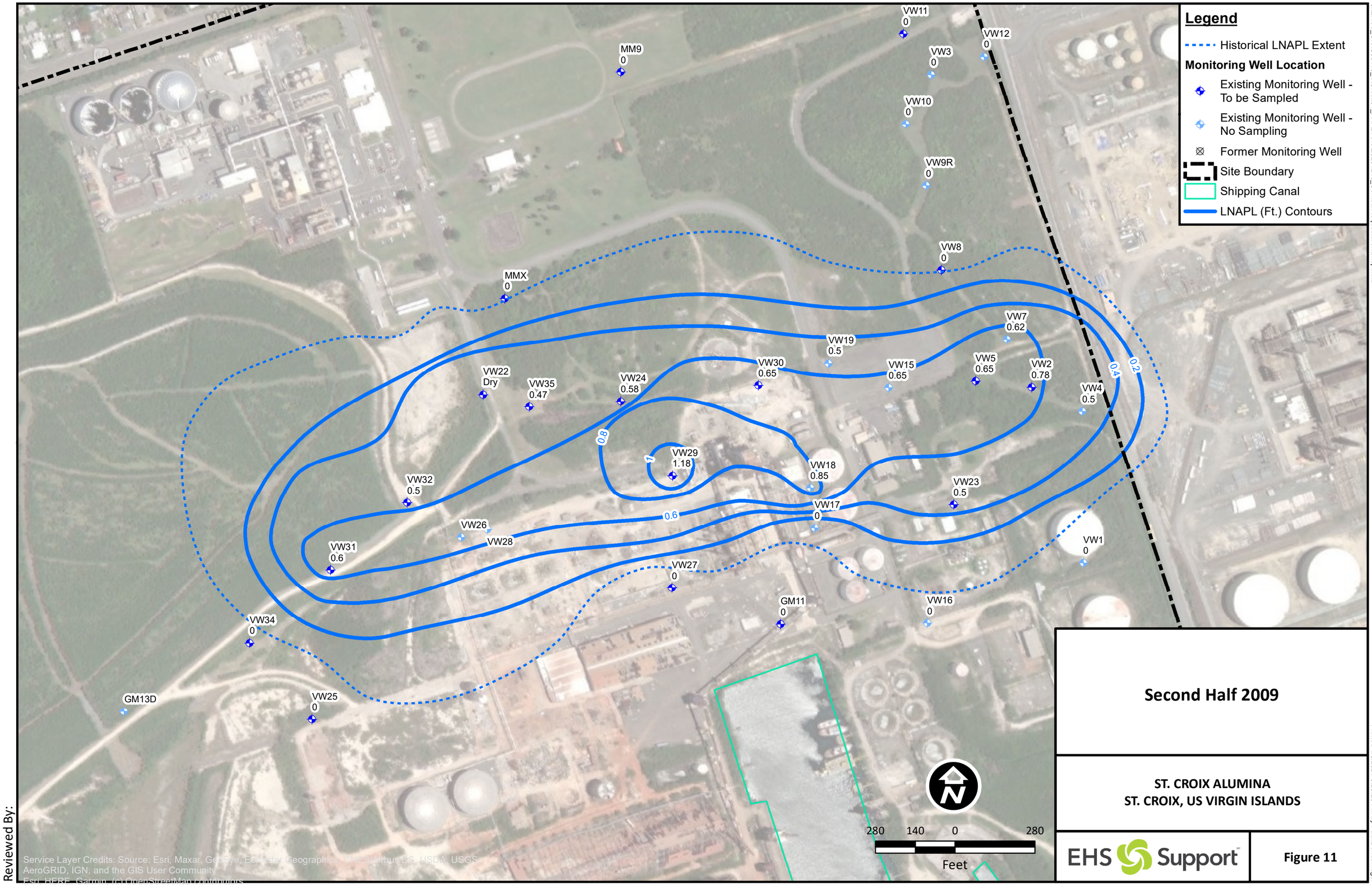

Second Half 2009

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Figure 11

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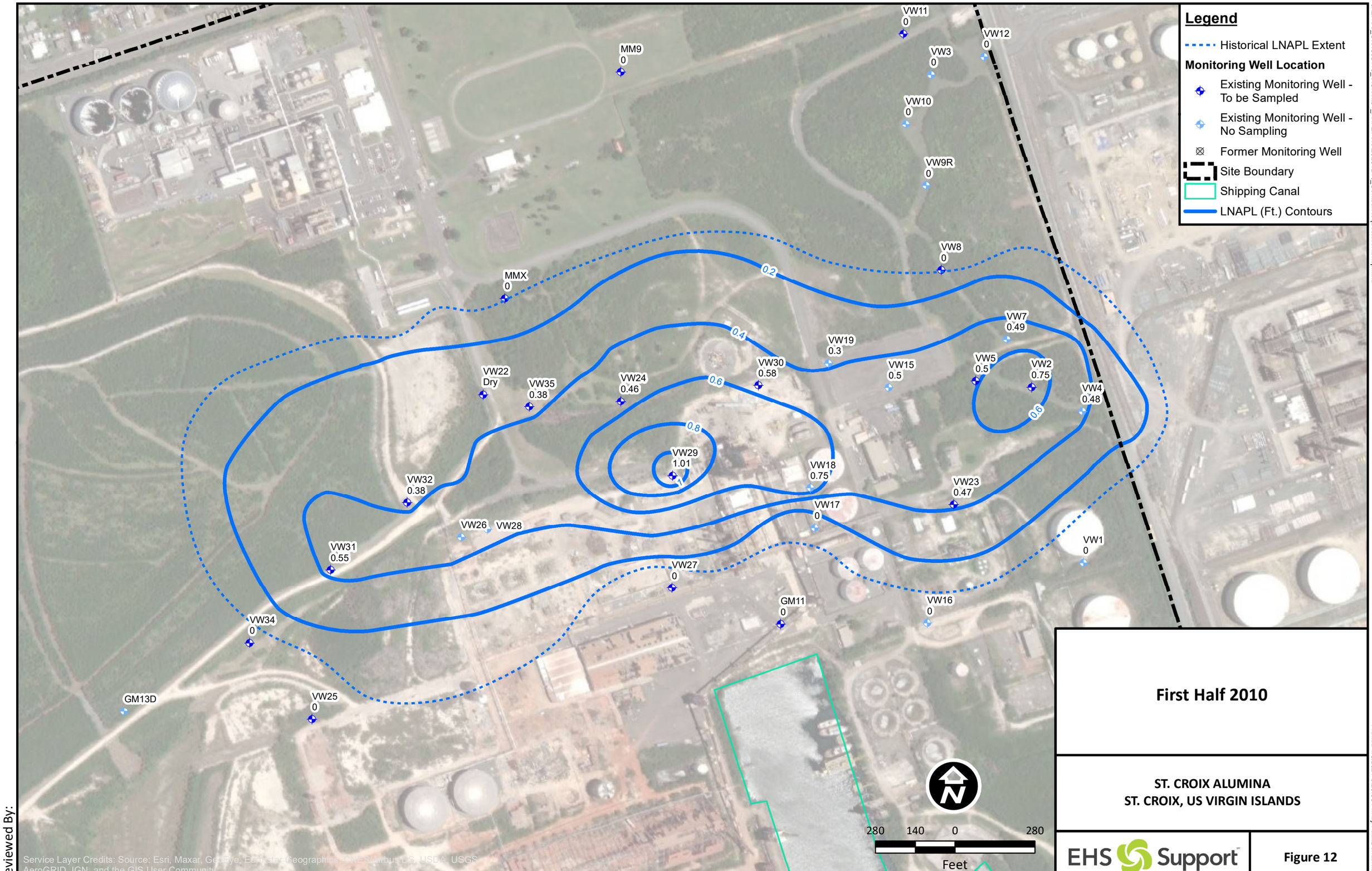

First Half 2010

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Figure 12

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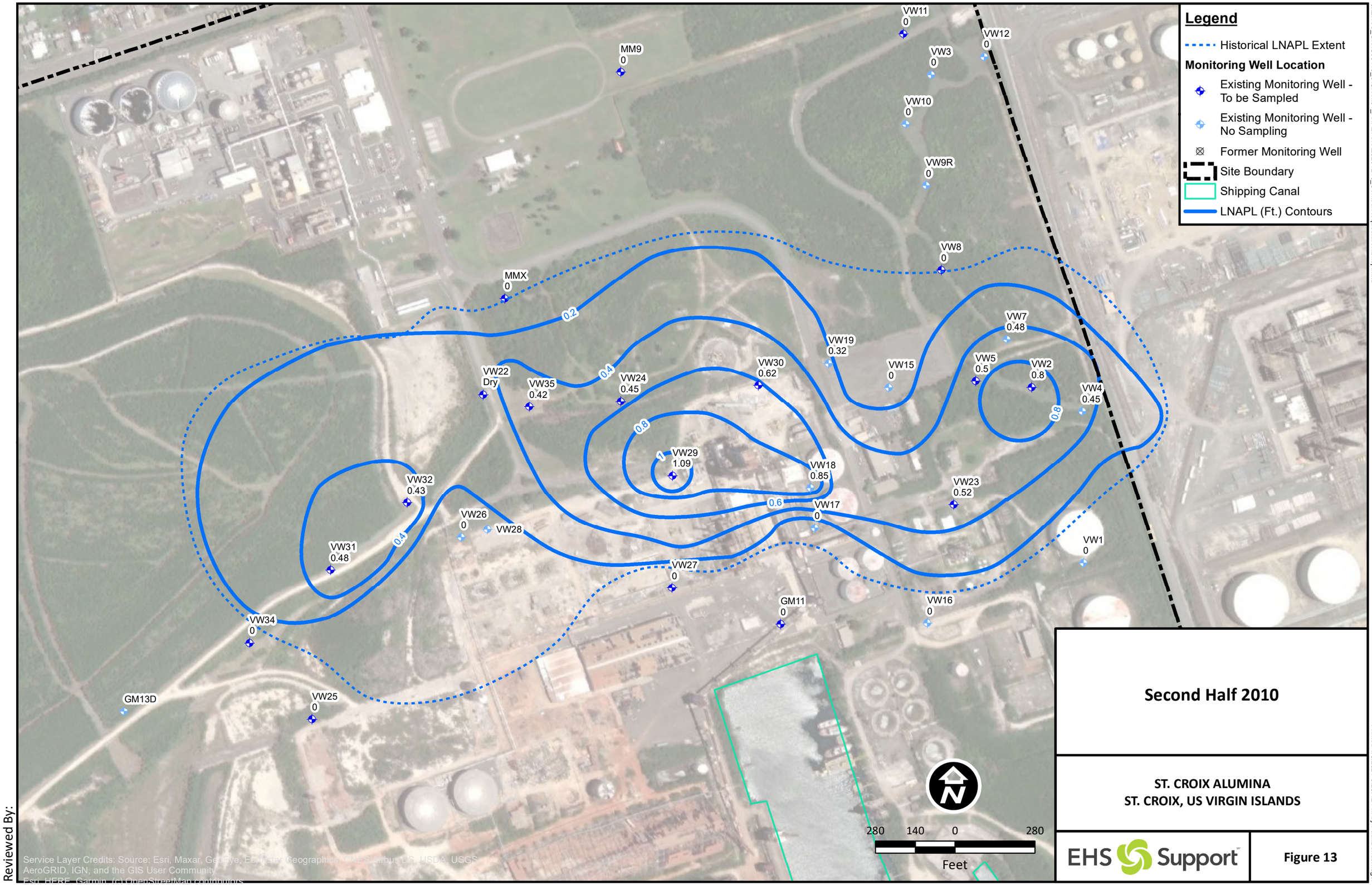
Legend
Historical LNAPL Extent
Monitoring Well Location
Existing Monitoring Well - To be Sampled
Existing Monitoring Well - No Sampling
Former Monitoring Well
Site Boundary
Shipping Canal
LNAPL (Ft.) Contours
MM9 0
VW11 0
VW12 0
VW3 0
VW10 0
VW9R 0
VW8 0
MMX 0
VW7 0.48
VW19 0.32
VW15 0
VW5 0.5
VW2 0.8
VW4 0.45
VW22 Dry
VW35 0.42
VW24 0.45
VW30 0.62
VW29 1.09
VW18 0.85
VW17 0
VW23 0.52
VW32 0.43
VW26 0
VW28
VW31 0.48
VW27 0
VW1 0
GM11 0
VW16 0
VW34 0
GM13D
VW25 0
0.2
0.4
0.6
0.8
1
280 140 0 280
Feet
N
Second Half 2010
ST. CROIX ALUMINA
ST. CROIX, US VIRGIN ISLANDS
EHS Support
Figure 13
Reviewed By:
Service Layer Credits: Source: Esri, Maxar, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community
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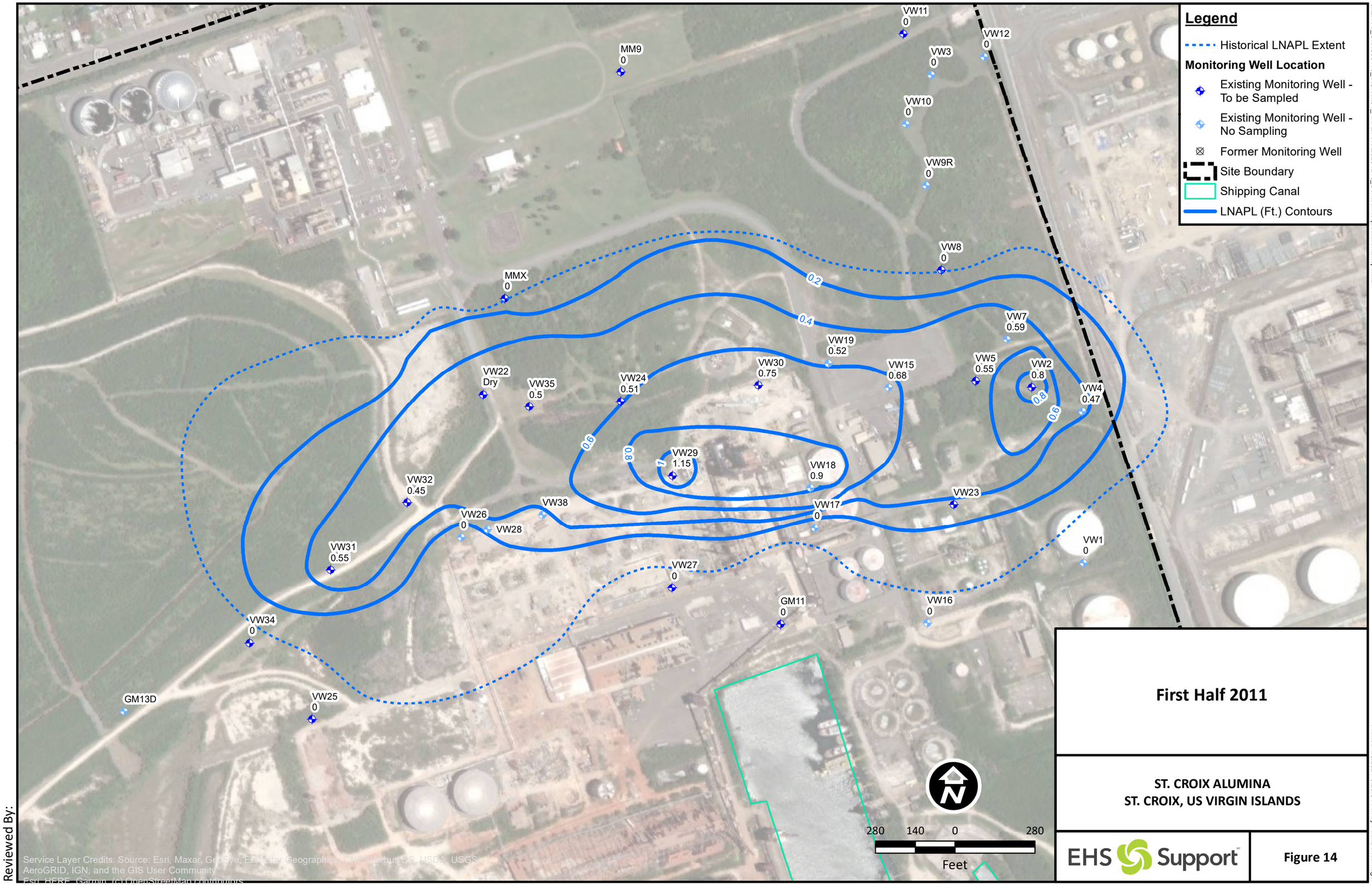

First Half 2011

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Figure 14

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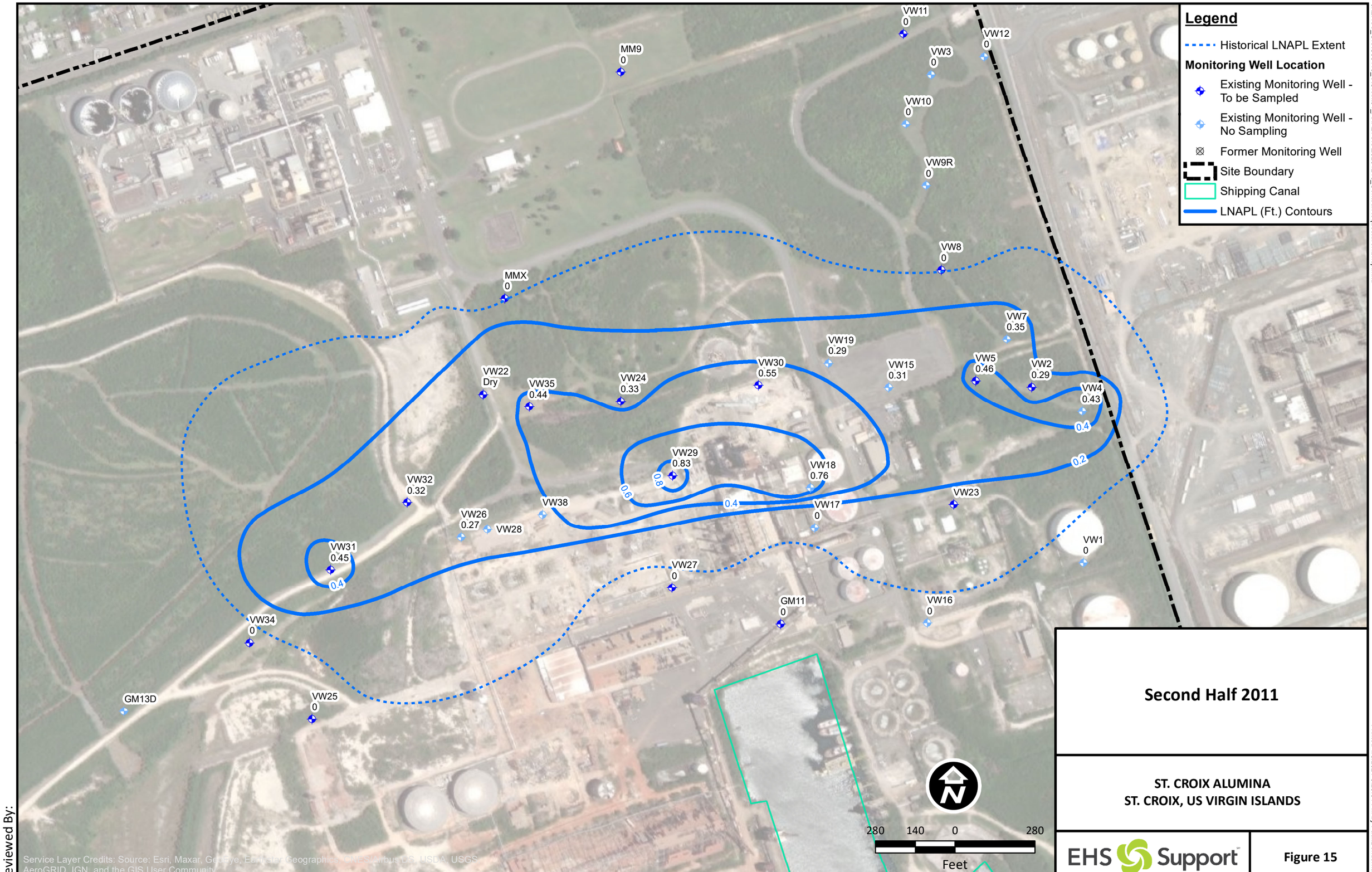

Second Half 2011

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Figure 15

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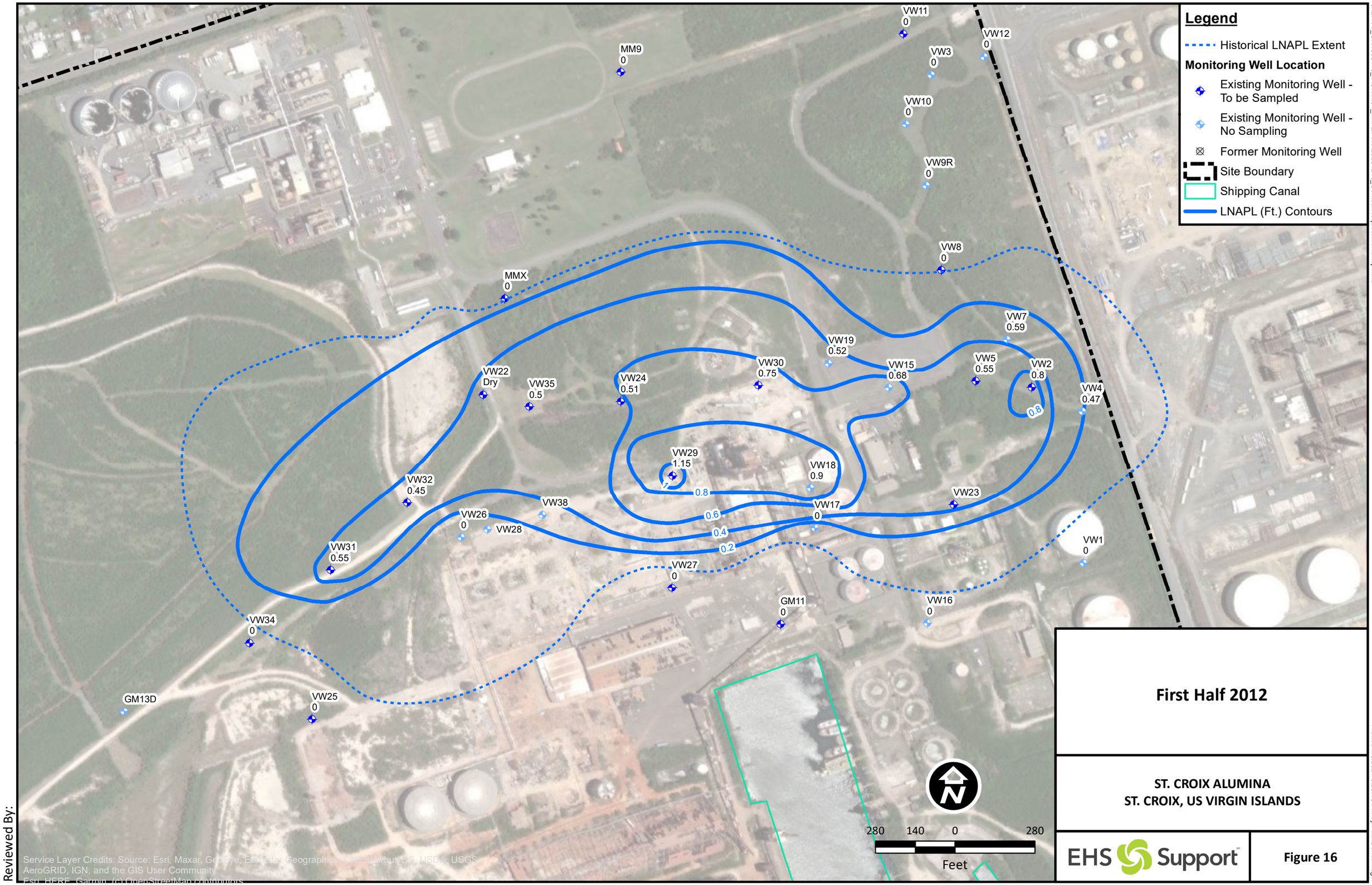

First Half 2012

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Figure 16

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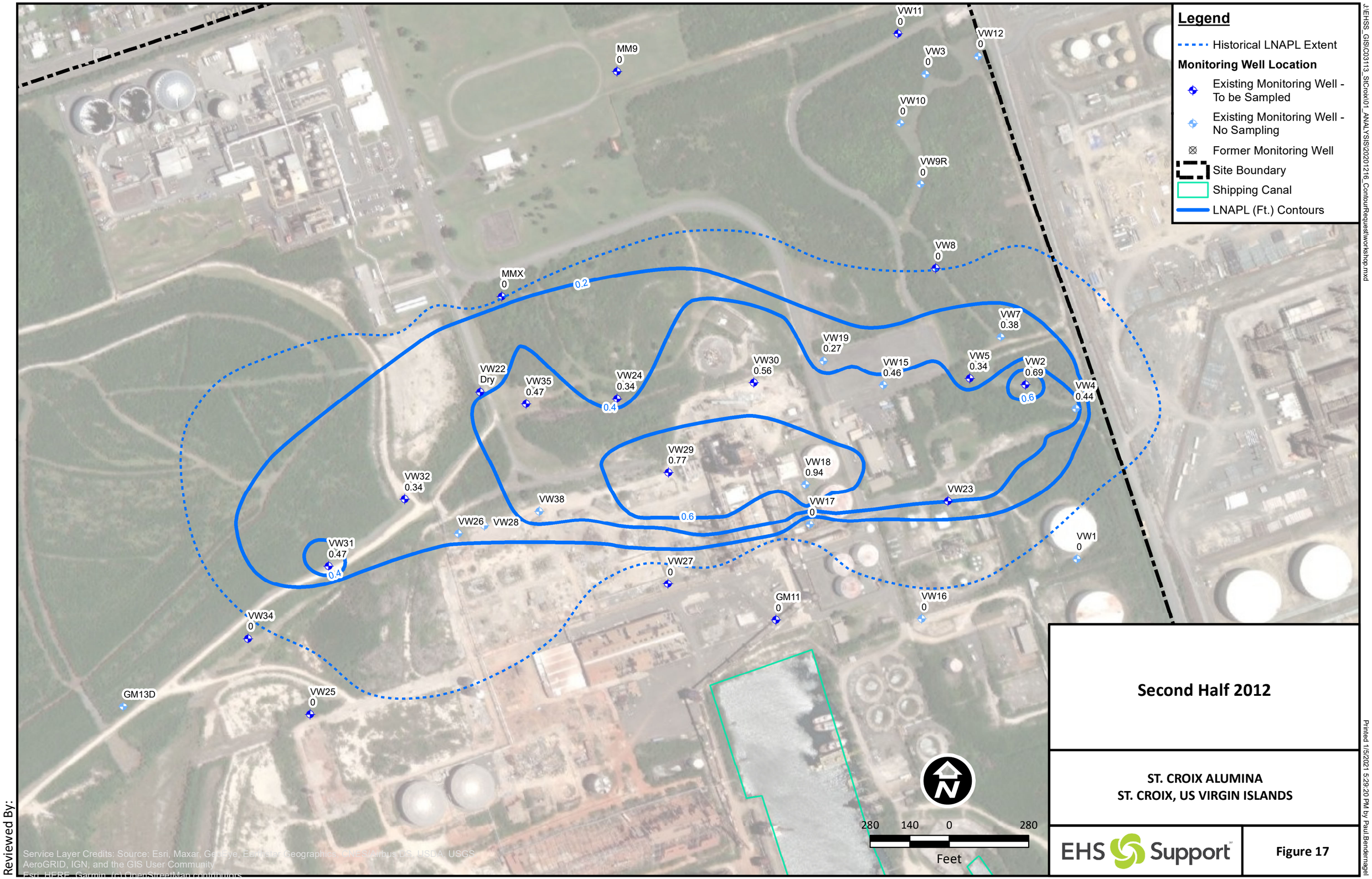

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Second Half 2012

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Figure 17

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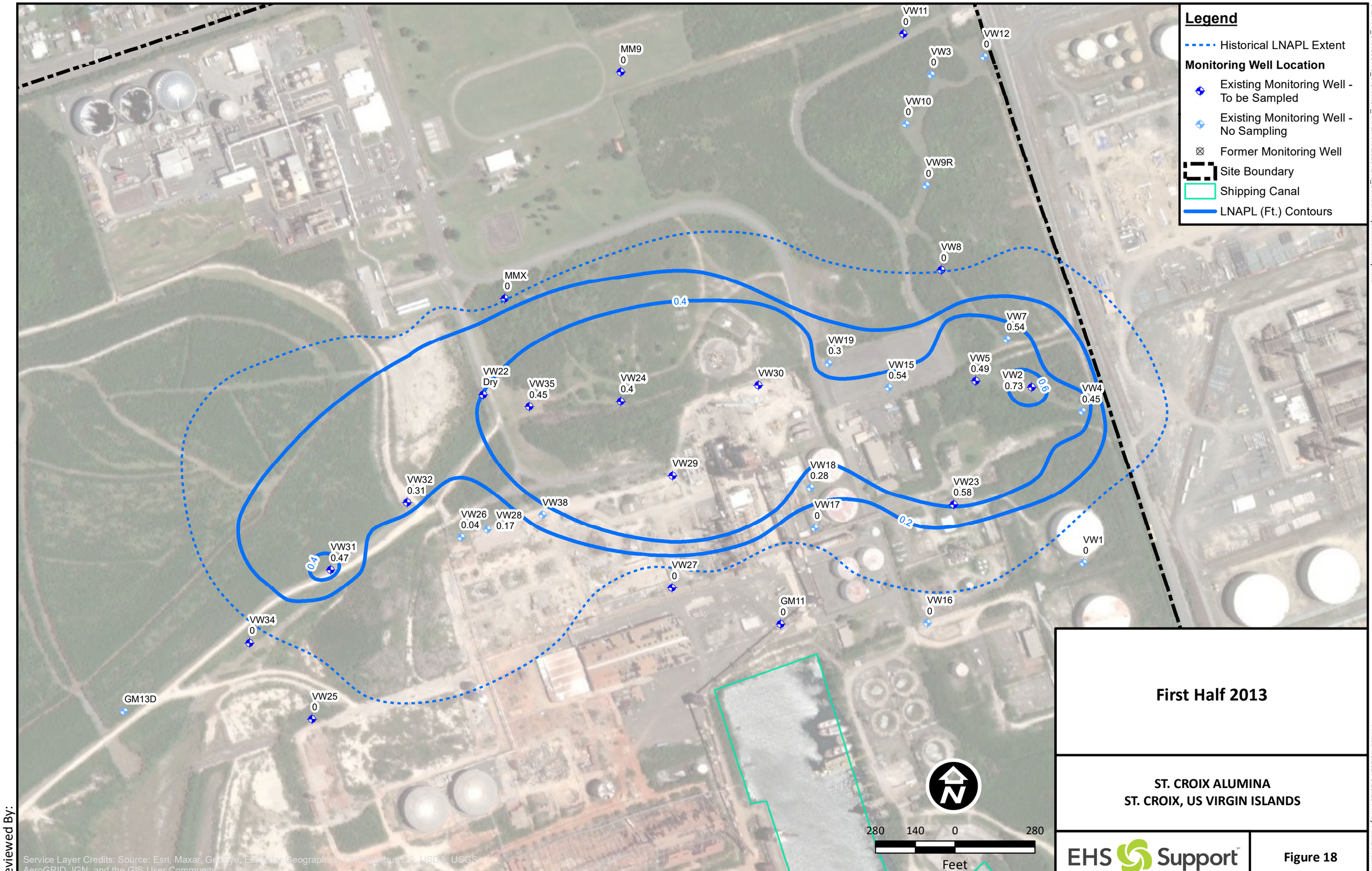

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First Half 2013

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Figure 18

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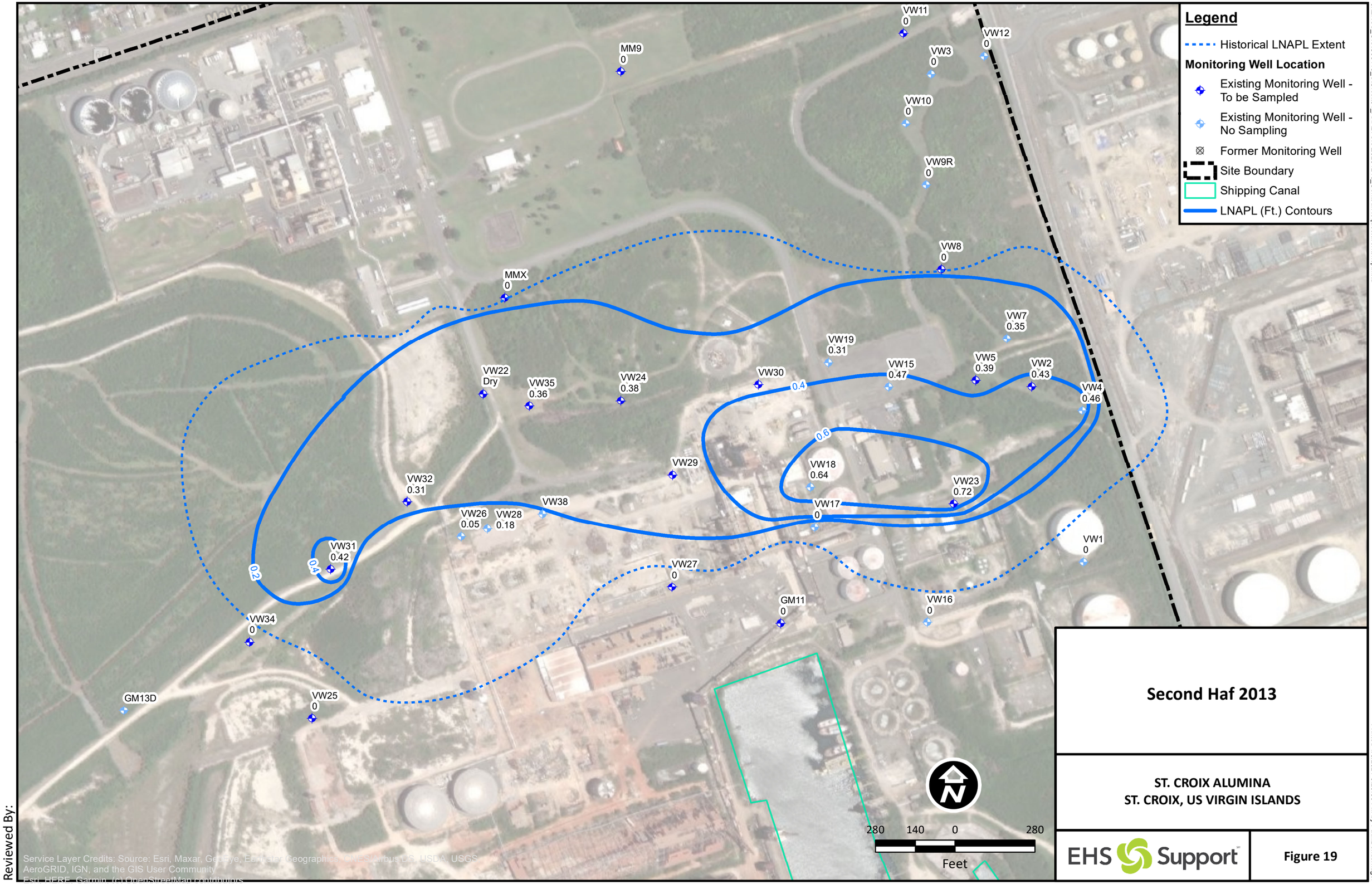

Second Haf 2013

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Figure 19

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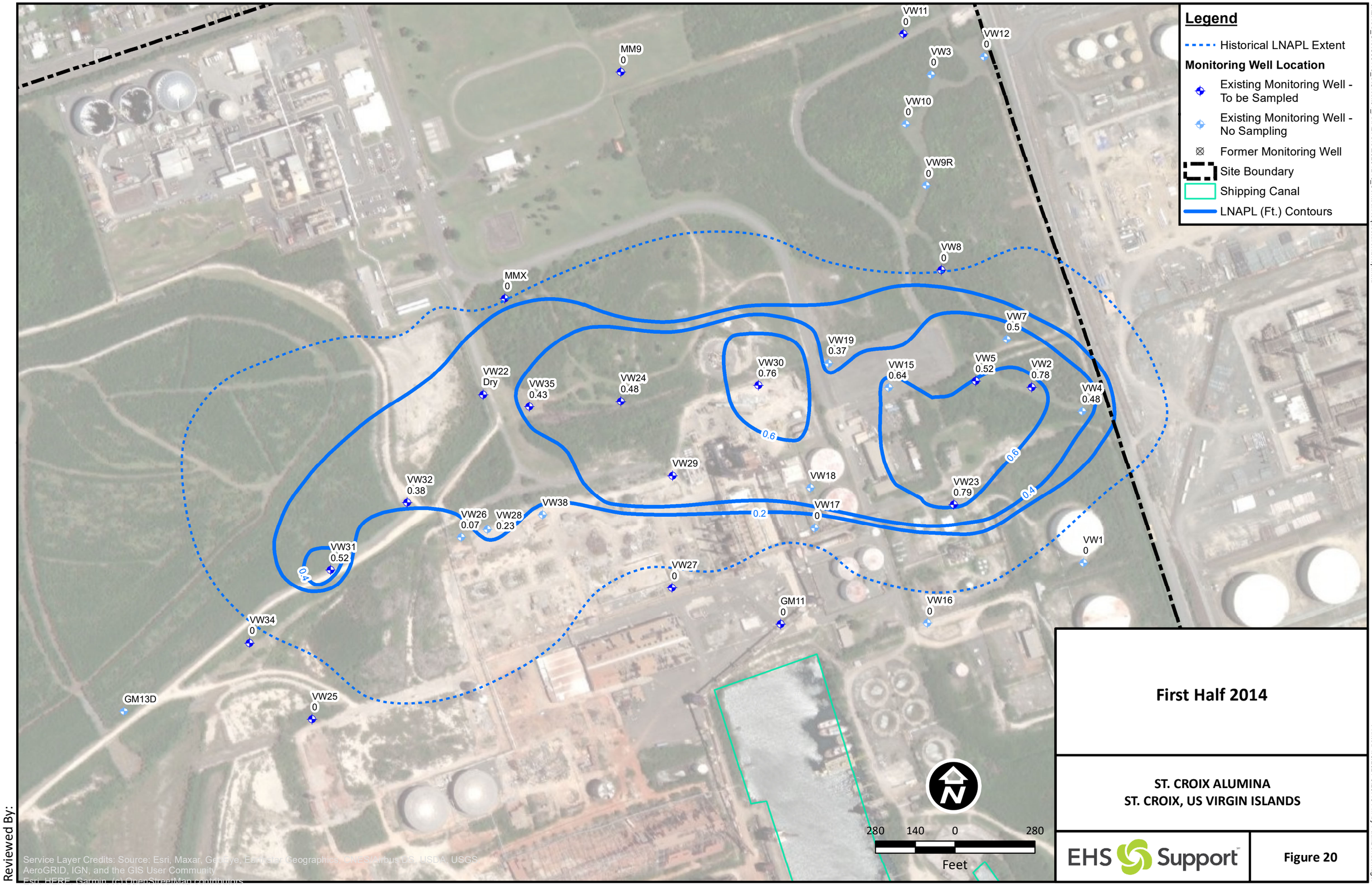

First Half 2014

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Figure 20

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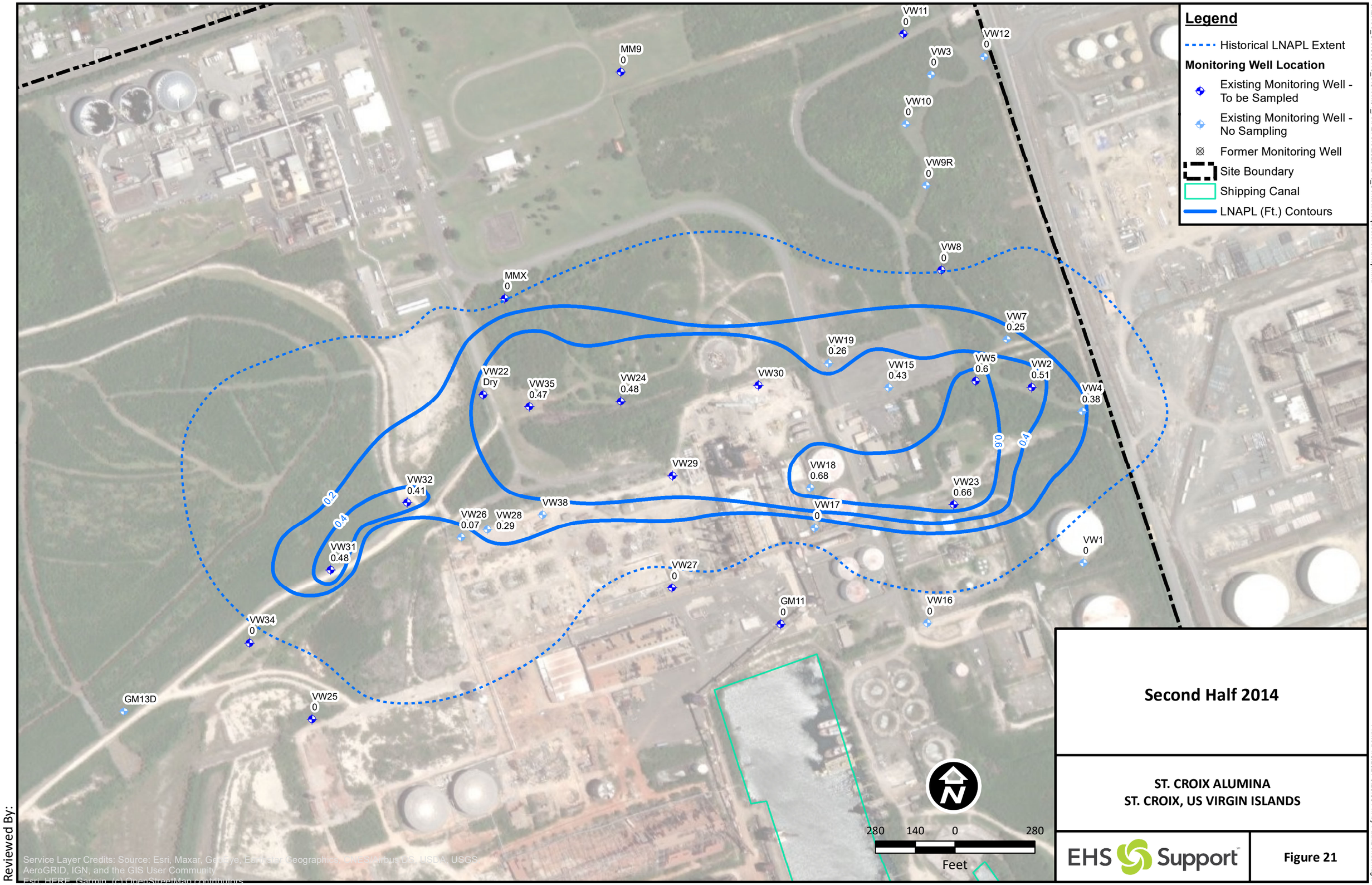
Legend
Historical LNAPL Extent
Monitoring Well Location
Existing Monitoring Well - To be Sampled
Existing Monitoring Well - No Sampling
Former Monitoring Well
Site Boundary
Shipping Canal
LNAPL (Ft.) Contours
VW11 0
VW12 0
MM9 0
VW3 0
VW10 0
VW9R 0
VW8 0
MMX 0
VW7 0.25
VW19 0.26
VW5 0.6
VW2 0.51
VW15 0.43
VW4 0.38
VW22 Dry
VW35 0.47
VW24 0.48
VW30
VW29
VW18 0.68
VW23 0.66
VW32 0.41
VW38
VW17 0
VW26 0.07
VW28 0.29
VW31 0.48
VW1 0
VW27 0
GM11 0
VW16 0
VW34 0
GM13D
VW25 0
0.2
0.4
0.6
0.4
280 140 0 280
Feet
Second Half 2014
ST. CROIX ALUMINA
ST. CROIX, US VIRGIN ISLANDS
EHS Support
Figure 21
Reviewed By:
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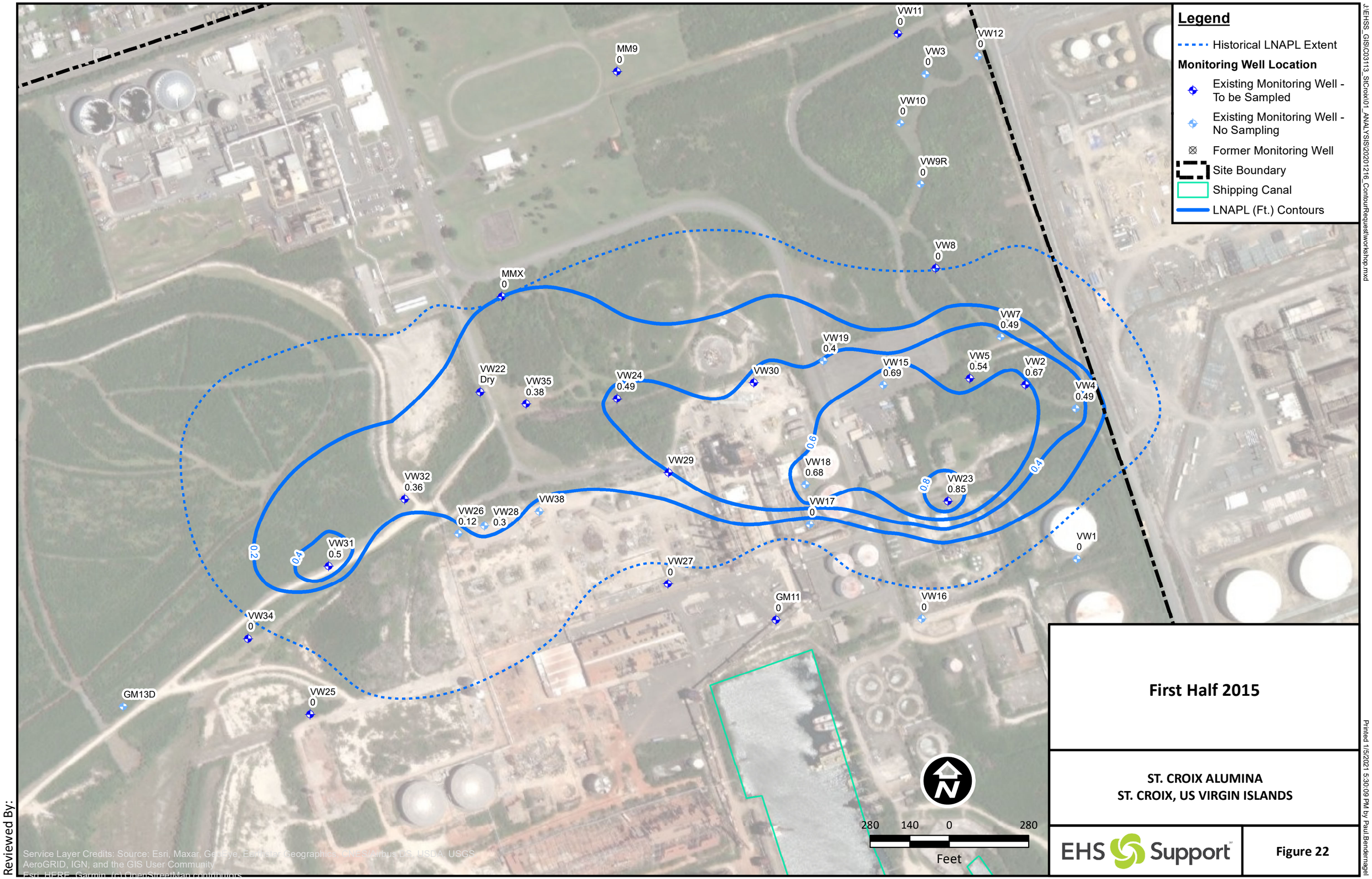

First Half 2015

ST. CROIX ALUMINA
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EHS Support

Figure 22

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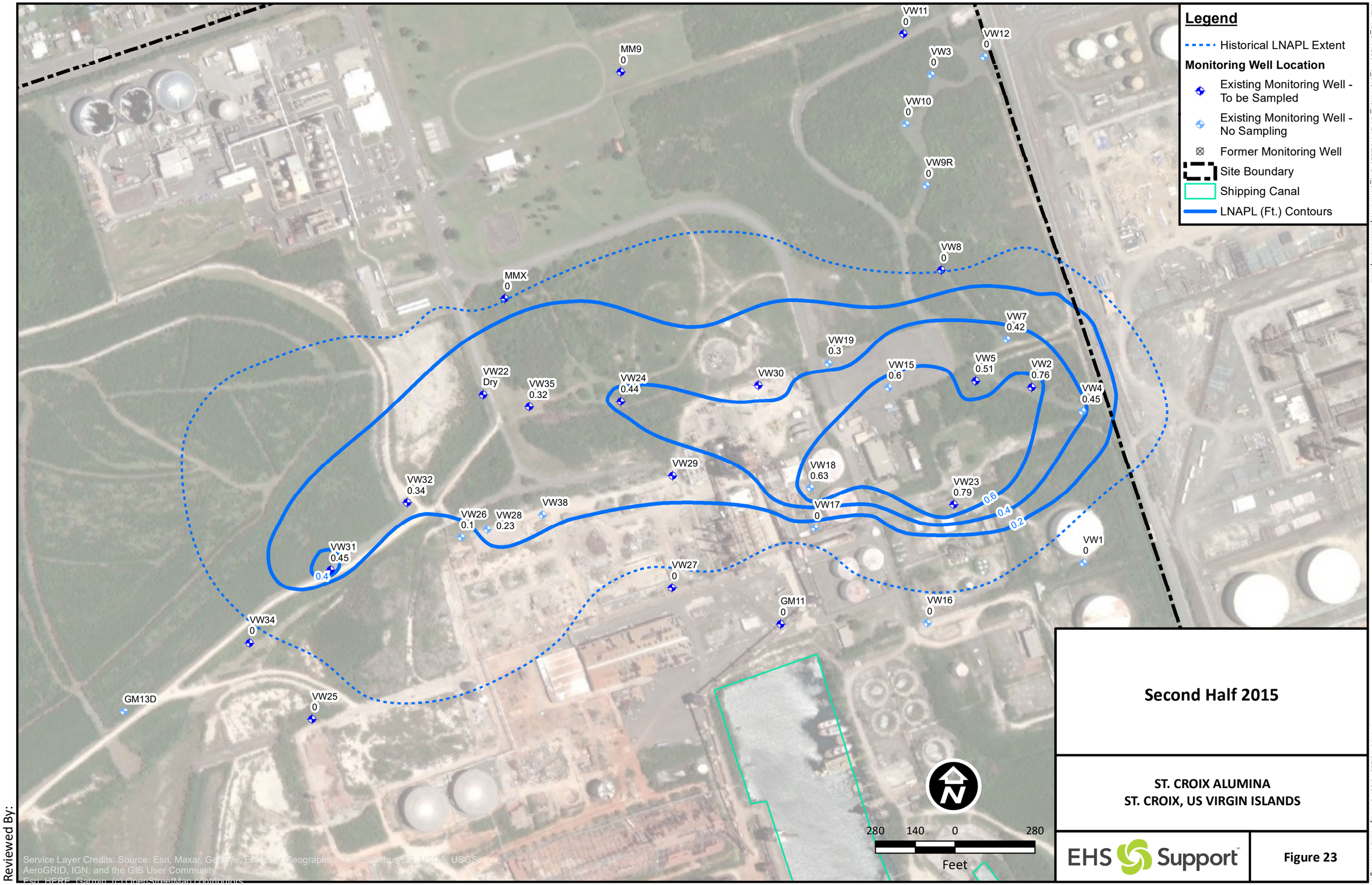

Second Half 2015

ST. CROIX ALUMINA
ST. CROIX, US VIRGIN ISLANDS

EHS Support

Figure 23

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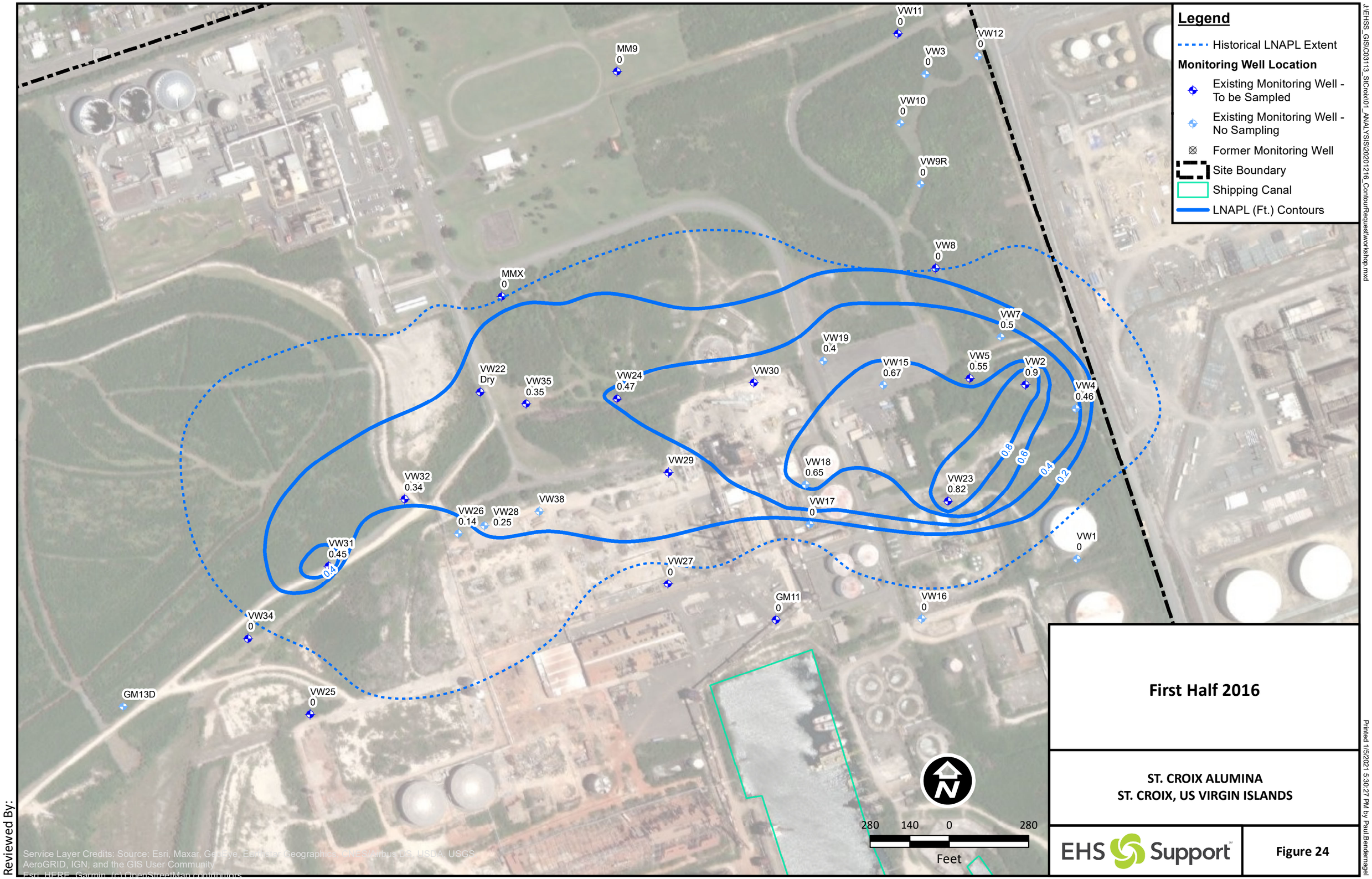

First Half 2016

ST. CROIX ALUMINA
ST. CROIX, US VIRGIN ISLANDS

EHS Support

Figure 24

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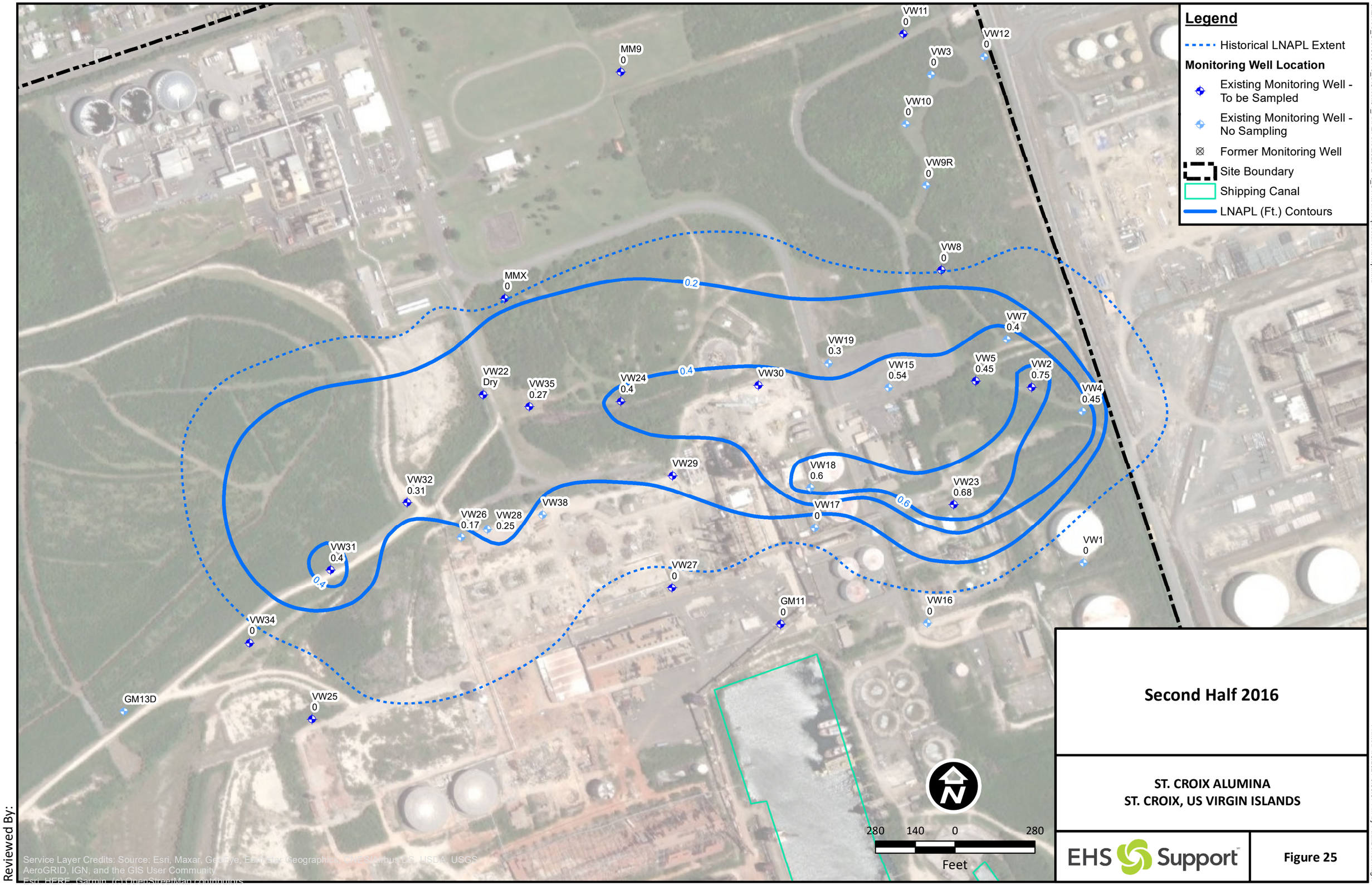
Legend
Historical LNAPL Extent
Monitoring Well Location
Existing Monitoring Well - To be Sampled
Existing Monitoring Well - No Sampling
Former Monitoring Well
Site Boundary
Shipping Canal
LNAPL (Ft.) Contours
VW11 0
VW12 0
MM9 0
VW3 0
VW10 0
VW9R 0
VW8 0
MMX 0
0.2
VW7 0.4
VW19 0.3
VW15 0.54
VW5 0.45
VW2 0.75
VW4 0.45
VW22 Dry
VW35 0.27
VW24 0.4
0.4
VW30
VW29
VW18 0.6
VW23 0.68
VW32 0.31
VW38
VW26 0.17
VW28 0.25
VW17 0
0.6
VW1 0
VW31 0.4
0.4
VW27 0
GM11 0
VW16 0
VW34 0
GM13D
VW25 0
280 140 0 280
Feet
Second Half 2016
ST. CROIX ALUMINA
ST. CROIX, US VIRGIN ISLANDS
EHS Support
Figure 25
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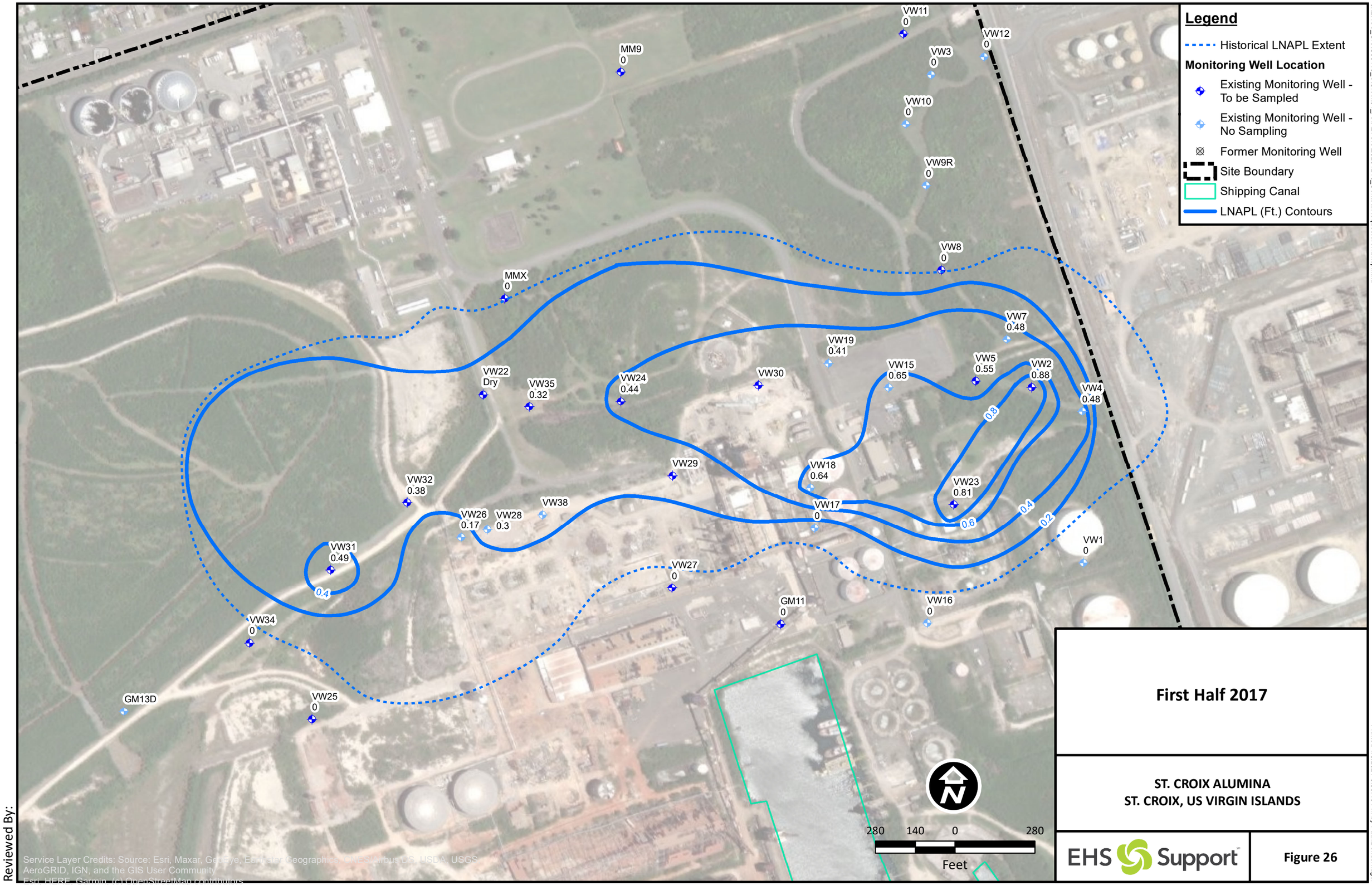

First Half 2017

ST. CROIX ALUMINA
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EHS Support

Figure 26

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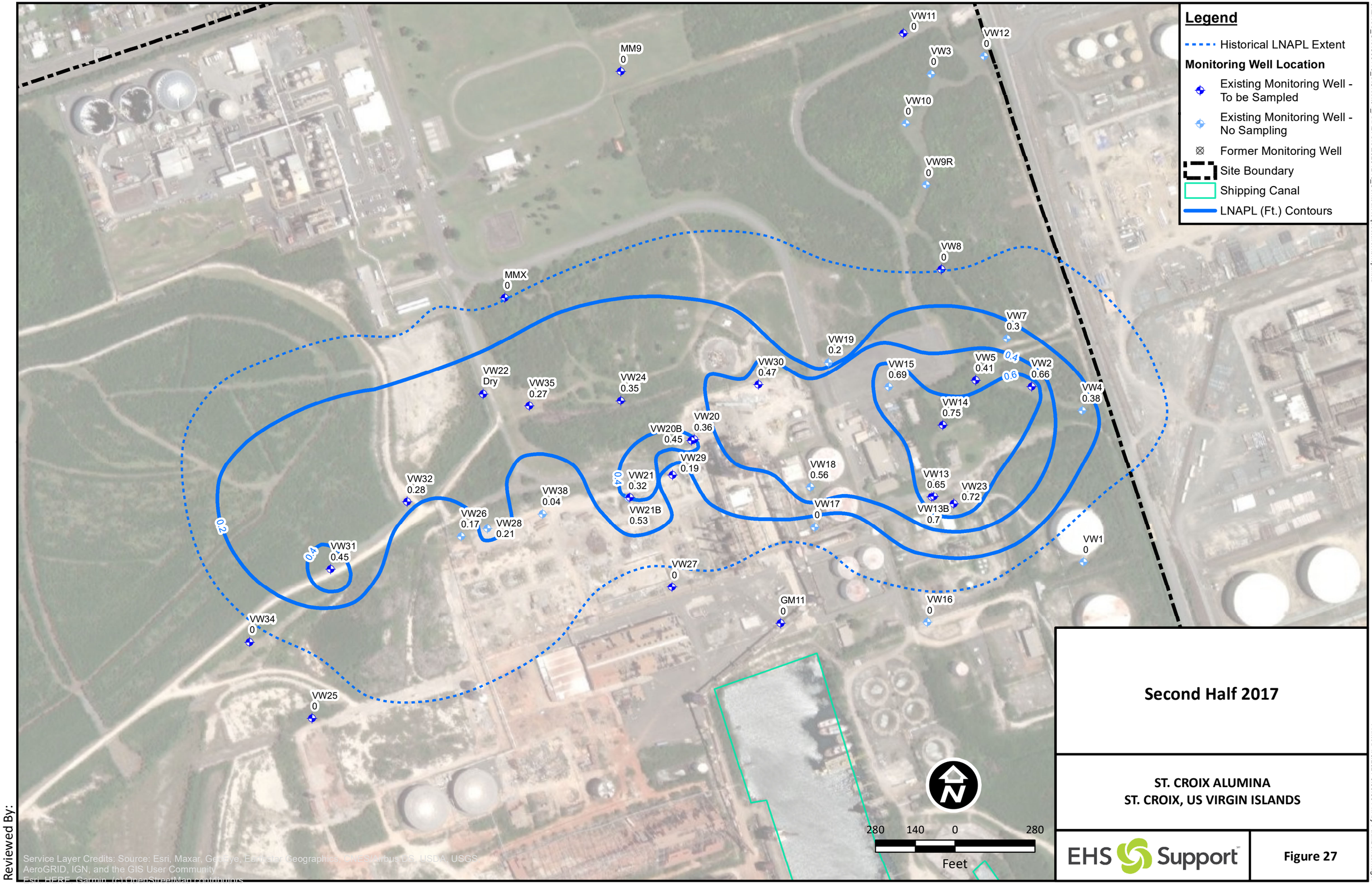

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Second Half 2017

ST. CROIX ALUMINA
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EHS Support

Figure 27

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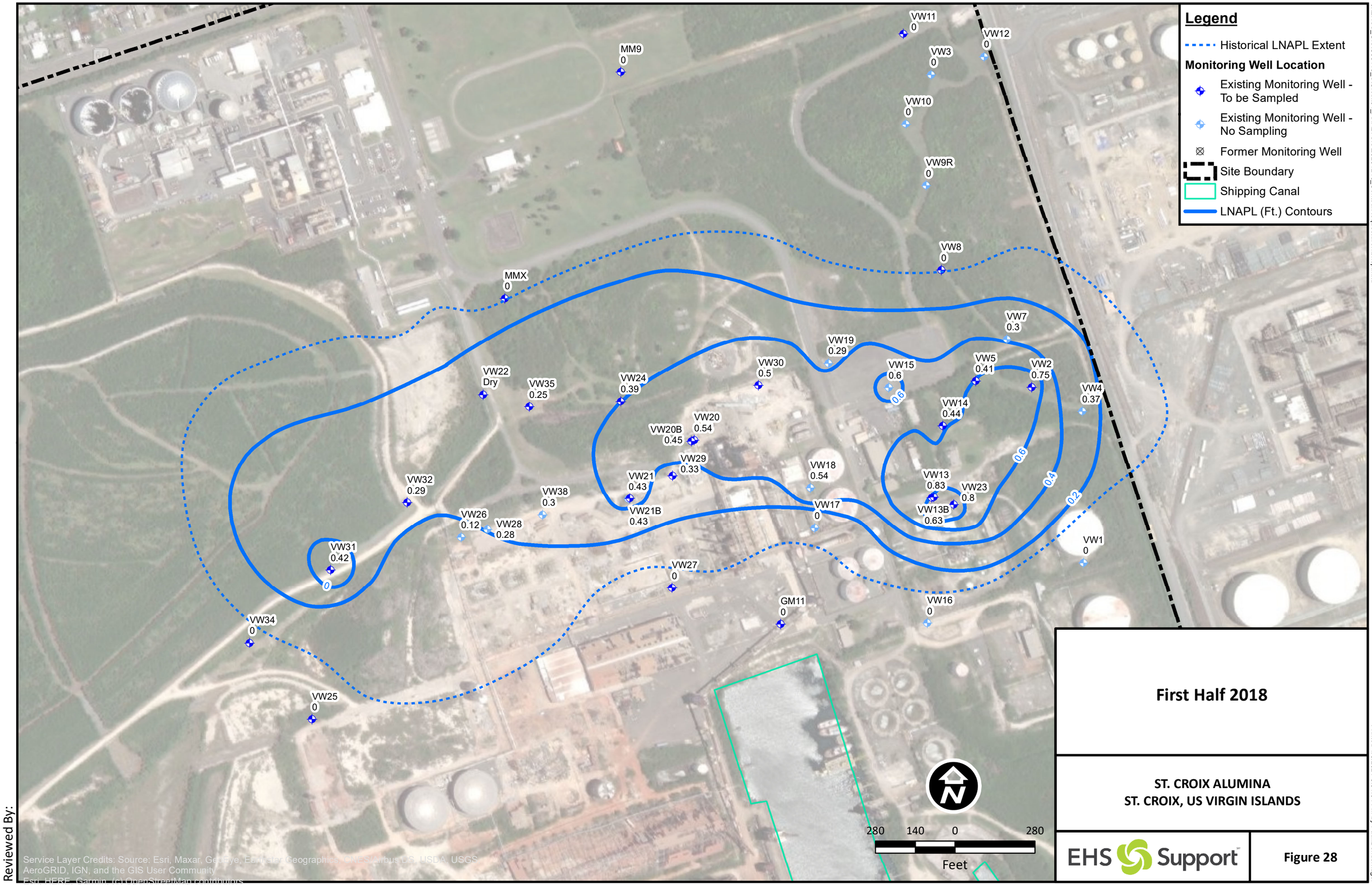

First Half 2018

ST. CROIX ALUMINA
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EHS Support

Figure 28

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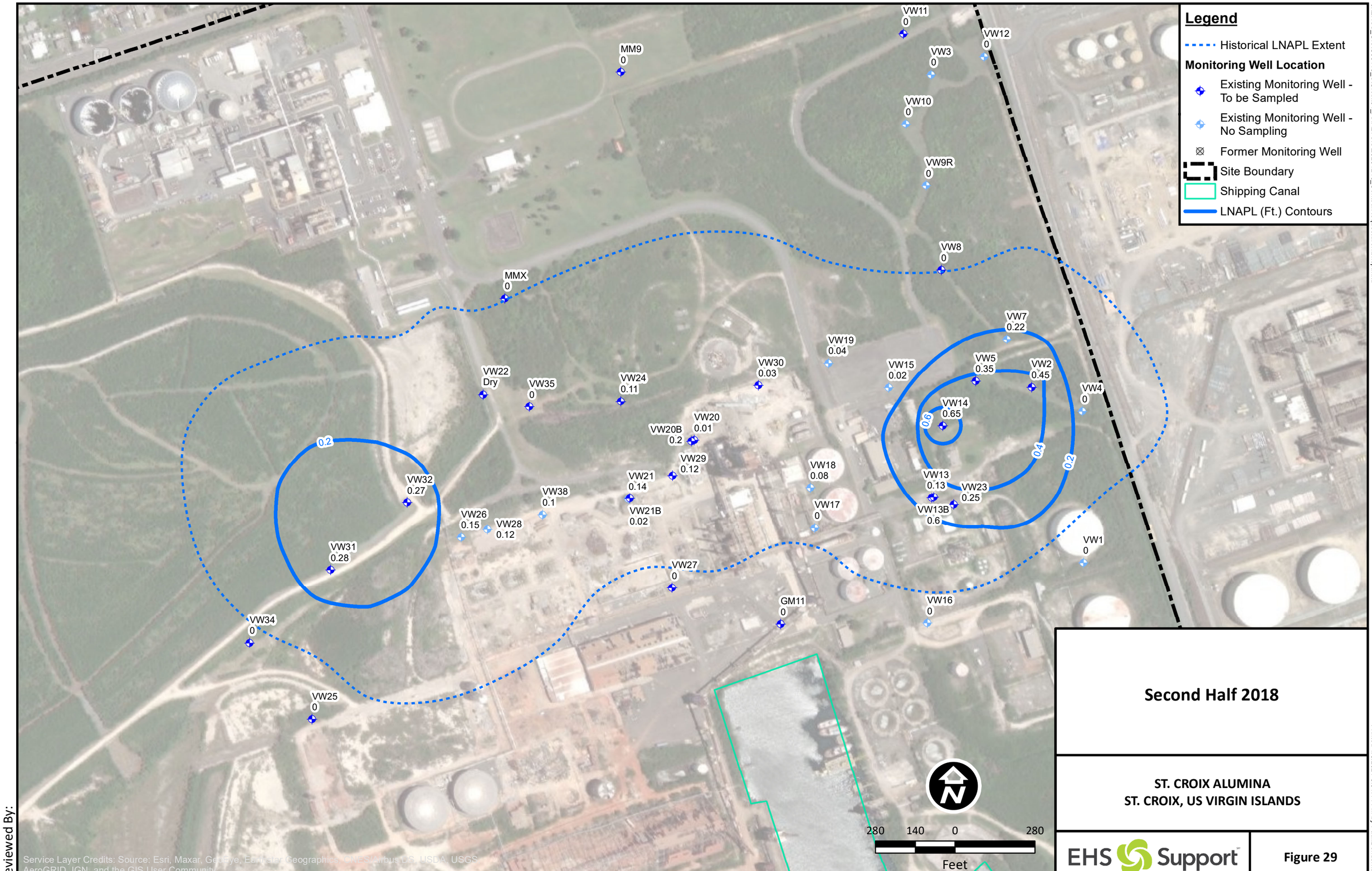
Legend
Historical LNAPL Extent
Monitoring Well Location
Existing Monitoring Well - To be Sampled
Existing Monitoring Well - No Sampling
Former Monitoring Well
Site Boundary
Shipping Canal
LNAPL (Ft.) Contours
MM9 0
VW11 0
VW12 0
VW3 0
VW10 0
VW9R 0
VW8 0
MMX 0
VW7 0.22
VW19 0.04
VW30 0.03
VW15 0.02
VW5 0.35
VW2 0.45
VW4 0
VW22 Dry
VW35 0
VW24 0.11
VW14 0.65
VW20 0.01
VW20B 0.2
VW29 0.12
VW18 0.08
VW13 0.13
VW23 0.25
VW13B 0.6
VW21 0.14
VW38 0.1
VW17 0
VW21B 0.02
VW26 0.15
VW28 0.12
VW32 0.27
VW31 0.28
VW1 0
VW27 0
GM11 0
VW16 0
VW34 0
VW25 0
0.2
0.4
0.6
280 140 0 280
Feet
Second Half 2018
ST. CROIX ALUMINA
ST. CROIX, US VIRGIN ISLANDS
EHS Support
Figure 29
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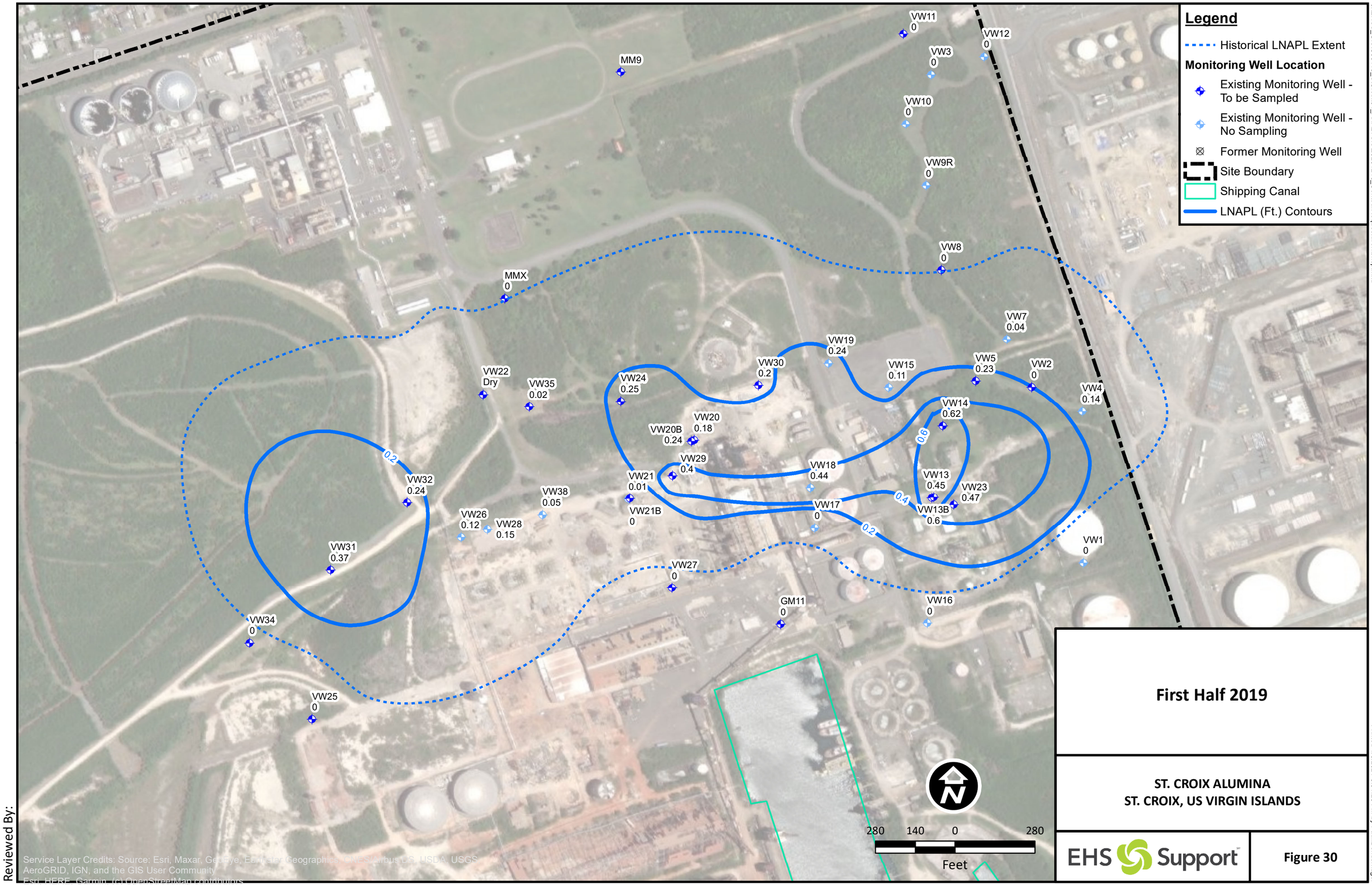
Legend
Historical LNAPL Extent
Monitoring Well Location
Existing Monitoring Well - To be Sampled
Existing Monitoring Well - No Sampling
Former Monitoring Well
Site Boundary
Shipping Canal
LNAPL (Ft.) Contours
VW11 0
VW12 0
VW3 0
MM9
VW10 0
VW9R 0
VW8 0
MMX 0
VW7 0.04
VW19 0.24
VW30 0.2
VW15 0.11
VW5 0.23
VW2 0
VW4 0.14
VW22 Dry
VW35 0.02
VW24 0.25
VW14 0.62
VW20 0.18
VW20B 0.24
VW29 0.4
VW18 0.44
VW21 0.01
VW13 0.45
VW23 0.47
VW38 0.05
VW21B 0
VW17 0
VW13B 0.6
VW26 0.12
VW28 0.15
VW32 0.24
VW31 0.37
VW1 0
VW27 0
GM11 0
VW16 0
VW34 0
VW25 0
0.2
0.4
0.6
280 140 0 280
Feet
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First Half 2019
ST. CROIX ALUMINA
ST. CROIX, US VIRGIN ISLANDS
EHS Support
Figure 30
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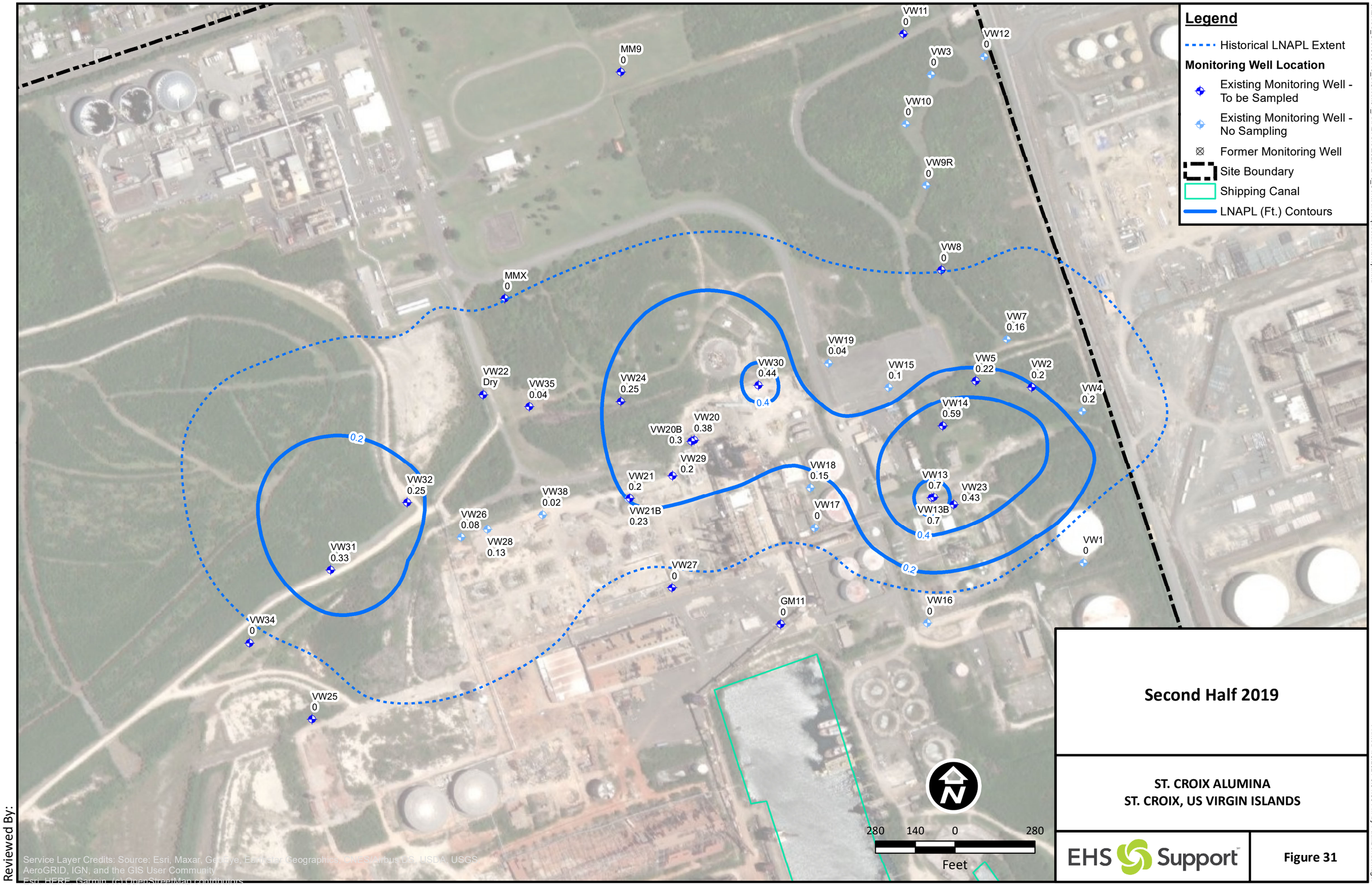
Legend
Historical LNAPL Extent
Monitoring Well Location
Existing Monitoring Well - To be Sampled
Existing Monitoring Well - No Sampling
Former Monitoring Well
Site Boundary
Shipping Canal
LNAPL (Ft.) Contours
VW11 0
VW12 0
MM9 0
VW3 0
VW10 0
VW9R 0
VW8 0
MMX 0
VW7 0.16
VW19 0.04
VW30 0.44
VW15 0.1
VW5 0.22
VW2 0.2
VW4 0.2
VW22 Dry
VW35 0.04
VW24 0.25
VW14 0.59
VW20 0.38
VW20B 0.3
VW29 0.2
VW18 0.15
VW13 0.7
VW23 0.43
VW13B 0.7
VW21 0.2
VW21B 0.23
VW17 0
VW38 0.02
VW32 0.25
VW26 0.08
VW28 0.13
VW31 0.33
VW1 0
VW27 0
GM11 0
VW16 0
VW34 0
VW25 0
0.2
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280 140 0 280
Feet
Second Half 2019
ST. CROIX ALUMINA
ST. CROIX, US VIRGIN ISLANDS
EHS Support
Figure 31
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Appendix C Standard Operating Procedures (SOPs)

SOP-02 Site Visit and Reconnaissance

Purpose

This SOP was developed to promote uniformity in investigating and evaluating potential health and safety hazards at sites. A site visit generally refers to inspection activities of the subject property. Site reconnaissance expands the site visit to include observations to identifying potential health and safety hazards, and in some cases recognized environmental conditions.

This SOP does not attempt to address all circumstances that could be encountered during a site visit or reconnaissance but can provide a baseline for recognition. It should be noted that seemingly safe sites or situations may still present life-threatening conditions. Personnel conducting site visits or site reconnaissance should be alert and aware of surroundings and conditions at all times.

Relevant EHS Support SOPs

- SOP-04 Field Documentation

Required Materials

- Field logbook and field documentation
- Site maps, site layouts, site plans
- Health and Safety Plan
- Appropriate personal protective equipment (PPE)
- Black waterproof and/or indelible ink pens
- Camera
- Monitoring or sampling equipment to evaluate hazards, as necessary.

1 Site Visit and Reconnaissance Procedure

1.1 Site Visit Preparation

A properly conducted site visit or reconnaissance should include procurement of available site details in preparation of a site visit as follows:

1. Obtain information about the site (current and historical).
2. Obtain information, if able, about hazardous materials or waste handling at the site. The hazardous material and waste handling information can be used to assess if any or all of the site conditions described below may require additional monitoring.
3. Obtain site-specific details to the on-site health and safety program and requirements.
4. Obtain site-specific information (current and historical), if able, about site practices and processes of hazards or potential hazards to the best extent possible and able. Considerations may include (but is not limited to):
    a. Facility occupancy (e.g., abandoned, operational)
    b. Locations that may require special training due to:
        - Oxygen-deficient atmospheres
        - Explosive atmospheric conditions
        - Potential for chemical vapors
        - Unexploded ordnance
        - Radioactivity
        - Confined space
        - Presence of asbestos or lead.
    c. Physical hazards:
        - Electrical hazards (down or exposed power lines)
        - Unsafe structures or deteriorated buildings, tanks, supports, or beams that are in the process of collapsing (or based on physical evidence may collapse at any time)
        - Pits (open or closed)
        - Trenches and sumps
        - Buried tanks or structures
        - Any type of elevated, surface, or subsurface structure that may fall, cause an employee to trip or fall, or cause an employee to fall into it
        - Hazards of concern with heavy equipment (backhoe, drill rig, etc.)
        - Biological hazards (plants, insects, snakes)
        - Noise hazards
        - Asbestos, lead, or other material that creates an exposure hazard
        - Weather (lightning, heat, and cold stress)
        - Traffic, including trains or facility-vehicles

5. Prepare a Health and Safety Plan (HASP) that satisfies the requirements of the Occupational Safety and Health Administration (OSHA) as defined in the Code of Federal Regulations 29 Code of Federal Regulations (CFR) 1910.120. Evaluation of health and safety hazards in the HASP should consist of reviewing and summarizing existing site data; preparing a site HASP; and use of monitoring or sampling equipment as necessary for the site visit, reconnaissance, or investigation.
6. Worker safety will be evaluated by the Project Manager and the EHS Support Health and Safety Manager prior to mobilization.
7. The HASP will be reviewed and signed by the EHS Support Health and Safety Manager. Team members must comply with the site HASP.

1.2 Site Walk Inspection

The site visual inspection will be conducted by doing a walkover of the entire site. Under some conditions (e.g., large facility, abandoned facility, unsafe site conditions), it may be required to have two or more persons conducting the reconnaissance. Attention should be given to potential health and safety hazards or hazard indicators associated with the site walk or the inspection. (Note: A hazard indicator may not represent a hazard directly but may indicate an activity has occurred in relation to a potential hazard. For example, an installed soil vapor extraction system may not be a hazard, but represents a condition exists in the soil that requires or required attention.)

During the site visit or reconnaissance, field observations should be given, but are not limited to:

- Physical features of man-made structures (e.g., locations and dimensions of buildings)
- Surface features (e.g., ditches, pits)
- Current site and facility use
- Building use (e.g., office, manufacturing, residential, including buildings having basements)
- Surrounding area use (e.g., residential, industrial, vacant)
- Facility or site features, including:
  - Site boundaries and fencing
  - Types, location, and layout of utilities
  - Presence and type of bulk storage vessels (underground or above ground)
  - Confined space locations
  - Water features (e.g., streams, ponds, impoundments)
  - Paved, non-paved, diked, or improved locations
  - Liquid and/or solid waste disposal practices
  - Location(s) and content(s) of managed or unmanaged waste
  - Location of drum or container storage areas
  - Waste water or liquid discharge types and locations
  - Location of outfalls, if applicable
  - Secondary containment
  - Type and location of treatment facilities (i.e., waste water treatment, disposal units)
  - Points of interest that may indicate the presence of potentially hazardous conditions (e.g., oxygen deficiency, explosive atmospheres, high vapor or radioactivity levels, pipelines, septic fields, leachate fields, oil/water separators, or other physical hazards)

  - Locations and types of tanks, floor drains, stained soil, or stressed vegetation
  - Pad or pole-mounted transformers that could polychlorinated biphenyls (PCBs)
  - Buildings or locations that could contain PCBs, asbestos, or lead
  - Dust conditions
  - Air emissions and control measures (e.g., production from spray painting, mechanical exhaust, burning fuel)
  - Presence of monitoring wells
  - Presence of historical or on-going remedial activities (e.g., groundwater extraction systems, soil vapor extraction systems, investigative., former boring locations)
- Other potential hazards identified by the field team (e.g., biological, noise, etc.)
- Photographs will be taken to document the site visit or reconnaissance. A photographic log will be maintained. Refer to SOP-04 Field Documentation for guidelines to photographic collection and maintaining a photographic log.
- Any site-specific documentation (e.g., drawings, MSDS, site processes) will be collected.
- Sketches or marked copies of the site layout should be maintained in the field logbook or field documentation.
- Record the site visit or reconnaissance observations in the field logbook or field documentation.

2 Records

Field logbook and field documentation will be completed in accordance with SOP-04: Field Documentation. Field documentation will be kept in the project file and may include:

- Field logbook or field documentation
- Site layout maps
- Sketches
- Photographs
- Obtained site-specific documents (e.g., tank inventory, utility drawings, reports, material safety data sheets).

SOP-04 Field Documentation

Purpose

The purpose of this SOP is to provide guidance to ensure that field documentation for any field activity is correct, complete, and adequate. Logbooks and field documentation forms are used for keeping a record of field activities and identifying, locating, labeling, and tracking samples. A field logbook should document any deviations from the applicable work plan, quality assurance project plans, and health and safety plans. A complete and accurate field logbook and field documentation aids in maintaining good quality control. All field records must be factual, objective, and legible.

Relevant EHS Support SOPs

- SOP-05 Sample Management and Shipping
- SOP-07 Investigation Derived Waste
- SOP-08 Field Equipment Operation and Calibration
- SOP-09 Equipment Decontamination
- SOP-21 Soil Sample Collection Methods
- SOP-22 Soil Sampling for Chemical Analysis
- SOP-23 Soil Sampling for Physical Analysis
- SOP-24 Hand Auger
- SOP-25 Drilling Methods using Direct Push Technology
- SOP-26 Drilling Methods using Hollow Stem Auger
- SOP-27 Drilling Methods using Sonic
- SOP-28 Drilling Methods using Rotary (Air, Mud, Water)
- SOP-29 Rock Coring
- SOP-30 Field Classification and Description of Soil
- SOP-31 Field Classification and Description of Rock
- SOP-32 Borehole and Well Abandonment
- SOP-40 Groundwater Monitoring Well Design and Installation
- SOP-42 Groundwater Monitoring Well Development
- SOP-43 Groundwater Sampling Using Low Flow Sampling
- SOP-44 Groundwater Sampling Using Volume Purge Techniques

Attachments

- Attachment A Examples of Chain of Custody
  - Environmental/Chemical
  - Physical

Required Materials

- Project work plan or instruction
- Field logbook and field documentation
- Black waterproof and/or indelible ink pens

1 Field Documentation

Field documentation serves as the primary record of collected data and activities used to support a given project. Subject to the requirements of the applicable work plan, documentation may include field logbooks, field documentation forms, or reports for the various field activities. Minimum expectations for field documentation are as follows:

- Field documentation must be accurate, legible, and written in indelible ink.
- Field documentation will be recorded and maintained on a daily basis as the work progresses, and should contain enough information to allow the activities to be reconstructed so that the work conducted and timeline are understood.
- The date, project name, and number of pages (e.g., 1/1, 2/3) will be written at the top of each page of the field document.
- Mistakes will be crossed out with one line, dated, and initialed. Any corrections/additions made to documentation will be dated and initialed.
- Materials that obliterate the original information (e.g., erasures, correction fluids, mark-out tapes) are prohibited.
- Skipped pages or blank sections at the end of a page in a field logbook should be crossed out with an "X" covering the entire page or blank section, dated, and initialed.
- The responsible field team member should sign and log the date at the bottom of each page in the field logbook and after the last entry for the day.
- Field logbooks and/or field documentation (e.g., boring logs, sampling forms) will contain all information of the field investigation. Use of approved field documentation forms for recording field data are at the discretion of the Project Manager.
- Original field documentation forms should have the date, project name, technician's name, and project activity at the top of the field document.
- The responsible field team member will sign and log the date at the bottom of each page of the field documentation form.
- Photographic documentation descriptions will be included in the field logbook during field investigations.
- All field documentation will be included with the project files. The location of the electronic project files will be confirmed with the Project Manager. The original hard copy field documentation will be scanned as an electronic copy and then placed in the project file folder, or sent to the Project Manager. The field logbook will be kept with the project file folder, Project Manager, or responsible field team leader.

1.1 Field Logbooks

A field logbook serves as the primary record for a field investigation. A field logbook will be maintained for every field investigation or operation undertaken during an investigation. The field logbook should contain detailed records of the field activities in as much detail as possible so personnel can accurately reconstruct the activities and events that have taken place during field assignments. Field logbooks are considered accountable documents in legal proceedings and may be subject to review. Therefore, the entries in the logbook must be accurate, detailed, and reflect the importance of the field events.

Field logbooks, generally in a 4⅝ by 7¼ inches or 8½ by 11 inches in format, should be bound with water resistant and acid-proof covers and have preprinted lines and wide columns. An indelible ink pen should be used to document the activities in the field logbook.

Various field tasks require observations pertaining to that task/activity. Documentation that should be provided in the field logbook for various field tasks is outlined below. The information may or may not be inclusive of the task performed, but is intended to provide an overview of the type of information and level of detail required for accurate and accountable record keeping.

1.1.1 General Field Logbook Requirements

All field personnel or field sampling teams are responsible for completing and providing a field logbook. Information that should generally be recorded in the field log includes

- Project and site name
- Site location (e.g. city and state)
- Health and safety activities
  - Record of tailgate meetings, topics discussed, attendees, company name of the attendees
  - Site contaminants of concern and/or other relevant hazards and steps to avoid, mitigate or remove hazards
  - Required personal protective equipment and decontamination procedures
  - Utility locate (one-call locate service, sketch, photographs), if applicable
- Time (24-hour clock)
- Personnel and subcontractors present for work activity and time spent on job site
- Weather, or changes in weather during the day
- Field operations and personnel assigned to the activities
- A documentary of the timeline detailing daily activities and operations, and summary of daily operations
- Problems encountered and corrective actions
- Quality control activities: e.g., decontamination procedures, quality assurance/quality control (QA/QC) samples taken, calibration of field equipment
- Deviations from the project work plan
- Visitors to the work area/site (date, time, name, company and contact information)
- Records of communications: discussions of job-related activities with the client, subcontractor, field team members, project manager, and/or visitors
- Records or documentation of equipment, supplies, or materials received or shipped invoices; copies of waste manifests or bill of lading, shipping information
- Field observations for inspections, monitoring, sampling, etc.
- Description and photographic log

1.1.2 Calibration Logs

Calibration will be conducted in accordance with SOP-08 Field Equipment Operation and Calibration. Calibration documentation logs are included as attachments to SOP-08. The following information should be provided in the field logbook or approved field documentation as applicable to the work:

- Calibration date and time for all equipment used for the project
- Type of equipment (e.g., photoionization detector (PID), pH meter, dust monitor, noise dosimeter, groundwater monitoring equipment) Serial number and model of equipment calibrated
- Calibration standard (gas or standard solution),concentration, and expiration
- Equipment response to calibration standard
- Adjustments made and recalibration
- Person performing calibration
- Manufacturer/vendor calibration sheet (for most recent maintenance calibration)

1.1.3 Drilling Log

Drilling activities will be conducted in accordance with subsurface borehole advancement SOPs (SOP-24 to SOP-29), SOP-21 Soil Sample Collection Methods, various media-specific sampling SOPs, SOP-40 Well Design/Construction, SOP-09 Equipment Decontamination, and/or SOP-32 Borehole and Well Abandonment. The following information should be provided in the field logbook or applicable field documentation:

- Borehole, well, or sample location (sketch)
- Borehole, well, or sample location identification
- Drilling activities
    - Name of drilling company and driller
    - Field geologist, hydrogeologist, engineer, or appropriate scientist logging the soil/bedrock
    - Time and date of drilling, stoppage, completion, and/or backfilling
    - Drilling method and equipment used (including soil sampler type and diameter)
    - Borehole and drill casing diameter
    - Reference elevation for depth measurements
    - Monitoring readings (e.g., PID readings)
    - Depth interval and recovery
    - Geologic information
    - Total drilling depth.
- Encountered obstructions or refusal
- Well construction information (e.g., materials used, total depth, screen interval, surface completion)
- Method of abandonment
- Type and amount of material used to abandon boreholes
- Sampling performed (soil, groundwater, waste, etc.)
    - Date and time of sample collection
    - Sample type (media) and method (e.g., grab, composite)
    - Sample interval

  - Number of samples collected, sample IDs/nomenclature used
  - Quality control samples collected (e.g., duplicates, equipment blanks)
  - Analyses to be performed on collected samples.
- Equipment decontamination procedures
- Investigation derived waste (IDW) containerization (number of drums, roll off-bins, etc.)
- Disposal of IDW (shipping/transport records or temporary storage details)
- Field observations
- Problems encountered and corrective action
- Signature and date of party generating log

1.1.4 Geologic Log

The preparation of geologic logs is the responsibility of the field geologist(s). A detailed description of unconsolidated soil logging is provided in SOP-30 Field Classification and Description of Soil and SOP-31 Field Classification and Description of Rock. A drilling log template is provided as an attachment to SOP-30 and SOP-31. The field logbook or approved field documentation forms for geologic logging should include:

- Type and volume of drilling fluids (e.g., mud, water, etc.)
- Depth, volume, and rate of drilling fluid loss, if applicable
- Blow counts, if applicable
- Geologic/Lithologic description of unconsolidated materials–Color, Unified Soil Classifications System (USCS) description, penetration resistance (consistency or density), moisture content, grain size information, minor lithologic information, miscellaneous information (e.g., odor, fractures, visible contamination, etc.)
- Geologic/Rock description of consolidated materials—Color, rock type, relative hardness, density, texture, weathering, bedding, structures (e.g., fractures, joints, bedding, etc.), minor lithologic information, miscellaneous information (e.g., presence of odor, visible contamination, etc.)
- Depth of stratigraphic/lithologic changes
- Depth to groundwater (first encountered, at completion, stabilized, absence of groundwater)
- Product description, if present (depth, thickness, visual and odor characteristics)
- Depth, type, and volume of grouting, grout mixes, sealing materials
- Field observations
- Problems encountered and corrective action
- Signature and date at the bottom of each page

1.1.5 Well Construction Log

The preparation of well construction diagrams is the responsibility of the field leader, geologist, technician, or engineer. Well construction is further discussed in the SOP-40 Groundwater Monitoring Well Design and Installation. A well construction form is provided as an attachment to SOP-40. The field logbook or approved field documentation form for well construction would include:

- Drilling and well installation dates
- Type, length, and diameter of well screening and casing

- Well screen perforation size
- Well screen and casing depths
- Depth, type, and volume of grouting, grouting mixes, and sealing materials
- Other construction details (e.g., depth and type of sumps, centralizers, multichannel tubing, permanent pumps, etc.)
- Surface construction details (e.g., flush mount, protective covers, concrete pads, weep hole)
- Surface elevation and reference elevation
- Problems encountered and corrective action
- Signature and date at the bottom of each page

1.1.6 Well Development and Groundwater Sampling Log

These topics are further discussed in SOP-42 Well Development, SOP-43 Groundwater Sampling Using Low Flow, and/or SOP-44 Groundwater Sampling Using Volume Purge Techniques. Respective field documentation forms are provided as attachments in each SOP. Basic information that is recorded in the field logbook or on approved field documentation forms for well development and groundwater sampling include:

- Calibration records (refer to Calibration Log documentation above)
- Date and time of well development or groundwater sampling
- Borehole, well, or sample location identification
- Water level and total depth of well
- Depth to product and product thickness, if present
- Reference elevation, if required
- Additional well information (e.g., casing diameter, filter pack thickness)
- Volume of water to be purged, if applicable
- Type of purging and sampling equipment
- Consistent time interval measurements of groundwater field parameters (e.g., pH, turbidity, conductivity, temperature, depth to water, etc.)
- Groundwater sampling details
  - Sample identification
  - Date and time of sample collection
  - Sample interval, if required
  - Quality control samples (e.g., duplicates, equipment blanks), if collected
  - Number of samples collected
  - Analyses to be performed on collected samples.
- Equipment decontamination procedures
- IDW containerization (volume, placement)
- Disposal of IDW (shipping/transport records or temporary storage details)
- Field observations
- Problems encountered and corrective action
- Signature and date at the bottom of each page.

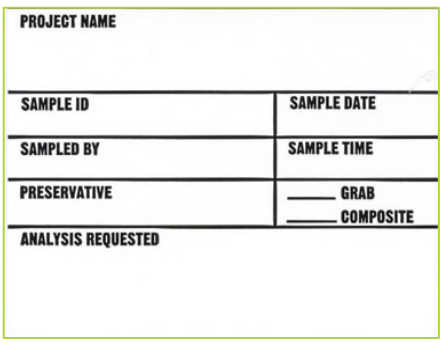
1.2 Documentation of Sampling Activities

Field documentation also includes sample labels, sample seals, chain of custody (COC) records, and the shipping airbill. Management of samples from collection to shipment to laboratory is further discussed in SOP-05 Sample Management and Shipping.

1.2.1 Sample Labels

Sample identification should be completed in accordance with the project work plan or sampling plan. A sample label will be completed using waterproof indelible marker. A sample label will be affixed to all sample containers and contain the:

- Sample identification
- Project location, project name, and/or project number
- Type of sample (grab or composite)
- Type of preservative, if applicable
- Date and time of collection
- Analytical method
- Initials of sampling personnel.



PROJECT NAME	
SAMPLE ID	SAMPLE DATE
SAMPLED BY	SAMPLE TIME
PRESERVATIVE	_____ GRAB _____ COMPOSITE
ANALYSIS REQUESTED	

Figure 1 Example of a Sample Label

1.2.2 Custody Seals

Custody seals consist of an initialed/signed and dated security tape covered with clear packing tape. The custody seal is to provide a line of evidence that sample coolers or containers have not been tampered since the cooler was packed and sealed. Custody seals will be placed on coolers prior to the sampling team's release to a second or third party (e.g., shipment to the laboratory).

Figure 2 Example of a Custody Seal

1.2.3 Chain-of-Custody Records

A COC record is the legal record that tracks the possession and handling of samples from the time of field collection through laboratory analysis and provides information on the sample condition and integrity as received by the laboratory. A sample is considered in custody if it meets any of the following criteria:

- Is in an individual's possession
- Is in view after being in an individual's physical possession
- Is locked or sealed so that no one can tamper with it after it has been in an individual's physical custody
- Is in a secured area that is restricted to authorized personnel.

The COC is documented through a record that lists each sample and the individuals responsible for sample collection, shipment, and receipt. Information recorded on the COC includes:

- Project name and project number
- Time and date of sample collection
- Sample identification number
- Sample matrix
- Sampler's signature
- Required analysis
- Number and type of containers and preservatives
- Other additional notations (e.g., sheen, odor, turnaround time, regulatory standards for analysis).

A copy of the COC record will be retained by the sampler prior to release to a second or third party. Prior to release the COC record will be properly signed, dated, and checked for completeness. Examples of COCs for chemical testing and physical testing are included as **Attachment A**.

1.2.4 Shipping Airbills

Samples shipped from the field to the laboratory or vendor via a commercial carrier (e.g., Federal Express) may require an airbill or receipt. Upon completion of the field sampling event, the sampling team or field leader will be responsible for submitting the sender's copy of the shipping airbills to be copied. While airbills may differ, the general shipping information includes:

- The date of shipment:
- The sender's mailing address and phone number
- The recipient's mailing address and phone number
- The EHS support shipping number
- The project number
- Shipping requirements.

A copy of the airbill or tracking number will be kept to verify sample shipment arrives as scheduled to the appropriate vendor or laboratory.

1.3 Photographs

Photographs provide the most accurate demonstration of the field worker's observations. Photographs can be significant to the project team during future inspections, data evaluation, report preparation, informal meetings, and hearings. Photographs should be taken with a camera-lens system having a perspective similar to that afforded by the naked eye. Telephoto or wide-angle shots cannot be used in enforcement proceedings. Video coverage of a sampling episode can be equally (or even more) valuable than photographs because the coverage can be used to prove that the investigation or sampling process was conducted properly as well as where they were taken.

A photograph must be documented by the photographer in the field logbook if it is to be a valid representation of an existing situation. The following information will be recorded in the field logbook for photographs taken:

- Site name and location
- Photographer
- Sequential photographic number
- Date and time photograph taken
- Directional reference or GPS coordinate of the photograph
- Subject of photographs and description.

Table 1 Example Format for Photographic Log

Site Name and Location:
Photographer:

Photo #	Date	Time	Photo Direction	Location/GPS Location	Subject	Subject Description

General Photographic Suggestions

- Some clients do not permit photographs. Confirm with the project manager or site manager that photographs are allowed.
- Take photographs before, during, and after to convey a timeline. Photographs should be taken for investigations, emergencies, incidents, and as appropriate.
- Be aware of the goal(s) of the project and capturing images that clearly demonstrate progress towards achieving the goal(s).
- The photographer should be prepared to take a variety of shots, from long range to close-up. Many shots will be repetitive in nature or format, especially close-up site feature photographs.
- Photographs taken to document sampling locations should include two or more reference points or include landscape features that are unlikely to change over several years (buildings, other structures, etc.) as to facilitate relocating the point at a later date.
- Consider the angle of light, cloud cover, background, shadows, and contrasts. Medium and long view photos are best shot with the sun at the photographer's back.
- Capture seasonal features such as foliage, stream flow, cloud cover, and site access as these features may help demonstrate passage of time.
- Use a ruler, person, farm animal, automobile, etc. when possible to convey the scale of the image. The angle (e.g., overhead, elevated shot from a bridge, peak, etc.) may provide better perspective of the intended subject.
- Photographs of soil or rock cores should have a location and depth interval label, as well as the boring/well ID and an "up" indicator.

Attachment A Examples of Chain of Custody

>>> Select a Laboratory <<<

#N/A
#N/A
#N/A
#N/A

Chain of Custody Record

Regulatory Program: ☐ DW ☐ NPDES ☐ RCRA ☐ Other:

Client Contact	Project Manager:	Site Contact:	Date:	COC No:
Your Company Name here	Tel/Fax:	Lab Contact:	Carrier:	_____ of _____ COCs
Address	**Analysis Turnaround Time**			Sampler:
City/State/Zip	☐ CALENDAR DAYS ☐ WORKING DAYS			**For Lab Use Only:**
(xxx) xxx-xxxx Phone	TAT if different from Below _____			Walk-in Client:
(xxx) xxx-xxxx FAX	☐ 2 weeks			Lab Sampling:
Project Name:	☐ 1 week			
Site:	☐ 2 days			Job / SDG No.:
P O #	☐ 1 day			

Sample Identification	Sample Date	Sample Time	Sample Type (C=Comp, G=Grab)	Matrix	# of Cont.	Filtered Sample (Y / N)	Perform MS / MSD (Y / N)																	Sample Specific Notes:

Preservation Used: 1= Ice, 2= HCl; 3= H2SO4; 4=HNO3; 5=NaOH; 6= Other _____

Possible Hazard Identification:
Are any samples from a listed EPA Hazardous Waste? Please List any EPA Waste Codes for the sample in the Comments Section if the lab is to dispose of the sample.

☐ Non-Hazard ☐ Flammable ☐ Skin Irritant ☐ Poison B ☐ Unknown

Sample Disposal (A fee may be assessed if samples are retained longer than 1 month)

☐ Return to Client ☐ Disposal by Lab ☐ Archive for_____ Months

Special Instructions/QC Requirements & Comments:

Custody Seals Intact: ☐ Yes ☐ No | Custody Seal No.: | Cooler Temp. (°C): Obs'd:_____ Corr'd:_____ Therm ID No.:_____

Relinquished by:	Company:	Date/Time:	Received by:	Company:	Date/Time:
Relinquished by:	Company:	Date/Time:	Received by:	Company:	Date/Time:
Relinquished by:	Company:	Date/Time:	Received in Laboratory by:	Company:	Date/Time:

PTS Laboratories, Inc.

CHAIN OF CUSTODY RECORD

PAGE OF

COMPANY

ADDRESS CITY ZIP CODE

PROJECT MANAGER

PROJECT NAME PHONE NUMBER

PROJECT NUMBER FAX NUMBER

SITE LOCATION

SAMPLER SIGNATURE

PO#

TURNAROUND TIME

24 HOURS ☐ 5 DAYS ☐
48 HOURS ☐ NORMAL ☐
72 HOURS ☐

OTHER: _____

SAMPLE INTEGRITY (CHECK):

INTACT _____ ON ICE _____

PTS QUOTE NO.

PTS FILE:

ANALYSIS REQUEST

SAMPLE ID NUMBER	DATE	TIME	DEPTH, FT	NUMBER OF SAMPLES	SOIL PROPERTIES PACKAGE	HYDRAULIC CONDUCTIVITY PACKAGE	PORE FLUID SATURATIONS PACKAGE	TCEQ/TNRCC PROPERTIES PACKAGE	CAPILLARITY PACKAGE	FLUID PROPERTIES PACKAGE	PHOTOLOG: CORE PHOTOGRAPHY	MOISTURE CONTENT, ASTM D2216	POROSITY: TOTAL, API RP40	POROSITY: EFFECTIVE, ASTM D425M	SPECIFIC GRAVITY, ASTM D854	BULK DENSITY (DRY), API RP40 or ASTM D2937	AIR PERMEABILITY, API RP40	HYDRAULIC CONDUCTIVITY, EPA9100, API RP40, D5084	GRAIN SIZE DISTRIBUTION, ASTM D422/4464M	TOC: WALKLEY-BLACK	ATTERBERG LIMITS, ASTM D4318					COMMENTS

1. RELINQUISHED BY	2. RECEIVED BY	3. RELINQUISHED BY	4. RECEIVED BY
COMPANY	COMPANY	COMPANY	COMPANY
DATE TIME	DATE TIME	DATE TIME	DATE TIME

PTS Laboratories, Inc. • 8100 Secura Way • Santa Fe Springs, CA 90670 • Phone (562) 347-2500 • Fax (562) 907-3610
PTS Laboratories, Inc. • 4342 W. 12th St. • Houston, TX 77055 • Phone (713) 316-1800 • Fax (713) 316-1882

SOP-05 Sample Management and Shipping

Purpose

The purpose of this standard operating procedure (SOP) is to provide a general reference for ensuring the integrity of samples from collection to their final disposition (e.g., laboratory) is met. This SOP considers general shipping of environmental (chemical) or geotechnical (physical) samples.

Shipping under this SOP includes direct delivery, courier, and/or air transport. Regulations for sample labeling, packing, and shipping of dangerous goods by air transport are promulgated by United States Department of Transportation (DOT) under Code of Federal Regulations, Title 49 [49 Code of Federal Regulations (CFR)], Subchapter C, Hazardous Materials Regulations, and the International Air Transport Authority (IATA).

Relevant EHS Support SOPs

- SOP-04 Field Documentation

Attachments

- Attachment A Example of Laboratory Holding Times

Required Materials

- Field logbook and field documentation
- Site maps, site layouts, site plans
- Health and Safety Plan
- Appropriate personal protective equipment (PPE)
- Black waterproof and/or indelible ink pens
- Sample labels
- Chain of Custody
- Custody seals
- Coolers
- Clear packing and duct tape
- Plastic baggies
- Trash bags, or drum liners
- Bubble wrap
- Ice
- Federal Express form (with EHS Support account)

1 Shipping of Hazardous Substances or Dangerous Goods

Shipment of hazardous substances and dangerous goods including non-aqueous phase liquids (quantity regulated), compressed gas, biological hazards, radioactive substances require special shipping procedures and training. Shipment of hazardous substances and dangerous goods requires additional training and regulatory-approved packaging if sent by common carrier. The shipment of hazardous substances and dangerous goods, their packaging, labeling, and shipping are regulated by the United States Department of Transportation (DOT) Hazardous Material Regulation (HMR), 49 CFR, Parts 106 through 180 and the IATA Dangerous Goods Regulation (DGR).

Shipment of a potentially hazardous substance or dangerous goods will be discussed with the Project Manager and the EHS Support Health and Safety Manger. Dangerous goods must not be offered for air transport by any personnel except for personnel trained and certified by IATA in dangerous goods shipment.

1.1 Definitions

Dangerous goods: Dangerous goods are articles or substances that can pose a significant risk to health, safety, or property when transported by air; they are classified as defined in Section 3 of the DGR (IATA 2007).

Environmental samples: Environmental samples include but are not limited to drinking water, groundwater, surface water, soil, sediment, mixed waste samples, treated municipal and industrial wastewater effluent, biological specimens, or any samples not expected to be contaminated with high levels of hazardous materials.

Hazardous Materials Regulations: The HMR are DOT regulations for the shipment of hazardous materials by air, water, and land; they are located in 49 CFR 106 through 180.

Hazardous samples: Hazardous samples include dangerous goods and hazardous substances. Hazardous samples shipped by air should be packaged and labeled in accordance with procedures specified by the DGR. Ground shipments should be packaged and labeled in accordance with the HMR.

Hazardous substance: A hazardous substance is any material, including its mixtures and solutions, that is listed in Attachment A of 49 CFR 172.101 and its quantity, in one package, equals or exceeds the reportable quantity listed in the attachment.

IATA Dangerous Goods Regulations: The DGR are regulations that govern the international transport of dangerous goods by air. The DGR are based on the International Civil Aviation Organization (ICAO) Technical Instructions. The DGR contain all of the requirements of the ICAO Technical Instructions and are more restrictive in some instances.

Nonhazardous samples: Nonhazardous samples are those samples that do not meet the definition of a hazardous sample and do not need to be packaged and shipped in accordance with the DGR or HMR.

1.2 Non-Hazardous Sample Management and Shipping

1.2.1 General Requirements

- Samples will be placed in contaminant-free containers stored in cool, dry, clean areas to prevent exposure to fuels, solvents, and other non-site related impacts.
- Sample containers will not be used if held for an extended period on the job site (some states dictate this time limit) or exposed to extreme heat conditions.
- Sample container will be kept out of the sun.

Samples will be shipped in an expeditious time to ensure samples are received by the laboratory within the holding time of the sample method. An example of sample container, preservative and holding times is included as **Attachment A**.

1.2.2 Sample Labels

Sample labels will be completed using black waterproof indelible marker. One sample label will be affixed to each sample container. The sample identification will be written as specified in the project work plan. Pre-printed sample labels should be used when available. Documentation for sample labeling can be referenced in SOP-04 Field Documentation.

1.2.3 Sample Packing

Protocols for sample temperature maintenance and sample packing are applicable to collection of samples year-round or as otherwise specified. The intent is to ensure samples arrive at the laboratory in good condition—both physically intact and appropriately preserved.

- Place each sample container in a re-sealable plastic baggie or similar
- Squeeze as much air as possible from the plastic baggie and seal
- Glass containers should be wrapped in bubble wrap

1.2.4 Cooler Packing for Samples on Ice

Determine the maximum allowable weight of each cooler (for example, the FedEx limit is 150 pounds. Most shippers will not accept a shipment for transportation when it appears if the shipment is:

- Improperly packed or packaged
- Of a kind or type likely to incur damage from high or low temperature under normal air transportation conditions
- Of an inherent nature or contains defects that may indicate transportation could not be furnished without loss or damage to the shipment or damage to the shippers facilities or equipment

Cooler Packing Instructions for Samples on Ice:

1. Tape the drain plug on the inside and outside of the cooler.
2. Place cushioning material (e.g., bubblewrap) in the bottom and around the sides of the cooler.
3. Place a large plastic bag (e.g., trash bag) in the bottom of cooler to contain samples. Allow the top edges of the plastic bag to hang over the outside of the cooler while filling.
4. Place the wrapped bottles upright in the cooler allowing enough room for ice bags and cushioning material to be placed between and around the containers.
5. If required, place a temperature blank in the cooler with the samples.
6. Insulate the samples with additional cushioning to deter breakage.
7. If using wet ice, place the ice in a plastic bags and seal (considered a double bagging to protect against possible leakage).
8. Distribute ice substitute bags (such as gel ice) or plastic bags containing wet ice between samples and over the containers to preserve them at approximately 4 degrees Celsius (°C).
9. Fill the remaining space in the cooler with additional ice and/or cushioning material to prevent the contents from shifting during shipment.
10. Pull the top edges of the large plastic bag up and together, force out any extra air, and twist the top of the plastic bag several times. Secure the twisted portion of the bag with a tie strap or tape.
11. If the cooler is being couriered or hand delivered to the laboratory, a signature will be required from the party releasing the cooler(s) and the party accepting responsibility for the cooler and its contents. If the cooler is being shipped via air carrier, a signature will be required from the party releasing the cooler (following the air carriers delivery to the laboratory, the laboratory will append their signature).
12. Place the chain-of-custody (C-O-C) in a plastic baggie outside, and on top of the large plastic bag containing the samples and ice. The baggie containing the C-O-C may be taped to the underside of the cooler top.
13. Retain an original carbon copy or photocopy of the completed C-O-C.
14. Complete two custody seals.
15. Seal the cooler by placing the one custody seal on the front and the other custody seal on the rear of the cooler across the edge where the cooler and cooler lid meet.
16. Use clear packing tape and encircle the tape around the cooler. The packing tape should cover the custody seals and should secure the lid.

1.2.5 Packing for Samples (not on ice)

1. Place cushioning material (e.g., bubblewrap) around the sample container.
2. Fill the remaining spaces of the container with additional packing material to secure the sample from movement.
3. If the container is being couriered or hand delivered to the laboratory, a signature will be required from the party releasing the cooler(s) and the party accepting responsibility for the cooler and its contents. If the cooler is being shipped via air carrier; a signature will be required from the party releasing the cooler (following the air carriers delivery to the laboratory, the laboratory will append their signature).
4. Place the COC in a plastic bag and place in container.
5. Retain an original carbon copy or photocopy of the completed C-O-C.

6. Complete a custody seal and attach along an opening of the container (e.g., the edge of a box).
7. Using clear packing tape, tape the container shut.

1.2.6 Shipping Airbills

1. Complete the shipping or airbill form.
2. It is recommended to ship coolers certified to ensure samples are received within a sample's required holding time.
3. Ship the samples. If necessary, notify the laboratory the samples have been shipped.
4. Retain a copy of the shipment airbill to use for tracking of the package.

1.2.7 Records

The documentation for sample packaging and shipping will consist of chain-of-custody records and shipper's records. Documentation should be kept and placed in with the project files.

Attachment A Example of Laboratory Holding Times

RECOMMENDED HOLDING TIMES FOR ENVIRONMENTAL SAMPLES

Parameters	Method*	Container	Recommended Quantity (mL)	Preservative	Holding Time
Acidity	305.1, 2310B	P,G	100	4^0C	14 days
Alkalinity	310.1, 310.2, 2320B	P,G	100	4^0C	14 days
Ammonia-N	4500NH3BE, 350.3	P,G	500	4^0C, H_2SO_4 to pH <2	28 days
Biochemical Oxygen Demand (BOD)	405.1, 5210B	P,G	1000	4^0C	48 hours
Bromide	300.0, 9056	P,G	200	None	28 days
Chemical Oxygen Demand (COD)	HACH 8000	P,G	100	4^0C, H_2SO_4 to pH <2	28 days
Chloride	325.3, 9251, 9056	P,G	200	None	28 days
Chlorine, Residual	330.3, 4500 CLG	P,G	200	None	Immediately
Coliform, Fecal	9222D	P,G (sterile)	100	4^0C, $Na_2S_2O_3$	6 hours
Color	2120C, 110.3	P,G	100	4^0C	48 hours
Cyanide	335.1, 335.2, 335.3 9012A	P,G	1000	4^0C, ascorbic acid, NaOH to pH > 12	14 days
Ferrous Iron	3500FED	P,G	100	2mHCl/100mL	Immediately
Flashpoint	1010	P,G	100	None	Not specified
Fluoride	300.0, 9056, 340.2	P	500	None	28 days
Hardness	130.2 2340B	P,G	100	HNO_3 to pH < 2	6 months
Nitrogen, Kjeldahl (TKN)	4500NH, 351.4	P,G	500	4^0C, H_2SO_4 to pH <2	28 days
Nitrate-N	353.2	P,G	100	4^0C	48 hours
Nitrate-Nitrite as N	353.2	P,G	200	4^0C, H_2SO_4 to pH <2	28 days
Oil and Grease	1664A	G	1000	4^0C, H_2SO_4 or HCl to pH < 2	28 days
Phenols	420.1, 420.2, 9066	P,G	1000	4^0C, H_2SO_4 to pH <2	28 days
Phosphorus, Total	365.1	P,G	200	4^0C, H_2SO_4 to pH <2	28 days
Phosphorus, Ortho	365.2, 4500PE	P,G	200	4^0C	48 hours
pH	150.1, 9040B, 9045C	P,G	100	None	Immediately
Radiochemisrty Alpha, Beta, Radium Tritium Radon, I-131	900 & 9000 series	 P,G P,G P,G	 2000 100 1000	 HNO_3 to pH < 2 None HNO_3 to pH < 2	 6 months 6 months 14 days
Reactivity	SW846 7.3.3.2, 7.3.4.2	G	100g	4^0C	Not Specified
Silica	370.1, 4500Si D	P, PFTE, Quartz	100	4^0C	28 days
Solids, Dissolved (TDS)	160.1, 2540C	P,G	100	4^0C	7 days
Solids, Suspended (TSS)	160.2, 2540D	P,G	500	4^0C	7 days
Solids, Volatile (TVS)	160.4, 2540E	P,G	100	4^0C	7 days
Solids, Total (TS)	160.3, 2.540B	P,G	100	4^0C	7 days
Specific Conductance	120.1, 9050	P,G	100	4^0C	28 days
Specific Gravity	2710F	P,G	100	4^0C	28 days
Sulfate	375.4, 9056, 9038	P,G	200	4^0C	28 days
Sulfide	376.1, 376.2, 9034	P,G	500	4^0C, Zn acetate, NaOH to pH > 9	7 days
Sulfite	4500S03B	P,G	200	None	Immediately
Surfactants (MBAS)	425.1, 5540C	P,G	250	4^0C	48 hours
Total Organic Carbon (TOC)	415.1, 9060	P,G	100	4^0C, HCl to pH < 2	28 days
Total Organic Halogens (TOX)	9020B	G-TLC (amber)	100	4^0C, H_2SO_4 to pH <2	28 days
Total Petroleum Hydrocarbon (TPH)	418.1	G-TLC	1000	4^0C, H_2SO_4 or HCl to pH < 2	28 days
Turbidity	180.1, 2130B	P,G	100	4^0C	48 hours
Viscosity	D2196	P,G	500	None	Not Specified

*The methods listed are from typical EPA references.
#Solid and waste samples: Quantity 1-100g, preservative 4 ° C
**Holding time for solids and samples is not defined
Organic Nitrogen = TKN – Ammonia-N

RECOMMENDED HOLDING TIMES FOR ENVIRONMENTAL SAMPLES

Metals

Parameters	Method*	Container	Recommended Quantity (mL)	Preservative	Holding Time
Metals (except Hexavalent Chromium and Mercury):					
Aqueous					
Total	6010B, 200.0, 7000 series	P,G	500	HNO_3 to pH < 2	6 months
Dissolved	6010B, 200.0, 7000 series	P,G	500	Filter on site HNO_3 to pH < 2	6 months
Solid					
Total	6010B, 200.0, 7000 series	P,G	100g	4^0C	6 months
Hexavalent Chromium					
Aqueous	7196A	P,G	500	4^0C	24 hours
Solid	3060A/7196A	P,G	100g	4^0C	30/7 days
Mercury					
Aqueous					
Total	245.2/7470	P,G	500	HNO_3 to pH < 2	28 days
Dissolved	245.2/7470	P,G	500	Filter on site HNO_3 to pH < 2	28 days
Solid					
Total	7471	P,G	100g	4^0C	28 days

Metals – Boron must be collected in a polyethylene container.

*The methods listed are from typical EPA references.
CrIII=Total Cr-Hexavalent Cr

Organic Parameters

Volatile Organics

Sample Matrix	Method*	Container	Minimum Quantity	Preservative	Holding Time
Concentrated Waste Samples	8021B, 8260B, 8015M	G-TLC or G-TLS	2 x 40mL vials or 4-oz wide mouth	4^0C	14 days
Aqueous Samples	8021B, 8260B, 8015M, 624, VPH	G-TLS	2 x 40mL vials	4^0C, HCl to pH < 2 , $Na_2S_2O_3$ if residual chlorine present	14 days, 7 days if not acid preserved
Solid Samples	8021B,8260B, 8015M, VPH	G-TLS or G-TLC	4-oz wide mouth and/or Terracore Kit	4^0C	14 days **

*The methods listed are from typical EPA references.

Semivolatile Organics, Pesticides/PCBs, Herbicides, PAHs, Petroleum

Hydrocarbons

Sample Matrix	Method*	Container	Minimum Quantity	Preservative	Holding Time
Concentrated Waste Samples	8270C, 8081, 8082, 8015M, 8151A, 8141A, FL-PRO	G-TLC (Amber)	1 Liter	None	14 days until extraction, 40 days after extraction
Aqueous Samples	8270C, 8081, 8082, 8015M, 8151A, 8141A, 8310,608, 625, FL-PRO,EPH ***	G-TLC (Amber)	2 x 1 Liter	4^0C	7 days until extraction, 40 days after extraction
Solid Samples	8270C, 8081, 8082,	G-TLC	8 oz.	4^0C	14 days until

RECOMMENDED HOLDING TIMES FOR ENVIRONMENTAL SAMPLES

	8015M, 8151A, 8141A, 8310,EPH FL-PRO ***				extraction, 40 days after extraction
Parameters	**Method***	**Container**	**Recommended Quantity (mL)**	**Preservative**	**Holding Time**
Dioxins and Furans**	613, 8280A, 8290, 1613	G-TLC(Amber)	2 x 1 Liter	4^0C	30 days until extraction, 45 days after extraction

*The methods listed are from typical EPA references.
**Concentrated wastes and soil samples are collected in 2 oz. to 1 Liter amber glass jars with TLC.
***1005/1006, Petroleum Hydrocarbons –14 days after extraction

TCLP/SPLP Parameters

Parameters	Holding Time from Collection to TCLP Extraction (days)	Holding Time from TCLP Extaction tor Preparative Extraction (days)	Holding Time from TCLP/Preparative Extraction to Analysis (days)	Total Time
Volatiles	14	NA	14	28
Semivolatiles	14	7	40	61
Mercury	28	NA	28	56
Metals	180	NA	180	360

Reference: 40CFR Part 136 Tables IA, IB, IC, ID & IE and Table II., SW846 Table 4-1 and Table 3-1, SW846 Method 1311 8.5,
*The methods listed are from typical EPA references
Acronymn Definitions: (Teflon is a registered trademark of E.I. DuPont)
CLP: EPA Contract Laboratory Program
G-TLC: Glass with Teflonâ-lined cap
NA: Not Applicable
G: Glass
G-TLS: Glass with Teflonâ-lined septrum
P: Polyethylene

RECOMMENDED HOLDING TIMES FOR ENVIRONMENTAL SAMPLES

Parameters	Method*	Container	Recommended Quantity (mL)	Preservative	Holding Time
Acidity	305.1, 2310B	P,G	100	4^0C	14 days
Alkalinity	310.1, 310.2, 2320B	P,G	100	4^0C	14 days
Ammonia-N	4500NH3BE, 350.3	P,G	500	4^0C, H_2SO_4 to pH <2	28 days
Biochemical Oxygen Demand (BOD)	405.1, 5210B	P,G	1000	4^0C	48 hours
Bromide	300.0, 9056	P,G	200	None	28 days
Chemical Oxygen Demand (COD)	HACH 8000	P,G	100	4^0C, H_2SO_4 to pH <2	28 days
Chloride	325.3, 9251, 9056	P,G	200	None	28 days
Chlorine, Residual	330.3, 4500 CLG	P,G	200	None	Immediately
Coliform, Fecal	9222D	P,G (sterile)	100	4^0C, $Na_2S_2O_3$	6 hours
Color	2120C, 110.3	P,G	100	4^0C	48 hours
Cyanide	335.1, 335.2, 335.3 9012A	P,G	1000	4^0C, ascorbic acid, NaOH to pH > 12	14 days
Ferrous Iron	3500FED	P,G	100	2mHCl/100mL	Immediately
Flashpoint	1010	P,G	100	None	Not specified
Fluoride	300.0, 9056, 340.2	P	500	None	28 days
Hardness	130.2 2340B	P,G	100	HNO_3 to pH < 2	6 months
Nitrogen, Kjeldahl (TKN)	4500NH, 351.4	P,G	500	4^0C, H_2SO_4 to pH <2	28 days
Nitrate-N	353.2	P,G	100	4^0C	48 hours
Nitrate-Nitrite as N	353.2	P,G	200	4^0C, H_2SO_4 to pH <2	28 days
Oil and Grease	1664A	G	1000	4^0C, H_2SO_4 or HCl to pH < 2	28 days
Phenols	420.1, 420.2, 9066	P,G	1000	4^0C, H_2SO_4 to pH <2	28 days
Phosphorus, Total	365.1	P,G	200	4^0C, H_2SO_4 to pH <2	28 days
Phosphorus, Ortho	365.2, 4500PE	P,G	200	4^0C	48 hours
pH	150.1, 9040B, 9045C	P,G	100	None	Immediately
Radiochemisrty Alpha, Beta, Radium Tritium Radon, I-131	900 & 9000 series	 P,G P,G P,G	 2000 100 1000	 HNO_3 to pH < 2 None HNO_3 to pH < 2	 6 months 6 months 14 days
Reactivity	SW846 7.3.3.2, 7.3.4.2	G	100g	4^0C	Not Specified
Silica	370.1, 4500Si D	P, PFTE, Quartz	100	4^0C	28 days
Solids, Dissolved (TDS)	160.1, 2540C	P,G	100	4^0C	7 days
Solids, Suspended (TSS)	160.2, 2540D	P,G	500	4^0C	7 days
Solids, Volatile (TVS)	160.4, 2540E	P,G	100	4^0C	7 days
Solids, Total (TS)	160.3, 2.540B	P,G	100	4^0C	7 days
Specific Conductance	120.1, 9050	P,G	100	4^0C	28 days
Specific Gravity	2710F	P,G	100	4^0C	28 days
Sulfate	375.4, 9056, 9038	P,G	200	4^0C	28 days
Sulfide	376.1, 376.2, 9034	P,G	500	4^0C, Zn acetate, NaOH to pH > 9	7 days
Sulfite	4500S03B	P,G	200	None	Immediately
Surfactants (MBAS)	425.1, 5540C	P,G	250	4^0C	48 hours
Total Organic Carbon (TOC)	415.1, 9060	P,G	100	4^0C, HCl to pH < 2	28 days
Total Organic Halogens (TOX)	9020B	G-TLC (amber)	100	4^0C, H_2SO_4 to pH <2	28 days
Total Petroleum Hydrocarbon (TPH)	418.1	G-TLC	1000	4^0C, H_2SO_4 or HCl to pH < 2	28 days
Turbidity	180.1, 2130B	P,G	100	4^0C	48 hours
Viscosity	D2196	P,G	500	None	Not Specified

*The methods listed are from typical EPA references.
#Solid and waste samples: Quantity 1-100g, preservative 4 ° C
**Holding time for solids and samples is not defined
Organic Nitrogen = TKN – Ammonia-N

RECOMMENDED HOLDING TIMES FOR ENVIRONMENTAL SAMPLES

Metals

Parameters	Method*	Container	Recommended Quantity (mL)	Preservative	Holding Time
Metals (except Hexavalent Chromium and Mercury):					
Aqueous					
Total	6010B, 200.0, 7000 series	P,G	500	HNO_3 to pH < 2	6 months
Dissolved	6010B, 200.0, 7000 series	P,G	500	Filter on site HNO_3 to pH < 2	6 months
Solid					
Total	6010B, 200.0, 7000 series	P,G	100g	4^0C	6 months
Hexavalent Chromium					
Aqueous	7196A	P,G	500	4^0C	24 hours
Solid	3060A/7196A	P,G	100g	4^0C	30/7 days
Mercury					
Aqueous					
Total	245.2/7470	P,G	500	HNO_3 to pH < 2	28 days
Dissolved	245.2/7470	P,G	500	Filter on site HNO_3 to pH < 2	28 days
Solid					
Total	7471	P,G	100g	4^0C	28 days

Metals – Boron must be collected in a polyethylene container.

*The methods listed are from typical EPA references.
CrIII=Total Cr-Hexavalent Cr

Organic Parameters

Volatile Organics

Sample Matrix	Method*	Container	Minimum Quantity	Preservative	Holding Time
Concentrated Waste Samples	8021B, 8260B, 8015M	G-TLC or G-TLS	2 x 40mL vials or 4-oz wide mouth	4^0C	14 days
Aqueous Samples	8021B, 8260B, 8015M, 624, VPH	G-TLS	2 x 40mL vials	4^0C, HCl to pH < 2 , $Na_2S_2O_3$ if residual chlorine present	14 days, 7 days if not acid preserved
Solid Samples	8021B,8260B, 8015M, VPH	G-TLS or G-TLC	4-oz wide mouth and/or Terracore Kit	4^0C	14 days **

*The methods listed are from typical EPA references.

Semivolatile Organics, Pesticides/PCBs, Herbicides, PAHs, Petroleum

Hydrocarbons

Sample Matrix	Method*	Container	Minimum Quantity	Preservative	Holding Time
Concentrated Waste Samples	8270C, 8081, 8082, 8015M, 8151A, 8141A, FL-PRO	G-TLC (Amber)	1 Liter	None	14 days until extraction, 40 days after extraction
Aqueous Samples	8270C, 8081, 8082, 8015M, 8151A, 8141A, 8310,608, 625, FL-PRO,EPH ***	G-TLC (Amber)	2 x 1 Liter	4^0C	7 days until extraction, 40 days after extraction
Solid Samples	8270C, 8081, 8082,	G-TLC	8 oz.	4^0C	14 days until

RECOMMENDED HOLDING TIMES FOR ENVIRONMENTAL SAMPLES

	8015M, 8151A, 8141A, 8310,EPH FL-PRO ***				extraction, 40 days after extraction
Parameters	**Method***	**Container**	**Recommended Quantity (mL)**	**Preservative**	**Holding Time**
Dioxins and Furans**	613, 8280A, 8290, 1613	G-TLC(Amber)	2 x 1 Liter	4^0C	30 days until extraction, 45 days after extraction

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**Concentrated wastes and soil samples are collected in 2 oz. to 1 Liter amber glass jars with TLC.
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TCLP/SPLP Parameters

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Reference: 40CFR Part 136 Tables IA, IB, IC, ID & IE and Table II., SW846 Table 4-1 and Table 3-1, SW846 Method 1311 8.5,
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G-TLS: Glass with Teflonâ-lined septrum
P: Polyethylene

SOP-07 Investigative Derived Waste Management

Purpose

This SOP is intended to assist the field staff in determining the appropriate manner to handle investigation derived wastes (IDW). It may be necessary to deviate from the guidelines presented in this SOP on the basis of the project requirements.

This document is intended to provide a general overview of appropriate IDW management practices; however, it is the Project Manager's responsibility to ensure that IDW is properly managed in accordance with applicable federal, state, and local law, the contract requirements, and good professional judgment.

Relevant EHS Support SOPs

- SOP-04 Field Documentation
- SOP-05 Sample Management and Shipping

Required Materials

- Field logbook and field documentation
- Site maps, site layouts, site plans
- Health and Safety Plan
- Appropriate personal protective equipment (PPE)
- Black waterproof and/or indelible ink pens
- Containers for waste (e.g., 55-gallon open and closed top drums) and material to cover waste to protect from weather (e.g., plastic covering)
- Hazardous /non-hazardous waste drum labels (weatherproof)
- Plastic garbage bags, zip lock storage bags, roll of plastic sheeting
- Drum socket/gloves/rubber mallet

Investigative Derived Waste General Considerations

IDW typically includes drilling cuttings, drilling muds, purged well water, decontamination fluids, sample residues, decontamination fluids, PPE, and other disposable equipment that is generated from sampling and investigation activities. Generally, the management of IDW must meet the following criteria:

- It must be protective of human health and the environment.
- It must comply with the applicable or relevant and appropriate requirements (ARARs) unless the ARAR is waived by the applicable regulatory authority. Potential ARARs for IDW include regulations under the Resource Conservation and Recovery Act (RCRA), which include the underground injection control regulations and the Land Disposal Restrictions (LDR); the Clean Water Act; the Clean Air Act; the Toxic Substances Control Act (TSCA); and applicable State environmental laws. To the extent that the United States Environmental Protection Agency (USEPA) has issued regulations relating to cleanup standards for specific chemicals, those standards must normally be followed unless either a waiver has been obtained or different site-specific cleanup standards have been established by the appropriate regulatory authority.

Important general elements of managing IDW include:

- Leaving a site in a condition that is similar to the condition that existed prior to the investigation.
- Minimizing the quantity of wastes generated.
- Removing wastes that pose an immediate threat to human health or the environment.
- Leaving on site those wastes that do not require off-site disposal or long-term above-ground containerization.
- Complying with federal and state ARARs.
- Planning and coordination for IDW management.

The following are general guidelines for the disposal for IDW, based on a review of existing USEPA guidance documents. These guidelines may be superseded by applicable state or local laws or other ARARs.

- Different waste streams should not be mixed (i.e., soils should be containerized in separate drums from water, potentially hazardous from non-hazardous, and so on).
- Soil--Generated soil (e.g., drill cuttings, excavated soil) and/or contaminated soil should be placed in an appropriate container and prepared for disposal at an appropriate disposal facility, as outlined in the site work plan. Soils contained in a roll off box may require the use of protective covers to minimize effects of weather (e.g., rain), odors, or dust.
- Hazardous water, or other aqueous liquid—Hazardous water or other aqueous liquids should be contained (drum, tanker) and disposed of at a treatment storage or disposal facility, as appropriate.
- Decontamination Fluids—Decontamination fluids should be drummed and disposed of at an appropriate disposal facility, whether on-site or off-site.
- Non-hazardous water—Non-hazardous water should be drummed and disposed of at an appropriate disposal facility, whether on-site or off-site.
- PPE and Disposable Equipment—Disposable PPE and equipment that has been decontaminated may be double-bagged and placed in appropriate solid waste containers.

- Such materials reasonably believed to be hazardous should be treated as if they are hazardous pending analytical confirmation.

1.1 Field Compliance with Requirements

Compliance with the applicable legal requirements can generally be achieved by complying with general principles:

- Identify the contaminants. The analysis can be based on reasonably available information and the application of reasonable professional judgment. Analytical testing may not be required under all circumstances.
- Characterization of the IDW. Use existing information (manifests, Safety Data Sheets (SDS), previous test results, knowledge of the waste generation process, and other relevant records), generator's knowledge, best professional judgment, and waste characterization analysis, to characterize IDW as hazardous, non-hazardous, or special (e.g., construction debris).
- Minimize the volume of the IDW. IDW containing hazardous substances or wastes should be carefully segregated from other non-hazardous IDW to minimize the volume of IDW that must be disposed of as hazardous waste, to the best extent feasible.
- Determine the ARARs. Attention should include RCRA, TSCA, and applicable state requirements. Individual State requirements may be more stringent than the corresponding federal requirements. Waivers should be sought when justified.
- Properly containerized IDW. Separate and contain potentially contaminated PPE, disposable equipment, decontamination fluids, sample media (e.g., drilling fluid, soil, groundwater). Comply with applicable containerization, labeling, and storage and recordkeeping requirements.

1.2 IDW Field Procedures

Procedures for IDW and disposal should include the following:

1. Inform the On-Site Facility Manager or personnel that containerized IDW may be temporarily stored on-site while awaiting pick up for off-site disposal.
2. Initiate and coordinate the procurement process for IDW analytical testing, pick up, and disposal.
3. Prepare the adequate numbers and types of containers for storage and, if necessary, analytical testing.
4. Consider using containers, such as roll-off boxes, Baker tanks, poly tanks, and bins (**Figure 1**), if a large quantity or volume of IDW is anticipated.

Figure 1 Example of a Roll-off Box, Baker Tank, and Various Sizes of Poly Tanks

5. Consult local, state, and federal regulations for additional requirements for the storage of IDW in tanks, as required.
6. Record the size of any storage container (e.g., roll-off bin, Baker tank, poly tank). The volume of water or soil can be obtained from a manifest or scale, if either are available during site activities. Alternatively, the volume of water or weight of soil in a large-quantity sized container can be estimated by:
    a. Reading the volume gage on the outside of the poly tank (usually in gallons or liters).
    b. Measuring the height of the water in a bin, tank or poly, and multiplying to the length and width of the bin or tank.
    c. Knowing the dimensions of the roll off bin or container and multiplying by the density of the material. Standard roll-off bins generally have an estimated volume or tonnage associated with them. If this volume or tonnage is available, it can be used. Weight or tonnage will vary based on the material type (e.g., clay, sand, construction material) and associated density.
7. Use and properly label 55-gallon (200-liter) steel drums if a small quantity or volume of IDW is anticipated, and confirm steel is compatible with the IDW characteristics (e.g., corrosive materials might require plastic).
8. Use Department of Transportation (DOT)-approved steel drums or equivalent.
    a. A typical DOT-approved steel drum (**Figure 2**) cover comes with 1.5-inch (25 mm) vent hole, a 2-inch (50 mm) opening (sometimes referred to as a bunghole), and a rubber seal that fits into the lip of the cover. The drum is sealed to the lid cover by tightening with a bolt and nuts.

Figure 2 Typical DOT-approved Steel Drum with Cover Showing Vent and Bunghole

   b. Inspect drums prior to use to ensure there is no denting, pitting, or other visual observations that would indicate wear. Drums should be clean and not have been used for storage of other materials or chemicals.
   c. Fill drums s to about 80 percent capacity. If working in cold weather conditions (i.e., temperatures below freezing), space should be left in water-based IDW drums to allow for expansion.
9. Maintain an IDW log or drum log during the investigation. An IDW log or drum log tracks the volume of IDW, roll-off or Baker Tank number, the contents, the start generation date, drum numbers, storage location, and the storage time requirements. In some cases, particularly for drum contents, it may be a good practice to further define the contents of the drum by location (e.g., Soil cuttings from SB-2, SB-4).
10. Container labels for hazardous wastes must indicate the content's hazards using the applicable hazardous waste characteristic, DOT label or placard, Occupational Safety and Health Administration hazard statement or pictogram, or a National Fire Protection Association label.
11. Consult with the waste hauler or location of final disposition (e.g., landfill) to determine the volume of sample needed and the analytical testing required, if a waste characterization sample is necessary. If a composite sample is required for waste characterization, a small volume of similar media (i.e., soil, water) from each drum and/or container will be mixed and placed in the appropriate laboratory jar or container. The sample will be analyzed by the subcontracted laboratory. Waste characterization samples will be managed in accordance with SOP-04 Sample Management and Shipping.
12. Store, transport, and dispose of IDW according to applicable federal, state, and local regulations. All wastes classified as hazardous will be disposed of at a licensed treatment storage and disposal facility or managed in other approved manners.
13. Remove hazardous IDW from the facility within 90 days. A state-certified hazardous waste hauler shall transport all wastes classified as hazardous. Typically, the facility receiving any waste can coordinate a hauler to transport the waste. Shipped hazardous waste shall be disposed of in accordance with all federal, state, or regulatory requirements.
14. If the IDW is determined characteristically non-hazardous, disposal of the waste may include:
   a. Off-site disposal. The approved waste facility can coordinate a hauler to transport the waste. Shipped waste shall be disposed of in accordance with all federal, state, or regulatory requirements.

b. On-site disposal. Under some conditions, the generated wastes may be disposed on site. For instance, soils or solids may be disposed in a facility-approved disposal unit, or water, groundwater, or decontamination water may be disposed in a facility water treatment plant. Prior to disposing of non-hazardous generated wastes on-site, obtain approval from the On-Site Facility Manager or personnel in charge of site-generated wastes.

15. Ensure the client or the client's designee sign all waste manifests or bills of lading. Under no circumstance should a representative from EHS Support sign a waste manifest or bill of lading.
16. Decontaminate all PPE and disposable equipment, as necessary and double-bag for disposal at a municipal landfill or collect in drums for disposal at a hazardous waste facility.
17. Dispose of non-hazardous trash that is generated as part of field activities as general refuse.

1.3 Labeling

Containers used to store IDW must be properly labeled. Two general conditions exist:

1. Waste characteristics are known to be either hazardous or nonhazardous; or
2. Waste characteristics are unknown until additional data are obtained.

Waste labels should be constructed of a weatherproof material and filled out with a permanent marker to prevent being washed off or becoming faded by sunlight. It is recommended that waste labels be placed on the side of the container, since the top is more subject to weathering. However, when multiple containers are accumulated, it may be helpful to include labels on the top of the containers to facilitate organization and disposal. If no sample labels are not available, a paint pen can be used to temporarily identify the contents until a sample label is available. Examples of hazardous and non-hazardous waste labels are included as **Figure 3.**

Figure 3 Examples of a Hazardous and Non-Hazardous Waste Label

For situations where the waste characteristics are known, the waste containers should be packaged and labeled in accordance with the federal, state, or applicable regulations that may govern the labeling of waste. In some cases, site-specific labels may be available.

1.3.1 Known Hazardous or Non-Hazardous Waste

The following information shall be placed on Non-Hazardous Waste Labels:

- Description of waste (e.g., purge water, soil cuttings)
- Client or Responsible Party contact information (e.g., contact name and telephone number)
- Date when the waste was first accumulated.

The following information shall be placed on Hazardous Waste Labels:

- Description of waste (e.g., purge water, soil cuttings)
- Generator information (e.g., Client or Responsible Party name, address, and telephone number)
- USEPA identification number (supplied by Site Client Representative)
- Date when the waste was first accumulated.

1.3.2 Unknown Hazardous or Non-Hazardous Waste

When the final characterization of a waste is unknown, a notification label should be placed on the drum and the following information included on the label:

- Include the words “Waste Characterization Pending Analysis” on the label
- Description of waste (e.g., purge water, soil cuttings)
- Client or Responsible Party contact information (e.g., contact name and telephone number)
- Date when the waste was first accumulated.

Once the waste has been characterized, the label should be changed as appropriate for a nonhazardous or hazardous waste.

1.4 Storage

A temporary storage facility or location is required for containers storing IDW. Waste may be stored either on-site or off-site and should only be accessible by authorized personnel or officials. If waste will be stored off-site, consult local, state and federal regulations prior to off-site transportation and storage to ensure all requirements are met. Ideally, the drums should be stored in a facility or structure that encloses the drum so that its contents are not visible to passers-by and to prevent precipitation collection, run on, or infiltration from occurring. Minimize the possibility of spilling, traffic incident, fire, explosion, or any unplanned release of the IDW waste to the environment. The storage area should be limited in access .by authorized personnel.

1.5 Regulatory Requirements

The following federal and state regulations shall be used as resources for determining waste characteristics and requirements for waste storage, transportation, and disposal:

- Code of Federal Regulations (CFR), Title 40, Part 261; 262. The EPA approved the Hazardous Waste Generator Improvements Rule (40 CFR Part 262) effective 30 May 2017. This rule is anticipated to impact state and local hazardous wastes at various dates for the next 1 to 2 years.
- CFR, Title 49, Parts 172, 173, 178, and 179.

Records

Each container of waste generated shall be recorded in the field notebook used by the person responsible for labeling the waste. After the waste is disposed of, either by transportation off-site or disposal on-site in an approved disposal area, an appropriate record shall be made in the same field notebook to document proper disposition of IDW.

Field notes will be kept in a bound field logbook or approved field documentation following the format specified in SOP-04 Field Documentation. Record the following information in an IDW log or drum log:

- Type of IDW (e.g., drilling mud, soil, purge water, etc.)
- Volume of IDW per media
- Roll-off bin or Baker tank unit number and rental company name
- Roll-off bin or Baker tank size
- Drum number
- Start date of IDW collection
- Storage location of the drums
- Label type affixed to drum (e.g., Non-hazardous, Hazardous)
- Storage time requirements
- Other applicable requirements (e.g., weekly inspections for hazardous wastes).

Additional documentation includes:

- Collection of Waste Characterization chain of custody, if required
- Copy of signed manifests or bill of lading, if applicable
- Weight tickets, if applicable
- Location of final disposition.

Provide information about the IDW generated to the site contact for waste reporting.

SOP-08 Field Equipment Operation and Calibration

Purpose

The purpose of this SOP is to provide general procedures for the calibration of field instruments used during field investigations for field screening and measurements. This SOP applies to calibration for equipment used during field investigations with additional focus on the more commonly used field instruments - a multi-parameter water quality indicator and a photo-ionization detector (PID).

The manufacturer's manual should be referred to for calibration and standard operating procedures as well as operating instructions for the various field equipment. It is beyond the scope of this SOP to describe all alternatives to equipment type, calibration procedures, and maintenance.

Relevant EHS Support SOPs

- SOP-04 Filed Documentation

Attachments

- **Attachment A** Examples of Instrument Calibrations Forms
  - Multi-probe Water Quality Meter Calibration Form
  - Photoionization Detector or Single Gas Meter Calibration Form
  - Bump Test Form
- **Attachment B** Water Quality Meter
  - Calibration and Maintenance of a Portable Multi-Probe Water Quality Meter (YSI 556)
- **Attachment C** Portable Gas Meter
  - Calibration and Maintenance of a Photo-ionization Detector (Rae System 2000)

Required Materials

- Field logbook or field documentation
- Black waterproof and/or indelible ink pens
- Appropriate personal protective equipment (PPE)
- Field equipment and supplies necessary to perform the task

1 Field Equipment Calibration

Calibration of field equipment is conducted to ensure observations obtained in the field obtain a level of accuracy. Calibrate field monitoring equipment within calibration acceptance criteria, based on contaminants of concern potentially encountered, and within the instruments operational limits. Equipment calibration is only as good as the quality and accuracy of the calibration standard used. Therefore, verify that the calibration standards meet the minimum requirements for source and purity recommended by the instrument manufacturer.

Field monitoring equipment will be properly calibrated and remain operable in the field. All field equipment will be thoroughly inspected for functionality and calibrated prior to use.

1.1 General Field Equipment Calibration Procedures

- The type of field equipment used should be consistent for the activities performed to ensure the variability when monitoring/sampling is minimized.
- Instruments used during the field activities will be checked for possible malfunctions, cleaned, and calibrated prior to use.
- A calibration log will be completed for all equipment requiring calibration. Examples of a water quality meter calibration, a portable gas meter calibration, and a bump test form are included as **Attachment A**.
- Common field equipment includes a multi-probe water quality meter and a photo-ionization meter. Field equipment calibration and maintenance for a multi-probe water quality meter, specifically a YSI 556, is included as **Attachment B**. Field equipment calibration and maintenance for a portable gas meter, specifically a RAE System 2000 PID, is included as **Attachment C**. Included in **Attachment C** is the function of a bump test on a multi-gas detector.
- Calibration verification will be performed on field instruments prior to their initial use, at least once daily, as specified in the work plan, and/or whenever indications of instrument malfunction or questions in the instrument's readings are observed. The calibration schedule is outlined in **Table 1**.

Table 1 Calibration Schedule

Equipment	Calibration Standard	Frequency
Water quality meter	As required for project	Daily
Photoionization Detector	Isobutylene	Daily

- Project-specific requirements may require calibration of field monitoring equipment at a greater frequency (e.g., mid-day, end of day).
- Attempt to recalibrate instruments before collecting additional data if instrument readings appear to be irregular or drifting.
- Calibrate sensors in a controlled environment such as in the designated field preparation room. Avoid calibrating units in the field since it can introduce error.

In general, instrument identification and calibration should include the following steps:

1. Determine which instruments are needed for the specific field tasks.
2. Obtain the necessary instruments and associated calibration gases and/or reference standards for calibration.
3. Check expiration dates on calibration gases and/or standard solutions. Replace the standard if out of date.
4. Assemble the instrument and turn it on, allowing the instrument to warm up.
5. Check the battery charge. Charge or replace if necessary.
6. Clean the instrument (if necessary).
7. Calibrate the instrument prior to field use in accordance with manufacturer's procedures, and if necessary adjust the instrument to meet calibration specifications.
8. If the instrument malfunctions and the malfunction cannot be corrected, obtain another instrument, and have the malfunctioning instrument repaired or returned.
9. For an instrument to be considered calibrated and ready for use, the instrument must read within at least 10% of the calibration standard, or as outlined in the project work plan.
10. If the instrument reads within 10% of the reference standard value upon first testing, the instrument will be considered calibrated. If the instrument reads >10% difference from the reference standard value it will be calibrated, recalibrated, or taken out of service. Consult the manufacturer's instruction manual for more specific details on the instrument in use.
11. Document calibration activities and results on the Instrument Calibration Log (**Attachment A**) and record the activity in the Field Log Book.
12. Recharge batteries and add carrier gases (if applicable) at the end of each day or as needed.

2 Records

A record will be maintained of the calibration, and/or calibration verification. The records will include the following information, where applicable:

- Date and time of calibration activity
- Project name and number
- Personnel conducting the calibration
- Serial number and/or meter numbers
- Instrument name and model number
- Calibration gases or reference standard used, concentration of the gases and solutions used, and the associated units (if applicable), and lot numbers of calibration intervals
- Instrument readings after calibration
- Instrument readings of calibration verification data.

Additional documentation that will be retained include:

- Equipment rental shipping and calibration documents (provided by the Rental Company)
- Service and repair records
- Certificates of traceability for reference standards.

The calibration activity will be recorded in the field logbook. Calibration data will be recorded in the Instrument Calibration Log and/or the field logbook. Examples of Instrument Calibration Log are included in **Attachment A.**

3 Corrective Action

Field instruments can be affected by changes in temperature, humidity, and barometric pressure. Instrument calibration should be checked when significant changes in weather occur. In addition, instrument calibration should be checked if maintenance activities (e.g. battery replacement, lamp replacement, or refueling) are required, if instrument malfunctions occur, or when questionable readings are observed.

Corrections and reviews of calibration records will be completed in accordance with the SOP for Field Notes and Documentation. Errors will be corrected by drawing a single line through the error, entering the correct information, initialing, and dating the change. Materials that obliterate the original information, such as correction fluids and/or mark-out tapes, are prohibited. All corrections will be initialed and dated.

Attachment A Examples of Instrument Calibration Forms

003 EHS Field Form
Instrument Calibration Log

Multi-Parameter Water Meter	
Project Name	Equipment Type
Project Location	Make/Model/Serial No.
Project Number	Page _____ of _____

Calibration Reference Solution					
	Parameter	Standard	Units	Buffer Expiration Date	
	pH	4.01	S.U.		
		7			
		10.01			
	Conductivity				
	ORP				

Date/Time	Calibrated By	Temp	pH Standard 1	pH Standard 2	pH Standard 3	Conductivity	ORP (Redox)	Dissolved Oxygen	Comment
		C°	*7*			*___ S/cm*	*mV*	*mg/L*	

004 EHS Field Form
PID Instrument Calibration Log

Photoionization Detector or Single Gas Meter	
Project Name	Equipment Type
Project Location	Make/Model/Serial No.
Project Number	Page _____ of _____
Calibration	
Calibration Gas Type	Calibration Standard Concentration

Date/Time	Calibrated By	Calibration Results	Comments

005 EHS Field Form
Bump Test Form

Multi-Gas Meter Bump Test Log	
Project Name	Equipment Type
Project Location	Make/Model/Serial No.
Project Number	Page _____ of _____
Calibration	
Calibration Gas Type	Calibration Standard Concentration

Bump Test

Date/Time	Calibrated By	Did Bump Test Pass?	Comments

Attachment B Calibration and Maintenance – Portable Multi-Probe Water Quality Meter

ATT B SOP-08 Field Equipment Operation and Calibration Attachment B – Water Quality Meter

EHS Support

July 2018

1 Portable Multi-Parameter Water Quality Probe Calibration

Water quality meters and instruments vary by manufacturer and model number. Instructions for maintenance and operation of all these field instruments are described in the operation manuals provided by the manufacturer. The manufacturer's manual should take precedent over the procedures described herein. The procedures described below are for portable multi-parameter water quality probes such as the YSI 556 or AquaProbe. Additional probes, such as a total dissolved solid or salinity, are available and should be used as directed by the Project Plan and calibrated according to the manufacturer's manual.

Figure 1 Example of AquaProbe® AP-5000 Multi-parameter Probe and Multi-parameter Readout Instrument (YSI 556).

If a "RapidCal" or "QuickCal" option is available for the instrument, initiate the calibration and follow the calibration prompts. The volume of the calibration solutions must be sufficient to cover both the probe and temperature sensor (see manufacturer's instructions for additional information). While calibrating or measuring, make sure there are no air bubbles lodged between the probe and the probe guard.

1.1 pH

Calibrate daily using at minimum a 2-point calibration method. A 2-point calibration uses two pH reference standard solutions (for example, pH 4 and pH 7 or pH 7 and pH 10) and is valuable only if the water being monitored is known to be either basic or acidic. For example, if the pH is known to vary between 5.5 and 7, a 2-point calibration with a pH 7 and pH 4 reference standard solution is sufficient.

If the pH of water being measured is unknown, a 3-point calibration method is preferred. Using this calibration, the pH sensor is calibrated with a pH 7 standard and two additional reference standards (such as pH 4 and pH 10). The 3-point calibration method accounts for the full pH range and assures maximum accuracy when the pH of the media to be monitored cannot be anticipated. Typically, the procedure for a 3-point calibration is the same as for a 2-point calibration, but the instrument may prompt you to select a third pH reference standard.

1.1.1 pH Calibration Procedure

1. Allow the reference standards to equilibrate to the ambient temperature.

ATT C SOP-08 Field Equipment Operation and Calibration Attachment B – Portable Gas Meter

EHS Support

July 2018

1 Portable Gas Meter

Many instruments are available for organic vapor monitoring, as well as monitoring of explosive atmosphere, oxygen levels, toxic gas, and airborne dust. Because it is beyond the scope of this SOP to describe all these alternatives, this SOP will focus on conducting air monitoring using a PID. In addition, the purpose of a function check (also known as a bump test) will be discussed; however, the calibration of a multi-gas meters (e.g., 4-gas meters, oxygen, hydrogen sulfide) will not be included in this SOP. Calibration of a multi-gas meters should follow recommended instructions in the manufacturer's manual.

All field air monitoring equipment will be calibrated onsite.

1.1 Function Check (Bump Test)

The function check (bump test) is a qualitative function check in which a challenge gas is passed over the sensor(s) at a concentration and exposure time sufficient to activate all alarm settings. The purpose of this check is to confirm that gas can get to the sensor(s) and that all the instrument's alarms are functional. The bump test or function check verifies that audible and visual alarms are activated and does not provide a measure of the instrument's accuracy.

Figure 1 Examples of Multi-Gas Meters (Rae System, BW Honeywell)

1.1.1 Bump Test Procedure

The bump test procedure is simple and easy, usually taking less than a minute to perform.

1. Turn on the equipment and allow the temperature of the unit to equilibrate to its surrounding.
2. Connect the tubing from the challenge gas to the gas monitor intake.
3. If tubing contains an in-line balloon, pinch off the middle of the tubing.
4. Turn on or open the challenge gas valve. If tubing contains an in-line balloon, allow balloon to inflate slightly, but not burst. If balloon bursts, replace balloon.
5. If visual and audible alarms come one, the bump test is successful. Turn off the challenge gas and remove the tubing from the meter.
6. If alarms do not come on, trouble shoot to assess cause (e.g., is challenge gas valve open, does the meter require calibration or repair).
7. Document the bump test results.
8. Return the PID to a secure area. Clean the instrument.

9. Connect the instrument to charger and plug in the charger. The probe must be connected to the readout unit to ensure that the unit accepts a charge.

1.2 Photoionization Detector

The PID is generally set to factory defaults for alarm limits, and unless directed, shipped to the renter with alarm limits specific to isobutylene (100 ppm). Calibrating the PID is a two-point process using "fresh air "and a standard reference gas (also known as span gas). First, a "Fresh air" calibration that contains no detectable volatile organic compounds (0.0 ppm) is used to set the zero point for the sensor. Then a standard reference gas that contains a known concentration of a given gas is used to set the second point of reference.

Figure 2 Examples of hand-held PIDs (RAE Systems, PhoCheck)

1.2.1 PID Calibration Procedures

1. Allow the temperature of the unit to equilibrate to its surrounding.
2. Verify the alarm limits are input correctly for the span gas (e.g., isobutylene). If the span gas or alarm limits on monitor do not match the span gas being used, consult with the manufacturer's manual, and change the limits as appropriate.
3. To perform a fresh air calibration, use the calibration adapter to connect to the PID to a "fresh" air source such as a "zero-gas" cylinder or "zero-gas" transferred into a Tedlar® bag. The "fresh" air is clean dry air without any organic impurities. If such an air cylinder is not available, any clean ambient air without detectable contaminants can be used.
4. Chose the "Fresh Air Cal" or similar under the menu prompt.
5. Open the Tedlar® bag valve or cylinder valve to initiate flow through the tubing into the instrument sensor. There can be a 3 to 5-second delay in read-out depending upon the instruments sensitivity.
6. Allow instrument to run during the test until prompted to accept the test result.
7. Turn off any flow of gas.
8. Record the reference standard and result in the Instrument Calibration Log.
9. To perform the span gas calibration, attach a flow-limiting regulator to span gas cylinder. The regulator flow must match or exceed the intake pump of the meter. Alternatively, the span gas can be transferred to a Tedlar® bag.
10. Chose the "Span Gas Cal" or similar under the menu prompt.
11. Open the Tedlar® bag valve containing the span gas or the span gas cylinder valve to initiate flow through the tubing into the instrument sensor.

12. Allow the instrument to run during the calibration test until prompted to accept the test results. The calibration results should be very close to the span gas concentration. If within 10% of the span gas concentration, the calibration is considered complete.
13. Turn off any flow of gas.
14. Record the reference standard and result in the Instrument Calibration Log.
15. Return to the "Ready" prompt and press "Yes" button to use the instrument during the day.
16. At the end of the day or work shift, turn the instrument to OFF.
17. Return the PID to a secure area. Clean the instrument.
18. Connect the instrument to charger and plug in the charger. The probe must be connected to the readout unit to ensure that the unit accepts a charge.

1.2.2 PID Equipment Maintenance

Daily maintenance generally includes cleaning of the outside of the equipment and ensuring the PID lamp remains free of moisture. The white filter tip used to protect the PID lamp should be discarded and replaced if it becomes soiled or wet. If the PID lamp needs to be cleaned or replaced, consult the manufacturer's manual. In many cases, a replacement or backup PID should be used so the malfunctioning instrument can be repaired.

2. The calibration container should be filled with the reference standard solution, so the pH probe and temperature sensor are immersed in the reference standard.
3. Record reference standard solution information and temperature on the Instrument Calibration Log (Attachment A). Temperature can affect the pH, therefore enter the pH calibration values based on the appropriate temperature as labeled on the pH calibration solutions used or according to **Table 1**, below.
4. Record the final pH calibration reading, with the corresponding temperature, on the Field Calibration Sheet.
5. Remove probe from its storage container and rinse with a small amount of reference standard.
6. Select monitoring/run mode for pH calibration on the data logger or screen prompt. Immerse probe into the initial reference standard (e.g., pH 7).
7. Enter the reference standard value (e.g., 7) into the instrument. The readings should remain within manufacturer's specifications. If they change, re-calibrate. If readings continue to change after re-calibration, consult manufacturer.
8. Remove probe from the reference standard and rinse with a small amount of initial standard.
9. Immerse probe into the second standard (e.g., pH 4). Repeat step 5
10. If instrument only accepts two standards, the calibration is complete. Go to step 10.
11. Immerse probe in third buffered standard (e.g., pH 10) and repeat steps 5 to 7.
12. Remove probe from the third standard and record results.
13. Toggle from Calibration Mode to Monitoring/Run mode. To ensure the initial calibration standard (e.g., pH 7) has not changed, immerse the probe into the initial standard. Wait for the readings to stabilize. The reading should read the initial standard. If not, recalibrate.

Table 1 pH Buffer Solution Values Based on Temperature

Temperature	pH Buffer			Temperature	pH Buffer		
°C	4.01	7.0	10.01	°C	4.01	7.0	10.01
0	4	7.11	10.32	24	4.01	7	10.02
1	4	7.11	10.31	25	4.01	7	10.01
2	4	7.1	10.29	26	4.01	6.99	10
3	4	7.09	10.28	27	4.01	6.99	9.99
4	4	7.09	10.26	28	4.01	6.99	9.98
5	4	7.08	10.25	29	4.01	6.99	9.98
6	4	7.08	10.23	30	4.02	6.98	9.97
7	4	7.07	10.22	31	4.02	6.98	9.96
8	4	7.07	10.21	32	4.02	6.98	9.95
9	4	7.06	10.2	33	4.02	6.98	9.94
10	4	7.06	10.18	34	4.02	6.98	9.93
11	4	7.05	10.17	35	4.02	6.97	9.93
12	4	7.05	10.16	36	4.03	6.97	9.92
13	4	7.04	10.14	37	4.03	6.97	9.91
14	4	7.04	10.13	38	4.03	6.97	9.9

Temperature	pH Buffer			Temperature	pH Buffer		
15	4	7.03	10.12	39	4.03	6.97	9.9
16	4	7.03	10.11	40	4.03	6.97	9.89
17	4	7.02	10.10	41	4.04	6.97	9.88
18	4	7.02	10.09	42	4.04	6.97	9.88
19	4	7.02	10.08	43	4.04	6.96	9.87
20	4	7.01	10.06	44	4.04	6.96	9.86
21	4.01	7.01	10.05	45	4.04	6.96	9.86
22	4.01	7.01	10.04	46	4.05	6.96	9.85
23	4.01	7	10.03	47	4.05	6.96	9.85

1.1.2 pH Probe Storage and Maintenance

A pH meter with a glass probe needs to be stored wet. It is best to use an "electrode storage solution" or a pH 4 or 7 buffer but tap water will sometimes work for short storage periods. Never use distilled or deionized water for storage; this will ruin the probe. During storage, the probe can be immersed in the storage solution or in contact with a soaked sponge or paper towel, the cap for the probe will typically have a sponge or a reservoir to fill with solution. If a probe dries out, usually it can be reconditioned by soaking in a storage or buffer solution for a few hours.

Electrodes with glass membranes can get dirty after heavy use, which affects the sensitivity of the electrode. Soaking the electrode in an “electrode cleaner solution” will help. The typical lifetime of a glass pH probe is about 6 months to 2 years, dependent upon if the pH probe is used correctly and is properly maintained. Most meters will allow you to change out the electrode when it is time for replacement.

1.2 Conductivity

Perform calibration for conductivity according to the recommended manufacturer’s calibration instructions. Conductivity is generally calibrated for Specific Conductance and entered as milliSiemens per centimeter (mS/cm) at 25 degrees Celsius (°C). Conductivity standard solution at 25°C has a specific conductance value of 1.413 mS/cm (also 1413 microSiemens per centimeter (µS/cm) or 1413 µmho/cm) when at a temperature of 25°C. If the temperature varies from 25°C, the conductivity will vary from the standard. Record the reference standard solution information and conductivity reading with the corresponding temperature on the Instrument Calibration Log.

1.2.1 Conductivity Calibration Procedure

1. Allow the calibration standard to equilibrate to the ambient temperature.
2. Remove probe from its storage container, rinse the probe with a small amount of the conductivity reference standard (discard the rinsate), and place the probe into the reference standard.
3. Select the Monitoring/Run mode. Allow the probe temperature to stabilize.

4. Look up the conductivity value at this temperature from the conductivity versus temperature correction table (**Table 2**). Select Calibration Mode, then Conductivity. Enter the temperature corrected conductivity value into the instrument.

Table 2 Value Relationship of a 1,413 µS/cm (1.413 mS/cm) Reference Standard to Temperature

Temperature	Conductivity Standard	Temperature	Conductivity Standard
°C	**1413 µS/cm**	**°C**	**1413 µS/cm**
0	776	24	1386
1	799	25	1413
2	822	26	1441
3	846	27	1468
4	870	28	1496
5	894	29	1524
6	918	30	1552
7	943	31	1580
8	968	32	1608
9	992	33	1636
10	1017	34	1665
11	1043	35	1693
12	1068	36	1722
13	1094	37	1751
14	1119	38	1780
15	1145	39	1808
16	1171	40	1837
17	1198	41	1866
18	1224	42	1896
19	1251	43	1925
20	1277	44	1954
21	1304	45	1983
22	1331	46	2013
23	1358	47	2042

5. Select Monitoring/Run Mode. The reading should remain within manufacturer's specifications. If it does not, recalibrate.

Read the conductivity value on the instrument and compare the value to the specific conductance value on Table 2. The instrument value should agree with the standard within the manufacturer's specifications. If not, re-calibrate. If the re-calibration does not correct the problem, the probe may need to be cleaned or serviced by the instrument manufacturer.

1.2.2 Conductivity Probe Storage and Maintenance

These probes can usually be stored dry. Conductivity probes can get dirty over time, which interferes with the flow of electricity and can skew measurements. Clean the probes as recommended in the manufacturer's manual.

1.3 Oxygen Reduction Potential (ORP)

Most ORP meters are pre-calibrated in the factory and do not need to be calibrated before use. If verification of accuracy is needed there are "validation solutions" which show if a meter is reading correctly. A calibration check of the ORP probe can be performed by placing it into a Zobell™ solution that is within approximately 10°C of the expected groundwater temperature, or as close to groundwater or surface water temperature as practical.

1.3.1 ORP Calibration Procedures

1. If the instrument instruction manual states that the instrument is factory calibrated, then verify the factory calibration against the standard. If they do not agree within the specifications of the instrument, the instrument will need to be re-calibrated by the manufacturer.
2. Remove the probe from its storage container and place it into the standard.
3. Select Monitoring/Run Mode.
4. Wait for the probe temperature to stabilize, then record the temperature.
5. Look up the millivolt (mv) value at this temperature from the millivolt versus temperature correction table usually found on the standard bottle, on the standard instruction sheet, or in the manufacturer's manual. You may need to interpolate millivolt value between temperatures.
6. Select Calibration Mode, then "ORP". Enter the temperature-corrected ORP value into the instrument.

Select Monitoring/Run Mode. The readings should remain unchanged within manufacturer's specifications. If they change, recalibrate.

1.3.2 ORP Probe Storage and Maintenance

ORP meters are stored wet in a storage or buffer solution, and not in deionized/distilled water. If left dry, the probe can be reconditioned by soaking in a storage or buffer solution for about one hour. Electrode cleaning solutions should be used as needed to keep the probe clean and working correctly.

1.4 Dissolved Oxygen

Most meters allow calibration of the DO meter in air or against a wet sponge or paper towel, which gives a "saturated air" calibration. The only solution typically used for calibrating a DO meter is a "zero-oxygen" solution. This solution is used only if the samples being measured have very low oxygen concentrations.

There are two primary types of dissolved oxygen sensing technologies available: the optical based sensing method, which is commonly referred to as luminescent, and the Clark electrochemical or membrane-covered electrode. Within these two types of technologies, there are slight variations to calibration and measurement. Check the manufacturer's manual to ascertain the requirements of the probe being used.

1.4.1 DO Calibration Procedure

1. Place a wet piece of cloth or paper towel in the cap that covers the probe. The probe should not come in contact with the wet cloth or towel. The probe must fit tightly into the container to prevent the escape of moisture evaporating from the sponge or towel.
2. Turn on the instrument to allow the DO probe to warm up.
3. Allow the confined air to become saturated with water vapor (saturation occurs in approximately 10 to 15 minutes). Select Monitoring/Run Mode. Check temperature. Readings must stabilize before continuing to the next step.
4. Select Calibration Mode; then select "DO %".
5. Enter the local barometric pressure (usually in millimeters of mercury) for the sampling location into the instrument. This measurement must be determined from a local barometer. Do not use barometric pressure obtained from the local weather services unless the pressure is corrected for the elevation of the sampling location. [Note: inches of mercury times 25.4 mm/inch equals mm of mercury or consult Oxygen Solubility at Indicated Pressure chart attached to the SOP for conversion at selected pressures].
6. The instrument should indicate that the calibration is in progress. The instrument will take one minute or more to calibrate. After calibration, the instrument should display %-saturated DO.
7. Record the result in the Instrument Calibration Log.
8. Select Monitoring/Run Mode. Compare the DO (mg/L) reading to the Oxygen Solubility at Indicated Pressure chart as provided in the Equipment Manual. The numbers should agree. If they do not agree to the accuracy of the instrument (usually ± 0.2 mg/L), repeat calibration. If this does not work, change the membrane and electrolyte solution.
9. If a DO reference standard is used, remove the probe from the container and place it into a 0.0 mg/L DO standard. The standard must be filled to the top of its container and the DO probe must fit tightly into the standard's container (no headspace). Check temperature readings, as they must stabilize before continuing.
10. Wait until the "mg/L DO" readings have stabilized. The instrument should read 0.0 mg/L or to the accuracy of the instrument (usually ± 0.2 mg/L). If the instrument cannot reach these values, it will be necessary to clean the probe, and change the membrane and electrolyte solution. If this does not work, prepare a new 0.0 mg/L DO standard. If these measures do not work, contact manufacturer.
11. Record the result in the Instrument Calibration Log.

Check the dissolved oxygen reading against the theoretical value of saturated oxygen at different elevations. If the instrument is not reading in the proper range, it should be recalibrated, or the dissolved oxygen probe membrane should be replaced.

1.4.2 DO Probe Storage and Maintenance

Dissolved oxygen meters that use membranes should be stored wet to prevent the electrolyte solution and membrane from drying out. This can be done by submerging the probe in tap water or placing it against a moistened sponge, which many meters include for storage. If the probe dries out, the electrolyte solution and membrane may have to be changed.

Dissolved oxygen probes with membranes should have the membrane and electrolyte solution changed about every 2 months with normal use. Continual use may also result in deposits accumulating on the metal cathode. The deposits can be removed by removing the membrane from the DO sensor tip, and lightly brushing the metal end with very fine sandpaper (400 grit). Multi-parameter meters typically come with a maintenance kit that includes membranes, electrolyte solution, and a sanding disk.

Optical DO meters do not contain electrolyte solution or membranes, so they can be stored dry. Optical DO meters do not need any maintenance except for changing the sensing element, typically once a year with normal use.

1.5 Turbidity

Turbidity meters have calibration standards that are usually between 0 and 1000 nephelometric units (NTU). Most turbidity meter kits come with a set of these standards. When choosing which calibration standards to use, choose a reference standard that is near the anticipated turbidity of the water sample. The more reference standards used during the calibration, the better the accuracy.

1.5.1 Turbidity Calibration Procedures

1. Using a standard in the range of 5 to 20 NTUs, calibrate according to manufacturer's instructions or verify calibration if instrument will not accept a second standard. If verifying, the instrument should read standard value to within the specifications of the instrument. If the instrument has range of scales, check each range that will be used during the sampling event with a standard that falls within that range.
2. Record the results in the Instrument Calibration Log.

1.5.2 Turbidity Probe Storage and Maintenance

There are no storage requirements. The only maintenance involves the glass cuvettes. Light must be able to pass through the cuvettes, so if there are scratches, dirt or even oils from fingers on the sides of the cuvettes, it could skew the measurements. Make sure the cuvettes are clean, dry, and free of scratches before placed in the turbidity meter.

Attachment C Portable Gas Meters

SOP-09 Field Equipment Decontamination

Purpose

The purpose of this SOP is to provide procedures for field decontamination of environmental sampling equipment and personal protective equipment (PPE). Decontamination of equipment and PPE is designed to ensure that sample cross-contamination, human-health exposure, and contamination transport is minimized.

This SOP covers field decontamination of small re-useable equipment using a manual cleaning application. Procedural modifications may be warranted depending on field conditions, equipment limitations, or limitations imposed by the procedure. Construction of a decontamination station, use of a high-pressure spray washer, and decontamination of heavy equipment and machinery is addressed under SOP-10 Drill Rig and Heavy Equipment Decontamination.

Relevant EHS Support SOPs

- SOP-04 Field Documentation
- SOP-06 Pre-Field Mobilization
- SOP-07 Investigative Derived Waste
- SOP-10 Drill Rig and Heavy Machinery Decontamination
- SOP-12 Quality Assurance/Quality Control Samples
- Any SOP that references using small equipment or re-used equipment

Attachments

Attachment A Soluble Contaminants and Recommended Solvent Rinse

Required Materials

- Field logbook and field documentation
- Site maps, site layouts, site plans
- Health and Safety Plan (HASP)
- Appropriate personal protective equipment (PPE)
- Brushes and flat-blade scrapers
- Hand-held spray bottles
- Water - potable water, rinsate water
- Laboratory-grade non-phosphate detergent
- Additional cleaning agents, as specified in the project work plan, with appropriate safety data sheets
- Plastic waste bags or sheeting
- Waste containers (55-gallon drum or similar)

- Wash basins, buckets, pails, or tubs
- Paper towels and/or disposable drying cloths
- Drying shelves, as needed

1 Small Field Equipment Decontamination Guidelines

Decontamination is performed as a quality assurance measure. Improperly decontaminated sampling equipment can lead to misinterpretation of environmental data due to interference caused by cross-contamination between samples or sample locations through use of contaminated equipment. Decontamination also protects field personnel from potential exposure to hazardous materials on equipment. Proper PPE will be worn when conducting decontamination procedures.

1.1 Decontamination Area

The decontamination area should be located, if possible, where decontamination fluids and soil wastes can be easily discarded or discharged in accordance with the project plan or waste management plan. Select the decontamination area so decontamination investigative derived wastes (IDW) can be managed in a controlled area with minimal risk to the surrounding environment. The decontamination area should be large enough to allow temporary storage of equipment and materials, drum or waste storage, and if required to contain a large area for decontamination of large equipment (e.g., for heavy equipment or hollow-stem auger). Large equipment decontamination and decontamination pad construction for large equipment decontamination procedures can be referenced in SOP-10 Drill Rig and Heavy Machinery Decontamination.

Smaller decontamination areas, such as equipment decontamination between groundwater or surface water sample locations, may take place at the sampling location. In this case, required decontamination supplies and equipment must be mobilized to the location. Bucket and decontamination stations may be placed on plastic sheeting, or in basins, or tubs to capture decontamination IDW. Decontamination materials, including wastes, should be stored in central location(s) to maintain control over the materials used or produced throughout the investigation program.

1.2 Decontamination Considerations

- No hand to mouth contact (e.g., eating, smoking, drinking, chewing) shall be permitted during decontamination activities.
- All contaminated equipment shall be disassembled to the extent practical to allow for thorough decontamination procedures.
- If heavy residuals (e.g., petroleum, creosote) are encountered during field activities, an appropriate solvent (e.g., methanol) should be considered to remove any residues from equipment. If additional solvents are required and approved per the project plan or Project Manager, the solvent must be properly used, collected, stored, and disposed of according to the investigative derived waste plan, health and safety plan, and/or material safety data sheet. Take care that materials and solutions used for decontamination procedures are not hazardous themselves or could potentially contaminate samples (that is, are acids and solvents). Necessary precautions should be used if handling detergents and reagents, if used. A generalized solvent or reagent summary for few contaminants is included in Attachment A.
- Personal protective equipment (PPE) shall be worn to avoid splashing, skin contact, and incidental ingestion during decontamination procedures.

- Necessary precautions shall be used when handling detergents and reagents, if used.
- Quality assurance/quality control measures, if required, will be specified in the Project's Work Plan.

1.3 General Decontamination Procedures

Field equipment for decontamination may include a variety of items used in the field for monitoring and/or for collection of soil, sediment, and/or water samples, such as water level meters, certain water quality monitoring meters (check with manufacturer for suggested decontamination procedure), split-spoon samplers, trowels, scoops, spoons, and pumps. Dedicated equipment is not usually decontaminated, as a general rule. Disposable equipment (e.g., bailers, rope, EnCore™ samplers, and filters) will be properly discarded after use.

Decontamination will occur before use, between sample locations, and prior to transporting off-site for re-used or non-disposable equipment. Rental equipment used in the field, which is being returned to the respective vendor, will be decontaminated prior to shipment. Conduct consistent decontamination of sampling equipment to ensure the quality of the samples collected.

Equipment decontamination is comprised of four general steps.

1. Removal of gross (visible) contamination
2. Removal of residual contamination
3. Prevention of recontamination
4. Disposal of wastes associated with the decontamination

Decontamination Caution: Some types of decontamination procedures require the use of solvents or rinsates which may be chemical specific. A general Soluble Contaminants and Recommended Solvent Rinse (EPA, 1994) is provided in **Attachment A**; however, the table may be limiting and not appropriate for the scope of work. Safety Data Sheets should be included in the project Health and Safety Plan or available for reference.

1.4 Small Equipment Decontamination Procedures

Small equipment generally includes soil sampling equipment (e.g., trowels, split spoon samplers, hand augers, water interface probes). Small equipment decontamination procedures will be generally conducted as follows:

1. Remove any gross contamination from the equipment. Gross contamination generally applies to soil sampling equipment that may have residue clinging to the equipment. The clinging residual soil can usually be removed by dry brushing or scraping, or in some cases using a high-pressure sprayer. Removal of gross contamination should be done close to the source of contamination.
2. Remove residual contamination including film or other particles. This generally consists of a series of sprayers, buckets, or basins used to wash and rinse the equipment.

3. Wash equipment vigorously with a bristle brush or similar in a bucket containing potable water with non-phosphate lab-grade detergent such as Liquinox®, Alconox®, or equivalent.
4. Rinse equipment thoroughly in a second bucket containing potable water (1st rinse).
5. Rinse equipment thoroughly with distilled or deionized water (2nd rinse).
6. In few instances, such as decontaminant of sensitive field instruments, it may be necessary to rinse equipment with distilled, deionized, or American Society for Testing and Materials International (ASTM) reagent grade water (3rd rinse).
7. Allow equipment to air dry in an area free from contact with contaminants. All decontaminated equipment should be dry prior to use. A decontaminated metal drying rack may be used to aid in the drying process.
8. Decontamination equipment should be stored to preserve the clean status. This step will vary on the nature of the equipment. Protection measures may include covering or wrapping the equipment in plastic or aluminum foil. Only personnel wearing clean protective gloves (e.g., nitrile, latex) should handle the decontaminated equipment to prevent re-contamination.
9. If the decontaminated equipment is not to be used immediately after cleaning, it should be covered or wrapped to protect the equipment from contaminants.
10. Replace dirty detergent water solution and rinsate(s) between borings, sample locations, or as deemed appropriate to limit cross-contamination.
11. Document the procedure used, fluids used, and any changes into a bound field notebook or on project-specific forms.
12. Waste decontamination materials such as spent liquids and solids will be collected and managed in accordance with SOP-07 Investigative Derived Waste.

1.5 Groundwater Sampling Decontamination Procedures

Proper decontamination between monitoring wells is essential on equipment such as submersible or bladder pumps in which mechanisms of the pump come in direct contact with potentially contaminated water. This SOP does not address decontamination of re-useable bailers. The following steps shall be used for contaminated pumps:

1. Disassemble the equipment to the extent practical.
2. Wash any small mechanism of the pump assembly (e.g., check valve, tube adapter)
3. Wash the exterior of the pump casing vigorously with a bristle brush or equivalent in a bucket containing potable water with non-phosphate lab-grade detergent such as Liquinox®, Alconox®, or equivalent. A bottle brush may be used to clean the interior of pump casing.
4. If decontaminating a pump in which sample water comes in contact with internal mechanisms of the pump system, place the pump into a potable water wash container containing non-phosphate lab-grade detergent. Ensure the pump intake is fully submerged and the pump outlet is allowed to flow directly back into the wash container. Energize the pump at a very low flow rate to allow the wash water to recirculate through the pump mechanism for 2 to 5 minutes.
5. Rinse the external portion of the pump using potable water (1st rinse). Submerge the pump intake into potable water (1st rinse) and energize the pump to recirculate the rinse water through the pump mechanism.
6. Use distilled, deionized, or ASTM reagent grade water (2nd rinse) as necessary to the external and internal portions of the pump and pump mechanisms.

7. Dry off excess water with a clean paper towel or disposable cloth.
8. Reassemble the pump.
9. Replace dirty detergent water solution and rinsate(s) between sample locations or as deemed appropriate to limit cross-contamination.
10. Document the procedure used, fluids used, and any changes into a bound field notebook or on project-specific forms.

2 Records

Field logbook and field documentation will be completed in accordance with SOP-04 Field Documentation. Detailed records will be maintained about decontamination procedures. Required records may include details about:

- Decontamination personnel
- Decontamination solutions types and methods
- Date and time of decontamination
- Decontamination station location
- Equipment type or identification numbers
- Decontamination solution Lot numbers
- Any problems encountered, observations, or alterations
- Safety Data Sheets for any specialized chemicals used in the decontamination process
- Volume of decontamination materials generated (IDW log)

Attachment A Soluble Contaminants and Recommended Solvent Rinse

APPENDIX A

Table

Table 1. Soluble Contaminants and Recommended Solvent Rinse

TABLE 1 Soluble Contaminants and Recommended Solvent Rinse		
SOLVENT[1]	EXAMPLES OF SOLVENTS	SOLUBLE CONTAMINANTS
Water	Deionized water Tap water	Low-chain hydrocarbons Inorganic compounds Salts Some organic acids and other polar compounds
Dilute Acids	Nitric acid Acetic acid Boric acid	Basic (caustic) compounds (e.g., amines and hydrazines)
Dilute Bases	Sodium bicarbonate (e.g., soap detergent)	Acidic compounds Phenol Thiols Some nitro and sulfonic compounds
Organic Solvents [2]	Alcohols Ethers Ketones Aromatics Straight chain alkalines (e.g., hexane) Common petroleum products (e.g., fuel, oil, kerosene)	Nonpolar compounds (e.g., some organic compounds)
Organic Solvent[2]	Hexane	PCBs

[1] - Material safety data sheets are required for all decontamination solvents or solutions as required by the Hazard Communication Standard

[2] - WARNING: Some organic solvents can permeate and/or degrade the protective clothing

SOP-12 Quality Assurance/Quality Control Samples

Purpose

The purpose of this standard operating procedure (SOP) is to give details to the quality control (QC) measures taken to ensure the integrity of the samples collected, and to establish the guidelines for the collection of QC samples. The objective of the QC program is to ensure that quality data of known and reliable quality are developed.

Documentation of representative data is essential to site investigations; therefore, the data must be validated though the performance of QC sampling. Verification performance sampling is necessary to evaluate and identify contradictory or suspect data. The project manager must determine the QC sampling requirements. Data validation measures must be specified as part of all environmental investigations. The collection of field QC samples serves to ensure proper field procedures, but can also serve as a mechanism for the laboratory to perform their quality assurance/quality control (QA/QC) program [such as collecting sufficient sample volume to allow the laboratory to perform a matrix spike (MS)/matrix spike duplicate (MSD) on their equipment or method].

Relevant EHS Support SOPs

- SOP-04 Field Documentation
- SOP-05 Sample Management and Shipping
- SOP-09 Equipment Decontamination
- SOP-22 Soil Sampling for Chemical Analysis
- SOP-46 Groundwater Sampling for Chemical Analysis
- SOP-61 Surface Water Sampling
- SOP-62 Sediment Sampling

Required Materials

Equipment used during collection of QC samples will be the same equipment utilized to collect the primary or parent sample, which may include a wide variety of tools depending upon the media sampled, type of sampling, and methods used.

- Field logbook and field documentation
- Site maps, site layouts, site plans
- Health and Safety Plan
- Appropriate personal protective equipment (PPE)
- Black waterproof and/or indelible ink pens
- Quality control bottle sets
- Other laboratory-supplied quality control bottle types (e.g., trip blanks, temperature blanks)

- Appropriate sample containers, sampling kits, labels, coolers and ice, Chain of Custody forms

1 Quality Assurance/Quality Control Samples

In order to assess the accuracy and precision of the field methods and laboratory analytical procedures, QA/QC samples are collected during the sampling program according to the project work plan. The QA/QC samples may be labeled with QA/QC identification numbers or fictitious identification numbers (if blind submittal is desired) and are sent to the laboratory with the other samples for analyses. The frequency, types, and locations of QC (field-specific) samples will be specified in the project work plan or the site specific quality assurance project plan (QAPP). Types of quality control samples may include duplicate, trip blank, equipment blank, field blank, matrix spike and matrix spike duplicate, and temperature blank.

The QA/QC samples could be sampled on any sample media such as soil, groundwater, surface water, sediments (SOP 22, SOP-42, SOP-61, and SOP-62) or project-specific media. Field documentation (SOP-04) and sample management and shipping (SOP-05) will be used for any QA/QC samples generated during the investigation process. Naming of QA/QC samples should be provided in the project work plan or QAPP.

1.1 Duplicate Samples

Duplicate sample analysis evaluates the precision of field and laboratory components of field samples and matrix heterogeneity. Duplicate samples are two physical samples collected simultaneously from the same location under identical conditions. The project work plan will determine if the duplicate sample is homogenized. A duplicate sample should be:

- Collected for any media sampled in the field.
- Collected in accordance with the sample collection procedures identified in the project work plan.
- The work plan should identify the ratio of duplicate sample collection per primary samples; however, if the ratio is not addressed in the project work plan, duplicate samples will be collected at a rate of 1 duplicate sampled per 20 samples (5%).
- Submitted for laboratory analysis for the same or a subset of the analysis requested for the primary (or parent) sample.
- Handled and preserved in the same manner as the primary sample.

To collect duplicate samples:

1. Collect the duplicate sample concurrently with the primary (or parent) sample (e.g., water, surface water, air) or in the next consecutive sample (e.g., soil, sediment). For soil or sediment samples collected in an 18-inch long split barrel that contains three 6-inch long (brass or stainless steel) sleeves of soil, the middle sleeve is designated as the primary sample, then the next sleeve (either the top or bottom sleeve) will be the duplicate sample.
2. Record the duplicate sample name in the field logbook or field documentation, including the chain of custody.

3. Record the duplicate sample location in the field logbook or field documentation. Do not indicate the duplicate location in the chain of custody if the sample will be considered a "blind duplicate."

1.2 Trip Blank

A trip blank sample is a sample of distilled or de-ionized water prepared in the laboratory, which accompanies the samples to and from the field, never opened, until all samples are ready for analysis. The trip blank assesses the potential for in-transit contamination of samples. The trip blank is later opened in the laboratory and analyzed along with field samples for constituent(s) of interest to ascertain whether cross-contamination has occurred during field handling, shipment, or in the laboratory.

- One trip blank (generally one or two 40-milliliter volatile organic analytical vials) should accompany each cooler containing volatile organic compound samples that are being submitted for lab analysis.
- The sample name convention should be dictated in the project work plan. If the nomenclature is not provided in the project work plan, the trip blank should be labeled with the date (e.g., TB-20140531) and/or sequence (TB-2-201405301). The addition of the date streamlines identification of the potentially affected samples in case cross-contamination is suspected during container or sample shipment.
- The trip blank is recorded on the chain of custody, at a minimum, and can be included in the field logbook or field documentation.

1.3 Equipment Blank

The collection of an equipment blank evaluates field decontamination procedures. To collect an equipment blank:

1. Decontaminate the reusable sample equipment (e.g., pump, split spoon sampler, bailer) in accordance with the project work plan or SOP-09 Field Decontamination. If equipment blank is being collected off a supplied material (e.g., tubing, disposable bailer), the supplied material will be unused (new).
2. Run "clean" (e.g., distilled/de-ionized/demonstrated analyte free) water through or down the equipment and into the appropriately labeled sample set.
3. The equipment blank sample set is identical to the sample set being analyzed. (For instance, if the project requires analysis for volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs), the equipment blank sample set will include a bottle set and analysis for VOCs and SVOCs.)
4. In some situations, one equipment blank will be required for each type of sampling procedure (e.g., bailer, soil sampling equipment, etc.).
5. Record the equipment blank sample name in the field logbook or field documentation, including the chain of custody.
6. Record the equipment blank sample location, type of equipment, etc. in the field logbook or field documentation.

7. The equipment blank can be collected one per equipment type, one per borehole, one per day, or as outlined in the project work plan or QAPP.

1.4 Field Blank

A field blank might be necessary where ambient air quality is poor. Taking this field blank would determine if airborne contaminants interfere with constituent identification or quantification.

- The field blank will be collected as outlined in the project work plan or QAPP.
- The field blank sample set is identical to the sample set being analyzed. (For instance, if the project work plan requires analysis for VOCs and SVOCs, the equipment blank sample set will include a bottle set and analysis for VOCs and SVOCs).

To collect a field blank:

1. The "clean" (e.g., distilled/de-ionized/demonstrated analyte free) water container will remain unopened until collection of the field blank sample occurs at the designated location.
2. Fill the sample bottle set with "clean" water. Pour clean water directly in to the sample bottles at the designated sample location. The clean water is exposed to the air as it travels from the “clean” water container to the sample container.
3. Record the field blank sample name in the field logbook or field documentation, including the chain of custody.
4. Record the field blank sample location in the field logbook or field documentation.

1.5 Matrix Spike and Matrix Spike Duplicates

An extra volume of sample media may be collected during the sampling event for performance of MS/MSD analyses by the laboratory to assess laboratory accuracy, precision, and matrix interference. The laboratory adds spikes of compounds (e.g., standard compound, test substance, etc.) to the additional sample volume to determine if the matrix is interfering with constituent identification or quantification. In addition, MS/MSD samples perform as a check for systematic errors and lack of sensitivity of analytical equipment.

Results of the laboratory analyses are compared with the results of the primary sample and the known concentrations of the spike compounds. The percent recovery and relative percent difference are calculated, and results are used to evaluate the precision and accuracy of the analytical method for various labeled "extra volume samples for MS/MSD." The MS/MSD sample should be:

- Collected for any media sampled in the field.
- Collected in accordance with the sample collection procedures identified in the project work plan.
- The work plan should identify the ratio of MS/MSD sample collection per primary samples; however, if the ratio is not addressed in the project work plan, MS/MSD samples will be collected at a rate of 1 MS/MSD sampled per 20 samples (5%).

- Submitted for laboratory analysis for the same or a subset of the analysis requested for the primary (or parent) sample.
- Handled and preserved in the same manner as the primary sample.

To collect a MS/MSD sample:

1. Collect the duplicate sample concurrently with the primary (or parent) sample (e.g., water, surface water, air) or in the next consecutive sample (e.g., soil, sediment). For soil or sediment samples collected in an 18-inch long split barrel that contains three 6-inch long (brass or stainless steel) sleeves of soil, the middle sleeve is designated as the primary sample, and the top and bottom sleeve will be the designated as the MS/MSD sample.
2. Generally, two to three times the volume of primary sample is required in an MS/MSD sample (or, the sample is collected in triplicate).
3. Identify the MS/MSD is on the chain of custody by indicating the extra volume or number of sample jars, and include a sample identifier or note to indicate the sample is an MS/MSD sample.
4. Record the MS/MSD sample name in the field logbook or field documentation, including the chain of custody.

1.6 Temperature Blank

A temperature blank is a vial of water that accompanies a sample cooler that will be opened and tested upon arrival at the laboratory to ensure the temperature of the contents of the sampling shipping container are within the required 4 degrees (°) Celsius ± 2°. Temperature blanks are generally included for chemical analysis samples that have a temperature requirement.

- The temperature blank requires little attention except to ensure one is in each cooler containing ice.
- Check with the laboratory if a temperature blank is not included in the cooler shipped to the site. A few laboratories are moving to temperature sensors (e.g., infrared sensors) to monitor cooler temperature upon arrival to the laboratory.
- Temperature blanks are generally required for those samples required to be preserved to 4° C ± 2°.
- No documentation is required on temperature blanks by the field staff.

2 Records

Field notes will be kept in a bound field logbook or approved field documentation following the format specified in SOP-04 Field Documentation. Detailed records will be maintained during sampling activities, particularly with respect to the location of QA/QC samples. The following information should be recorded:

- Location of QA/QC sample
- QA/QC sample name
- Type of QA/QC sample
- Sample analysis
- If needed, equipment type the QC sample was collected from
- "Clean" water type (laboratory supplied, grocery store)
- If applicable, weather conditions (e.g., air quality for field blanks)

SOP-41 Fluid Measurement

Purpose

This SOP provides personnel procedures to use in measuring the depth to water, the depth to non-aqueous phase liquids, and the total depths in monitoring wells, piezometers, water bores, or other wells or access points (extraction wells, injection wells, etc.). For this SOP, the term "well," "monitoring well," or "water bore" will be used as the generic term for a water monitoring point.

Relevant EHS Support SOPs

- SOP-04 Field Documentation
- SOP-09 Equipment Decontamination
- SOP-42 Well Development
- SOP-43 to SOP-47 Groundwater Sampling SOPs
- SOP-48 to SOP-50 Aquifer Testing SOPs

Attachments

- Attachment A Fluid Level Monitoring Forms

Required Materials

- Air monitoring instrumentation (e.g., PID) and supplies
- Field logbook and field documentation
- Site plan showing borehole locations
- Health and Safety Plan (HASP)
- Indelible ink pens and waterproof marking pen
- Fluid measurement device (e.g., water level indicator, interface probe)
- Extra batteries
- Paper towels and trash bags
- Decontamination supplies
- Information about the well or borehole including well construction details, previous well gauging data, if available.

1 Fluid Level Monitoring

Water level data is generally used for several purposes during a site investigation, including:

- Determination of horizontal and vertical hydraulic gradients
- Monitoring of changes in groundwater levels over time
- Assessment of surface water/groundwater interaction that occurs during various flow conditions
- Estimation of aquifer properties after aquifer testing
- Calculation of purge volume of standing water in the well for well development or water sampling
- Monitoring recharge during and after purging and aquifer testing.

A water level meter will typically be used to measure the groundwater levels and total depths. If non-aqueous phase liquid (NAPL) is present in the well, an oil-water interface probe will be used. NAPL level data is generally used for purposes of estimating NAPL volume, extent, or properties; and NAPL stabilization or stability.
A number of devices are available for the collection of fluid level measurements in monitoring wells. The most commonly used (and covered in this SOP) include an electric water level sounder and an interface probe (often times called a membrane interface probe or an oil-water interface probe). Other types of water level indicators and recorders include weighted steel tape, chalked tape, sliding float method, airline pressure method, and automatic recording methods (data loggers). These methods are primarily used for closed systems or permanent monitoring wells.

1.1 General Well Monitoring Considerations

General knowledge of the well construction, former fluid levels, and groundwater analytical data is helpful before field mobilization. This data can be useful in determining the monitoring order of the well (less contaminated to more contamination), and can be used to confirm or deny that current measurements comply (within a certain level of accuracy) with historical measurements.

Fluid levels and well depth measurements should be made relative to an established reference point on the well casing and should be documented in the field records. This reference point is usually identified by a permanent marker marking on the top of a polyvinyl chloride (PVC) well riser or by notching the top of casing with a chisel for stainless steel wells. Whether a marking is present or not, the north side of the top of casing is considered the general convention reference point.

Fluid levels should be allowed to equilibrate to atmospheric conditions after removing the sealing caps. Changes in fluid levels generally occur due to:

- Atmospheric pressure changes
- Tidal influences
- Changes in river stage, impoundments levels, or flow in unlined ditches
- Pumping of nearby wells
- Precipitation.

There are no set guidelines and appropriate equilibration times can range from minutes to hours depending on well recharge, local geology and topography, and project objectives. If fluid levels appear to rise or fall during the measurement process, allow at least three to five minutes to assess if levels have stabilized. If levels appear to change, a best determination should be made (i.e., allow more stabilization time) when to collect the water level.

1.2 Water Level Monitoring

Water level meters use a battery-powered probe assembly attached to a cable marked in 0.01-foot (5 millimeters) increments. These types of instruments consist of a spool of dual conductor wire and a probe attached to the end and an indicator. When the probe comes in contact with a fluid, the circuit is closed and a meter light and/or audible buzzer attached to the spool will signal contact. Note: A water level indicator is not capable of distinguishing between water and other fluids with a density close to that of water. Commonly used water level indicators are shown in **Figure 1**.

Figure 1 Water Level Indicators (Solinst and Heron)

Water level measurements are commonly taken in each monitoring well immediately prior to, during, and following well development (SOP-42 Well Development), prior to, during, after well purging and sampling depending on the sampling method (SOP-43 to SOP-47), and for any aquifer testing (SOP-48 to SOP-50). Water level measurements may also be taken to monitor or generate water table or piezometric surfaces. When measuring wells for monitoring potentiometric surface, and if the analytical concentrations in groundwater is known for each of the wells, it is advisable to collect water levels beginning with the least contaminated well(s) and progressing to the most contaminated well(s).

1.2.1 Water Level Measurement Procedures

1. Decontaminate the water level indicator in accordance with the procedures described in SOP-09 Equipment Decontamination.
2. Note well ID, time of day, and date in site logbook or the appropriate field form.
3. Open well and remove well cap.
4. If required in the project work plan, monitor headspace of well with a PID or plan-specified detector to assess presence of volatile organic compounds. Record results.
5. Turn on the indicator. Depress the “test button” to ensure the indicator is operating correctly. When the “test button” is depressed, the meter light should illuminate and the audible buzzer should emit a tone. If not, assess problem.
6. Ensure the indicator’s reel is not “locked.” If it is, loosen the lock.

7. Slowly lower the water level indicator probe down the monitoring well until the probe contacts the water surface, as indicated by the audible alarm. Do not let the probe tip and tape free-fall down the well. Always hold onto the meter's reel handle.
8. Raise the probe slowly out of the water until the audible alarm stops. Continue raising and lowering the probe until a precise level is determined within 0.01 foot or 5 millimeters.
9. Record the water level in the field logbook or approved field documentation.
10. Decontaminate the water level indicator for measurement at the following well.

1.2.2 Total Well Depth Measurements Procedures

Total depth measurements should be routinely conducted on wells as part of routine maintenance (i.e., ensuring the well has not been compromised or is filling with sediment). Collection of total depths for this SOP refers to wells or boreholes that do not have dedicated pumps or extraction equipment (e.g., monitoring wells, piezometers). If total depths are requested on wells that have dedicated equipment, construction, operation, and extraction equipment details should be made available to assess the ability to collect a total depth reading, if a system needs to be de-energized, etc.

A water level indicator should be used to measure the total depths of wells that do not a separate-phase liquid.

Use the following procedures to measure the total depth of a monitoring well:

1. Visually inspect the probe tip. Confirm the zero measurement point **(Figure 2)**.
2. Slowly lower the water level meter until the cable goes slack (assume to be the bottom of the well). Do not let the probe tip and tape free-fall down the well. Always hold onto the meter's reel handle.
3. Gently raise and lower the water level meter probe to tap the bottom of the well.
4. Record the reading on the cable at the established reference point to the nearest 0.01 foot or 5 millimeters.
5. If there is an offset [.g., 0.3 feet (9 cm) for some Solinst or Heron indicators] between the bottom of the probe and the water level sensor **(Figure 2)**, adjust the total depth measurement accordingly (i.e., add the additional length from the zero measurement point).
6. Record the total depth measurement in the field logbook or approved field documentation.

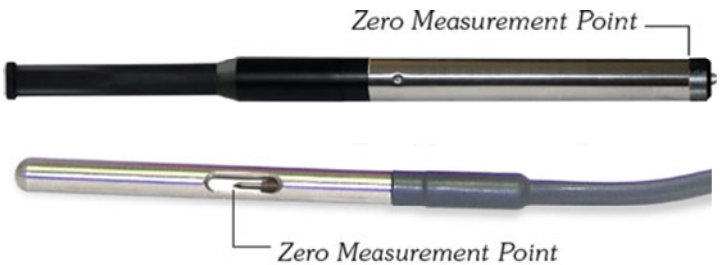

Figure 2 Comparison of Zero Measurement Points at the Top of the Probe and 0.3 Feet (9 cm) Above the Tip of the Probe

1.3 NAPL Monitoring and Procedures

The interface probe device is very similar to a water level indicator in that the probe is operated from a 9-volt battery, is connected to a measuring tape that measures to the nearest 0.01 foot or 5 millimeters, and contains a receiver with an audio and/or visual signal that indicates when phase changes occur. The difference from the water level indicator is that the device detects the difference in conductivity or specific gravity between the aqueous and nonaqueous phases in the well. The device detects the presence of both light NAPL (LNAPL) (floating) and dense NAPL (DNAPL) (sinking) in water wells.

1. Decontaminate the interface probe in accordance with the decontamination procedure described in SOP-09 Equipment Decontamination.
2. Note well ID, time of day, and date in site logbook or the appropriate field form.
3. Open well and remove well cap.
4. If required in the project work plan, monitor headspace of well with a PID or plan-specified detector to assess presence of volatile organic compounds. Record results.
5. Turn on the indicator. Depress the "test button" to ensure the indicator is operating correctly. When the "test button" is depressed, the meter light should illuminate and the audible buzzer should emit a tome. If not, assess problem.
6. Ensure the indicator's reel is not "locked." If it is, loosen.
7. Slowly lower the indicator probe down the monitoring well until the probe contacts the water surface or LNAPL, as indicated by the audible alarm. Do not let the probe tip and tape free-fall down the well. Always hold onto the meter's reel handle.
8. For LNAPL:
   - Raise probe out of LNAPL until the audible alarm stops. Continue raising and lowering the probe until a precise top measurement level is determined within 0.01 foot. Record the depth.
   - Very slowly lower the probe through the LNAPL until any audio (or visual queue) is emitted from the indicator (it is important to go slowly to avoid potential mixing at the LNAPL and water interface). The audio (or visual queue) indicates the phase has passed into water. Raise and lower the probe slowly through the alternative sound depth 2 to 3 times to achieve a better lower depth for the LNAPL depth.
   - Measure the lower LNAPL depth to the nearest 0.01 foot or 5 millimters. Record the depth.
9. For DNAPL:
   - Once the water level depth has been recorded, continue to lower the interface probe through the water column slowly. Do not let the probe tip and tape free-fall down the well.
   - Measure the upper depth of the DNAPL once an audio or visual change is emitted from the indicator. Raise and lower the probe through the alternative sound depth 2 to 3 time to achieve a better upper depth measurement for the DNAPL. Record the depth.
   - Do not continue any measurements through the DNAPL. Retrieve the probe.
10. Decontaminate the interface probe for NAPL measurement at the following well.

Note any change in the tone emitting from the interface probe when gaging for NAPL (along the length of the water column). If changes are noted at a mid-well depth, the indicator may be sensing a NAPL phase or dissolved phase present in the middle of the aquifer (i.e., neither LNAPL nor DNAPL).

1.4 Common Problems and Corrective Actions

All measuring tapes should be inspected prior to use for kinks, cracks, or tears and, if present, repaired or replaced with undamaged equipment. Bends and kinks may affect depth accuracy. The most-common problems that occur during fluid level measurement include:

No signal (audible or visible) when unit is turned on.

- Corrective Action:
  - The battery is discharged. Check or change battery.
  - The circuit is malfunctioning.

No indication of water.

Corrective Action:

- The conductive contact is dirty. Clean the contact.
- There is an open connection in the tape. Replace tape and/or probe. The circuit is malfunctioning.

The signal (audible or visible) is intermittent.
Corrective Action:

- There is an open connection in the tape. Replace tape and/or probe.
- There is a loose connection in the circuit or the probe. Repair the connection.
- Water may be cascading in from a damaged well riser or in from soil or rock layers is in an open-hole or rock well. Continue to lower the tape until the probe contacts water to emit a solid tone.

The signal (audible or visible) is continuous when not in water.
Corrective Action:

- The conductive contact is dirty (causing bridging). Clean the contact.
- There is a short in the tape and/or probe. A short in the tape usually is observed by missing plastic along the tape and exposure to the underlying wire. Replace tape and/or probe.

2 Records

Field notes will be kept in a bound field logbook or approved field documentation following the format specified in SOP-04 Field Documentation. The following information should be recorded when conducting fluid measurements:

- Well identification
- Depths to water, NAPL, and total depth
- Date and time
- Site conditions (e.g., floating oil or debris, gassing)
- Weather observations (e.g.,, wind speed, sunny or cloudy sky)
- Monitoring equipment used
- Any unusual well or groundwater observations.

Attachment A Fluid Level Monitoring Forms

EHS Support

FLUID LEVEL MONITORING FORM

Project: _____

Project Number: _____

Project Location: _____

Field Technician(s): _____

Weather: _____

Equipment: _____

Well ID	Top of Casing Elevation	Ground Surface Elevation	Well Info (from boring logs)			Date	Time	Product Level	Water Level	Total Depth	Comments
	(feet msl)	(feet msl)	Total Depth (feet bgs)	Screened Interval (feet bgs)	Screened Elevation (feet msl)			(feet bTOC)	(feet bTOC)	(feet bTOC)	

msl - mean sea level
bgs - below ground surface
bTOC - below top of casing

Signature: _____

EHS Field Form 021
Issue Date: August 18, 2014
Revision No: 00
Revision Date:

SOP-43 Low Flow Groundwater Sampling

Purpose

The purpose of this standard operating procedure (SOP) is to describe groundwater purging and collection procedures for groundwater samples from wells using low-flow purging and sampling techniques.

This procedure is based on the assumption that groundwater samples are able to be collected using low-flow (minimal drawdown) sampling techniques. Low-flow sampling techniques may not be practical or the best method for the collection of representative groundwater samples in all wells. In the event low-flow sampling techniques are insufficient for use, SOP 44: Groundwater Sampling Using a Volume Purge Technique will be followed to collect the groundwater sample.

Relevant EHS Support SOPs

- SOP-04 Field Documentation
- SOP-05 Sample Management and Shipping
- SOP-08 Field Equipment Operation and Calibration
- SOP-09 Equipment Decontamination
- SOP-41 Fluid Measurement
- SOP-46 Water Sampling for Chemical Analysis.

Attachments

- **Attachment A** EHS Support Low Flow Groundwater Sampling Form
- **Attachment B** Low-Flow (Minimal Drawdown) Groundwater Sampling Procedures

Required Materials

- Air monitoring instrumentation (e.g., photoionization detector [PID]) and supplies
- Water quality meters for temperature, specific conductance, pH, dissolved oxygen (DO), oxidation-reduction potential (ORP), and turbidity
- Field logbook and field documentation
- Site plan showing well or water bore locations
- Health and Safety Plan (HASP)
- Indelible ink pens and waterproof marking pen
- Pump, controller, and power source—generator or battery
- Teflon or polyethylene tubing
- Decontamination equipment and supplies
- Bucket, drums, or other large container for storing and/or transporting development water.
- Measuring equipment (tape, water level indicator)

- GPS
- Camera
- Appropriate sample containers, sampling kits, labels, coolers, ice, Chain-of-Custody forms, tape, plastic baggies
- Duct tape and wrapping tape.

1 Low Flow Groundwater Sampling

Low-flow sampling purges stagnant water out of the well to allow sampling of formation water; however, it is intended to purge and sample only a limited interval of the well/formation. The term "low-flow" refers to the velocity at which water enters the pump or tubing intake from the surrounding formation in the immediate vicinity of the well screen. Purging at a low flow rate within the screened interval of a well should result in minimal drawdown of the water level, minimize the mixing of stagnant water in the well with formation water, and should result in a representative sample of the formation water. The low-flow technique described in this SOP complies with the guidelines provided by Puls and Barcelona (USEPA Low-Flow (Minimal Drawdown) Groundwater Sampling Procedures, 1996).

1.1 Low Flow Groundwater Sampling Considerations

Low-flow purging has advantages and disadvantages.

Advantages	Disadvantages
• Improved sample quality by minimizing the disturbance in the well • Less mixing of the stagnant casing water with the formation water • Samples are more representative of the mobile load of contaminants present in the aquifer reducing the need for filtering the water samples • Turbidity can be lower due to the slower discharge rate • The purging and sampling time is reduced • Less operator variability, greater operator control • Better sample consistency; reduced artificial sample variability • Purge quantity is smaller resulting in less wastewater	• The necessity for more equipment such as variable speed pump with the capability to pump at low rates, a flow-through cell that includes pH, oxidation-reduction potential (ORP), dissolved oxygen (DO), temperature, specific conductance, and a turbidity probe and meter(s) • Additional cost and time can be incurred since stabilization of water parameters may require relatively longer times • Sample results may not be reproducible if the pump is placed at a different depth within the screened interval each time the well is sampled
Low-flow purging is generally most effective • with short-screened intervals (e.g., < 20 feet, < 6 m).	Low-flow purging is generally not suitable for: • aquifers with very low hydraulic conductivities where minimal drawdown cannot be maintained • long screened intervals (e.g., > 9 m) or open-hole wells where the hydraulic flow pathways are unknown • use where the aquifer is contaminated by non-aqueous phase liquids.

Selecting equipment for purging and sampling a well requires site and project specific considerations to ensure that all collected samples meet the project objectives and data quality requirements. Groundwater chemistry can be altered by changes in temperature, pressure, and exposure to air that are brought on by the sampling process. Therefore, it is important to select sample equipment and follow sampling procedures that minimize changes.

Factors to consider when selecting sample equipment include: the analytes being evaluated, the type and location of well being sampled, physical characteristics of the well (diameter and total depth), depth to water, geology adjacent to the screened interval and the groundwater chemistry.

1.2 Equipment

1.2.1 Pumps

Pumps transport water from depth to the land surface by two methods, suction lift or positive pressure. The pumping mechanism for most suction-lift pumps is at land surface. Positive-displacement pumps (e.g. submersible and bladder) are placed below the static water level.

Control of the pumping rate is an important consideration when selecting dedicated or portable pumps. Sampling rates should be high enough to fill sample containers efficiently and with minimal exposure to the atmosphere, but low enough to minimize sample alteration by agitation or aeration. This is especially important for sensitive analytes, such as volatile organic compounds (VOCs) and trace metals. Other considerations in pump selection:

- Suction pumps, (e.g., peristaltic pumps) may be inappropriate for collecting VOCs, semi-VOCs (SVOCs), volatile petroleum compounds, and some (pH-dependent) metals. Suction lift pumps are not recommended for sampling VOCs because a vacuum is created at the intake to draw the sample to the land surface and can result in the loss of volatile organics or other dissolved gases. The lift capacity of the peristaltic pump is about 25 feet (8 to 10 meters) below ground surface.
- Positive-displacement pumps are generally preferred over suction-lift pumps.
- Dedicated pumps are preferable to portable pumps because portable pumps can create a disturbance in the water column during installation and require decontamination between wells.
- If a portable pump is selected for low-flow pumping, new or dedicated tubing must be used at each sampling location, and the pump must be lowered gently into the well to minimize disturbance to the water column.
- Depth to water effects positive-displacement pump operation. The pumping rate will typically decrease with increased depth to water.
- If a gasoline- or diesel-powered generator is used to energize the sampling pump, the power source must be located at least 10- to 20-feet (5 to 10 meters) downwind of the wellhead.
- Inertial pumps (e.g., Waterra) or bailers should never be used for low- flow sampling because they generate turbulence in the well and exacerbate degasing.

1.2.2 Tubing

Teflon or Teflon-lined polyethylene tubing is preferred when sampling VOCs, SVOCs, pesticides, polychlorinated biphenyls (PCBs), and inorganics. Polyvinyl chloride (PVC), polypropylene, or polyethylene tubing are to be used when collecting samples for metal and other inorganic analyses. Tubing used in low-flow purging effort generally range have an inside diameter ranging from 1/4 inch or 3/8 inch (4 to 8 mm).

Silastic tubing is recommended for the section of tubing around the rotor head of the peristaltic pump and should be less than a foot in length.

1.2.3 Other Equipment

A multi-parameter instrument, capable of measuring pH, specific conductance, temperature, ORP, DO, and turbidity, with a flow-through cell is preferred when measuring indicator field parameters. Field instruments will be calibrated in accordance with SOP-08 Field Equipment Calibration and Operation. Details about a multi-probe water quality meter is included as Attachment B in the SOP-08.

1.3 Low-Flow Sampling Precautions

The following precautions should be considered when collecting groundwater samples using low-flow sampling procedures.

- Inaccurate sample results may be caused by using contaminated equipment, cleaning materials, or sample containers.
- Establish the order the wells will be sampled. Sample order is based on logistics or the known or suspected water quality of a sample location. For contaminated sites, wells should be sampled in order of increasing chemical concentrations (known or anticipated). This minimizes the possibility for cross contamination of the sample equipment.
- Uncontrolled ambient/surrounding air conditions (i.e., truck/vehicle exhaust) can also influence the samples.
- If groundwater is extremely turbid on initiation of purge, consider bypassing the flow-through cell until groundwater clears to a visually lower turbidity level. The length of time this may take can vary on how turbid the water is, the formation around the well screen, and the analysis required on the sample. If turbidity does not decrease, the well may need to be re-developed.
- The pump or tubing intake must be in an appropriate depth within the well screen and located at a depth specified in the work plan or QAPP. The sample depth should be consistent from sample event to sample event. Suggested intake depths might consider the following:
    - For wells with screens <10-feet (<5 m) in length, the intake should be placed approximately in the middle of the saturated portion of the screen.
    - For wells with well screens > 10 feet (>5 m), the primary flow zones and contaminant concentration intervals must be identified. Recommendations may include the middle of the saturated portion of the screen, or mid-screen.

- For wells that have measureable non-aqueous phase liquid (NAPL), a determination if the well should be sampled should be discussed with the PM. Groundwater that has NAPL may interfere with laboratory analytical equipment and has a higher potential of cross contamination if a displacement-pressure pump is used. If low-flow sampling in a well that has NAPL is determined to be appropriate, the following is recommended:
  i. Choose a purge technique such as a peristaltic pump in which the tubing can be discarded after use. A displacement-pressure pump is not recommended.
  ii. The preferred procedure is to remove the light NAPL (LNAPL) from the top of the water column prior to purging the well. Removal is generally accomplished by using a bailer, pumping/skimming the LNAPL, or absorbent pads.
  iii. If the NAPL is LNAPL and the LNAPL is not removed, lower the tubing intake a minimum of 2 feet (0.5 m) below the LNAPL/water interface. Purge at a low discharge rate and monitor the interface depth, so the drawdown of the interface does not allow LNAPL into the tubing intake.
  iv. If the NAPL is dense NAPL (DNAPL), measure the depth to the DNAPL/water interface and place the tubing intake a minimum of 2 feet (0.5 m) above the depth of the interface. Purge at a low discharge rate and monitor the water level for drawdown. Avoid purge rates that would disturb the DNAPL and allow the DNAPL to enter the tubing intake.

1.4 Low-Flow Sampling Procedures

The low-flow process can vary based on project work plan and well-specific details, and procedures may need to be adjusted to accompany variations. In general, the low-flow sampling procedures are as follows:

1. Field equipment will be calibrated in accordance with the guidelines provided in SOP-08 Field Equipment Operation and Calibration or the manufacturer's manual.
2. Field equipment will be decontaminated in accordance with SOP-09 Field Decontamination or new disposable equipment will be used as appropriate.
3. Open the well. If required, use a photoionization detector or equivalent to measure for the presence of volatile organic compounds. Record the results of the photoionization detector measurement in field logbook or approved field documentation.
4. Measure the depth to water and total depth of the well using a water level indicator. If NAPL is present, use an interface probe for fluid measurements and total depth. Fluid levels or total depths will be measured in accordance with the guidelines provided in SOP-41 Fluid Measurements. Record the measurements in the field logbook or approved field documentation.
5. Lower the pump or tubing intake slowly to the desired depth within the well screen. The determined depth should be outlined in the work plan or QAPP, or the midsection of the well screen or saturated water column of the well screen.
6. Once the pump or tubing intake is to depth, energize the pump. Set the pump controller to the desired pumping rate. Start the pump at a relatively low pumping rate--about 100 to 200 milliliters per minute (mL/min).
7. Record the purge start time.

8. Water levels, pump discharge rates, and groundwater field parameters will be measured and recorded at consistent intervals (e.g., 2, to 5 minute intervals) during purging activities.
9. Groundwater discharge rates will be measured using a graduated cylinder or equivalent to ensure purge rates are discharging between 100 to 500 milliliters per minute (ml/min). Preferably, pumping rates will be maintained between 200 to 300 mL/min.
10. Use water level measurements to help establish the optimum pump rate. Water level drawdown provides the best indication of the stress imparted by a given flow-rate for a given hydrological condition. Water level measurements during the purge will be less than 0.33 feet from the initially measured groundwater depth. If drawdown is greater than 0.33 feet, lower the pumping rate and continue to monitor the water level. If drawdown continues, lower the pumping rate until water levels are consistent or rebound. If drawdown is greater than 0.33 feet but the water level depth remains at the same water level depth or rebounds, groundwater depths will be considered stable or re-entering faster than being discharged. If water level continues to drawdown at the lowest achievable pumping rate, note on field logs.
11. During purging and sample collection the water flow should be a smooth, solid stream of water with no air or gas bubbles in the tubing or flow cell. Gradually adjust the pumping rate to eliminate bubbles, if present and able.
12. Observations of clarity, color, and odor of the purged water should be recorded at successive intervals.
13. Field indicator parameters will be recorded during purging for pH, temperature (°C or °F), specific conductance (µS/cm or mS/cm), ORP (mV), DO (mg/L), and turbidity (NTU). If other units of measurement are used, the unit of measurement will be documented in the field log book or approved field documents.
14. Turbidity will be monitored as turbidity may potentially interfere with some laboratory analyses, such as metals. Turbidity may be reduced in the sample by lowering the pumping rate.
15. Purging is considered complete when the water extraction rate and water level are consistent, and the indicators parameters have stabilized for 3 consecutive readings as outlined below:

Parameter	Stabilization Criteria
Temperature	± 3% of reading (minimum of ± 0.2 C)
pH	+/- 0.1
specific conductance	+/- 3%
ORP	+/- 10 millivolts
DO	+/- 0.3 milligrams per liter
Turbidity	No stabilization criteria, however, an NTU reading less than 10 NTU is preferred

16. If the field indicator parameters do not stabilize, a groundwater sample will be collected after removal of 1 well volume, or 1 hour, whichever occurs first. Calculation of a well volume is provided in SOP-44 Volume Purge Sampling.
17. If the well purges dry, the well should be sampled as soon as a sufficient volume of groundwater has re-entered the well.
18. Re-purging of the well will be performed if a well is inactive for more than 24 hours after full recharge.

19. Record the volume of water discharged during the purge event from the start time to the time of sample collection.
20. The pump should not be moved or turned off between purging and sampling. The pumping rate can be decreased for sample collection but should never be increased.
21. Prior to sampling, disconnect the tubing leading to the flow-through cell.
22. Groundwater samples will be collected in laboratory-supplied jars once purging is completed. Groundwater samples will be collected directly from the tubing (i.e., the sample will not be collected from the flow-through cell port) with the pump rate consistent with stabilization purging flow rates.
23. Groundwater samples will be collected in accordance with the work plan or QAPP and will follow the sampling guidelines provided in SOP-46 Water Sampling for Chemical Analysis.
24. Collected samples will be placed in insulated coolers containing ice to maintain a temperature of 4°C. Samples will be labeled, managed, and shipped in accordance SOP-05 Sample Management and Shipping.
25. Place the discharged water into a bucket or pump directly into an appropriate container. Dispose of the discharge water or wastes in accordance with SOP-07 Investigative Derived Waste.
26. Secure the well and restore the location and area to previous site conditions.

2 Records

Field notes will be kept in a bound field logbook or approved field documentation following the format specified in SOP-04 Field Documentation. Specific documentation may include health and safety documentation, precipitation data, and photographs. Hardcopy discharge records, including all related quality control documentation, must be maintained in permanent project files. A Low-Flow Sample Sheet is contained as **Attachment A**. Documentation of the sampling event should include (at a minimum):

- Required site maps and HASP forms
- Instrument calibration
- Equipment calibration sheet from rental agency
- Well identification and location
- Type of equipment and supplies
- Well construction details
- Previous sample event or water level details
- Air monitoring readings, if required
- Low-Flow Sampling Form details
  - Physical water observation
  - Containment and volume of water removed
  - Name of the sample collectors
  - Water level depth and total depth
  - Pump or tubing intake depth in screen
  - Pumping rates, drawdown, indicator field parameters values, calculated or measured total volume pumped, and clock time of each set of measurements.
  - Times (start, finish, sample time)
  - Laboratory information (sample ID, preservative, QA/QC)
- Weather observations (e.g., temperature, wind speed and direction, cloud coverage).
- Any problems encountered or deviations from this SOP.
- Summary of daily activities and personnel onsite.

Attachment A Low-Flow Groundwater Sampling Form

EHS Support

LOW FLOW GROUNDWATER SAMPLING FORM

Project Name: _____

Project Number: _____

Time (Initial): _____

Initial Water Level: _____ ft

Depth to Product: _____ ft

Total Well Depth: _____ ft

Well Identification: _____

Sample Date: _____

Field Technician(s): _____

Inner Casing Diameter (in): _____

Pump and Tubing Type: _____

Start Purge Time: _____

Time	Flow Rate	Water Level	Temp.	pH	Conductivity	Turbidity	DO	ORP	Odor	Color	Comments
	__L/min	ft	°C / °F	S.U.	__S/cm	NTU	mg/L	mV			

Comments: _____

End Purge Time: _____

Final Water Level: _____ ft

Total Volume Purged: _____ gal

One Well Volume (prior to purging, if applicable): _____ gal

Well Purged Dry? ☐ Yes ☐ No

Tubing Inlet Depth: _____

SAMPLE ID	TIME	ANALYSES	QA/QC SAMPLE	REMARKS

Gas Concentration in Well: _____ ppm

Formula for Calculating Well Casing Volume

$$[A] = \frac{\pi D^2 L}{4} * 7.48 \frac{gal}{ft^3}$$

D = Well casing inner diameter *(converted to feet)*

L = Height of water column (ft)

Parameter	Stabilization Criteria*
Temperature	± 3% of reading (minimum of ± 0.2 C)
pH	+/- 0.1
Specific Conductance	+/- 3%
ORP	+/- 10 millivolts
Dissolved Oxygen	+/- 0.3 milligrams per liter
Turbidity	Not a stabilization criteria; however, the lower the turbidity the better

* - USEPA, 1996 (Puls and Barcelona) Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures

Signature: _____

Attachment B Low-Flow (Minimal Drawdown) Groundwater Sampling Form (Puls and Barcelona, 1996)

United States Environmental Protection Agency | Office of Research and Development | Office of Solid Waste and Emergency Response | EPA/540/S-95/504 April 1996

Ground Water Issue

LOW-FLOW (MINIMAL DRAWDOWN) GROUND-WATER SAMPLING PROCEDURES

by Robert W. Puls[1] and Michael J. Barcelona[2]

Background

The Regional Superfund Ground Water Forum is a group of ground-water scientists, representing EPA's Regional Superfund Offices, organized to exchange information related to ground-water remediation at Superfund sites. One of the major concerns of the Forum is the sampling of ground water to support site assessment and remedial performance monitoring objectives. This paper is intended to provide background information on the development of low-flow sampling procedures and its application under a variety of hydrogeologic settings. It is hoped that the paper will support the production of standard operating procedures for use by EPA Regional personnel and other environmental professionals engaged in ground-water sampling.

For further information contact: Robert Puls, 405-436-8543, Subsurface Remediation and Protection Division, NRMRL, Ada, Oklahoma.

I. Introduction

The methods and objectives of ground-water sampling to assess water quality have evolved over time. Initially the emphasis was on the assessment of water quality of aquifers as sources of drinking water. Large water-bearing units were identified and sampled in keeping with that objective. These were highly productive aquifers that supplied drinking water via private wells or through public water supply systems. Gradually, with the increasing awareness of subsurface pollution of these water resources, the understanding of complex hydrogeochemical processes which govern the fate and transport of contaminants in the subsurface increased. This increase in understanding was also due to advances in a number of scientific disciplines and improvements in tools used for site characterization and ground-water sampling. Ground-water quality investigations where pollution was detected initially borrowed ideas, methods, and materials for site characterization from the water supply field and water analysis from public health practices. This included the materials and manner in which monitoring wells were installed and the way in which water was brought to the surface, treated, preserved and analyzed. The prevailing conceptual ideas included convenient generalizations of ground-water resources in terms of large and relatively homogeneous hydrologic *units*. With time it became apparent that conventional water supply generalizations of *homogeneity* did not adequately represent field data regarding pollution of these subsurface resources. The important role of *heterogeneity* became increasingly clear not only in geologic terms, but also in terms of complex physical,

[1]National Risk Management Research Laboratory, U.S. EPA
[2]University of Michigan

Superfund Technology Support Center for Ground Water

National Risk Management Research Laboratory
Subsurface Protection and Remediation Division
Robert S. Kerr Environmental Research Center
Ada, Oklahoma

Technology Innovation Office
Office of Solid Waste and Emergency Response, US EPA, Washington, DC

Walter W. Kovalick, Jr., Ph.D.
Director

chemical and biological subsurface processes. With greater appreciation of the role of heterogeneity, it became evident that subsurface pollution was ubiquitous and encompassed the unsaturated zone to the deep subsurface and included unconsolidated sediments, fractured rock, and *aquitards* or low-yielding or impermeable formations. Small-scale processes and heterogeneities were shown to be important in identifying contaminant distributions and in controlling water and contaminant flow paths.

It is beyond the scope of this paper to summarize all the advances in the field of ground-water quality investigations and remediation, but two particular issues have bearing on ground-water sampling today: aquifer heterogeneity and colloidal transport. Aquifer heterogeneities affect contaminant flow paths and include variations in geology, geochemistry, hydrology and microbiology. As methods and the tools available for subsurface investigations have become increasingly sophisticated and understanding of the subsurface environment has advanced, there is an awareness that in most cases a primary concern for site investigations is characterization of contaminant flow paths rather than entire aquifers. In fact, in many cases, plume thickness can be less than well screen lengths (e.g., 3-6 m) typically installed at hazardous waste sites to detect and monitor plume movement over time. Small-scale differences have increasingly been shown to be important and there is a general trend toward smaller diameter wells and shorter screens.

The hydrogeochemical significance of colloidal-size particles in subsurface systems has been realized during the past several years (Gschwend and Reynolds, 1987; McCarthy and Zachara, 1989; Puls, 1990; Ryan and Gschwend, 1990). This realization resulted from both field and laboratory studies that showed faster contaminant migration over greater distances and at higher concentrations than flow and transport model predictions would suggest (Buddemeier and Hunt, 1988; Enfield and Bengtsson, 1988; Penrose et al., 1990). Such models typically account for interaction between the mobile aqueous and immobile solid phases, but do not allow for a mobile, reactive solid phase. It is recognition of this third *phase* as a possible means of contaminant transport that has brought increasing attention to the manner in which samples are collected and processed for analysis (Puls et al., 1990; McCarthy and Degueldre, 1993; Backhus et al., 1993; U. S. EPA, 1995). If such a phase is present in sufficient mass, possesses high sorption reactivity, large surface area, and remains stable in suspension, it can serve as an important mechanism to facilitate contaminant transport in many types of subsurface systems.

Colloids are particles that are sufficiently small so that the surface free energy of the particle dominates the bulk free energy. Typically, in ground water, this includes particles with diameters between 1 and 1000 nm. The most commonly observed mobile particles include: secondary clay minerals; hydrous iron, aluminum, and manganese oxides; dissolved and particulate organic materials, and viruses and bacteria. These reactive particles have been shown to be mobile under a variety of conditions in both field studies and laboratory column experiments, and as such need to be included in monitoring programs where identification of the *total* mobile contaminant loading (dissolved + naturally suspended particles) at a site is an objective. To that end, sampling methodologies must be used which do not artificially bias *naturally* suspended particle concentrations.

Currently the most common ground-water purging and sampling methodology is to purge a well using bailers or high speed pumps to remove 3 to 5 casing volumes followed by sample collection. This method can cause adverse impacts on sample quality through collection of samples with high levels of turbidity. This results in the inclusion of otherwise immobile artifactual particles which produce an overestimation of certain analytes of interest (e.g., metals or hydrophobic organic compounds). Numerous documented problems associated with filtration (Danielsson, 1982; Laxen and Chandler, 1982; Horowitz et al., 1992) make this an undesirable method of rectifying the turbidity problem, and include the removal of potentially mobile (contaminant-associated) particles during filtration, thus artificially biasing contaminant concentrations low. Sampling-induced turbidity problems can often be mitigated by using low-flow purging and sampling techniques.

Current subsurface conceptual models have undergone considerable refinement due to the recent development and increased use of field screening tools. So-called hydraulic *push* technologies (e.g., cone penetrometer, Geoprobe®, QED HydroPunch®) enable relatively fast screening site characterization which can then be used to design and install a monitoring well network. Indeed, alternatives to conventional monitoring wells are now being considered for some hydrogeologic settings. The ultimate design of any monitoring system should however be based upon adequate site characterization and be consistent with established monitoring objectives.

If the sampling program objectives include accurate assessment of the magnitude and extent of subsurface contamination over time and/or accurate assessment of subsequent remedial performance, then some information regarding plume delineation in three-dimensional space is necessary prior to monitoring well network design and installation. This can be accomplished with a variety of different tools and equipment ranging from hand-operated augers to screening tools mentioned above and large drilling rigs. Detailed information on ground-water flow velocity, direction, and horizontal and vertical variability are essential baseline data requirements. Detailed soil and geologic data are required prior to and during the installation of sampling points. This includes historical as well as detailed soil and geologic logs which accumulate during the site investigation. The use of borehole geophysical techniques is also recommended. With this information (together with other site characterization data) and a clear understanding of sampling

objectives, then appropriate location, screen length, well diameter, slot size, etc. for the monitoring well network can be decided. This is especially critical for new in situ remedial approaches or natural attenuation assessments at hazardous waste sites.

In general, the overall goal of any ground-water sampling program is to collect water samples with no alteration in water chemistry; analytical data thus obtained may be used for a variety of specific monitoring programs depending on the regulatory requirements. The sampling methodology described in this paper assumes that the monitoring goal is to sample monitoring wells for the presence of contaminants and it is applicable whether mobile colloids are a concern or not and whether the analytes of concern are metals (and metalloids) or organic compounds.

II. Monitoring Objectives and Design Considerations

The following issues are important to consider prior to the design and implementation of any ground-water monitoring program, including those which anticipate using low-flow purging and sampling procedures.

A. Data Quality Objectives (DQOs)

Monitoring objectives include four main types: detection, assessment, corrective-action evaluation and resource evaluation, along with *hybrid* variations such as site-assessments for property transfers and water availability investigations. Monitoring objectives may change as contamination or water quality problems are discovered. However, there are a number of common components of monitoring programs which should be recognized as important regardless of initial objectives. These components include:

1) Development of a conceptual model that incorporates elements of the regional geology to the local geologic framework. The conceptual model development also includes initial site characterization efforts to identify hydrostratigraphic units and likely flow-paths using a minimum number of borings and well completions;

2) Cost-effective and well documented collection of high quality data utilizing simple, accurate, and reproducible techniques; and

3) Refinement of the conceptual model based on supplementary data collection and analysis.

These fundamental components serve many types of monitoring programs and provide a basis for future efforts that evolve in complexity and level of spatial detail as purposes and objectives expand. High quality, reproducible data collection is a common goal regardless of program objectives.

High quality data collection implies data of sufficient accuracy, precision, and completeness (i.e., ratio of valid analytical results to the minimum sample number called for by the program design) to meet the program objectives. Accuracy depends on the correct choice of monitoring tools and procedures to minimize sample and subsurface disturbance from collection to analysis. Precision depends on the repeatability of sampling and analytical protocols. It can be assured or improved by replication of sample analyses including blanks, field/lab standards and reference standards.

B. Sample Representativeness

An important goal of any monitoring program is collection of data that is truly representative of conditions at the site. The term *representativeness* applies to chemical and hydrogeologic data collected via wells, borings, piezometers, geophysical and soil gas measurements, lysimeters, and temporary sampling points. It involves a recognition of the statistical variability of individual subsurface physical properties, and contaminant or major ion concentration levels, while explaining extreme values. Subsurface temporal and spatial variability are facts. Good professional practice seeks to maximize representativeness by using proven accurate and reproducible techniques to define limits on the distribution of measurements collected at a site. However, measures of representativeness are dynamic and are controlled by evolving site characterization and monitoring objectives. An evolutionary site characterization model, as shown in Figure 1, provides a systematic approach to the goal of consistent data collection.

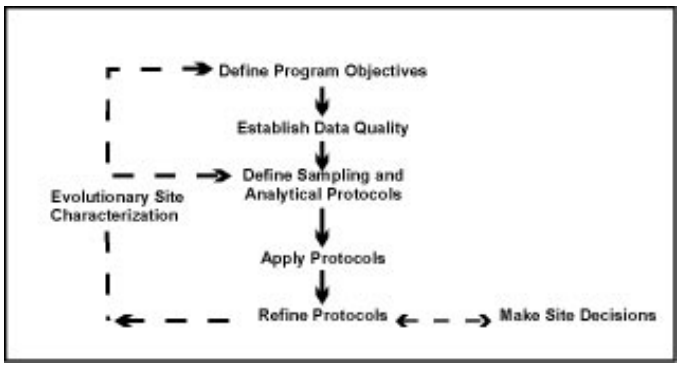

Figure 1. Evolutionary Site Characterization Model

The model emphasizes a recognition of the causes of the variability (e.g., use of inappropriate technology such as using bailers to purge wells; imprecise or operator-dependent methods) and the need to control avoidable errors.

1) Questions of Scale

A sampling plan designed to collect representative samples must take into account the potential scale of changes in site conditions through space and time as well as the chemical associations and behavior of the parameters that are targeted for investigation. In subsurface systems, physical (i.e., aquifer) and chemical properties over time or space are not statistically independent. In fact, samples taken in close proximity (i.e., within distances of a few meters) or within short time periods (i.e., more frequently than monthly) are highly auto-correlated. This means that designs employing high-sampling frequency (e.g., monthly) or dense spatial monitoring designs run the risk of redundant data collection and misleading inferences regarding trends in values that aren't statistically valid. In practice, contaminant detection and assessment monitoring programs rarely suffer these *over-sampling* concerns. In corrective-action evaluation programs, it is also possible that too little data may be collected over space or time. In these cases, false interpretation of the spatial extent of contamination or underestimation of temporal concentration variability may result.

2) Target Parameters

Parameter selection in monitoring program design is most often dictated by the regulatory status of the site. However, background water quality constituents, purging indicator parameters, and contaminants, all represent targets for data collection programs. The tools and procedures used in these programs should be equally rigorous and applicable to all categories of data, since all may be needed to determine or support regulatory action.

C. Sampling Point Design and Construction

Detailed site characterization is central to all decision-making purposes and the basis for this characterization resides in identification of the geologic framework and major hydro-stratigraphic units. Fundamental data for sample point location include: subsurface lithology, head-differences and background geochemical conditions. Each sampling point has a proper use or uses which should be documented at a level which is appropriate for the program's data quality objectives. Individual sampling points may not always be able to fulfill multiple monitoring objectives (e.g., detection, assessment, corrective action).

1) Compatibility with Monitoring Program and Data Quality Objectives

Specifics of sampling point location and design will be dictated by the complexity of subsurface lithology and variability in contaminant and/or geochemical conditions. It should be noted that, regardless of the ground-water sampling approach, few sampling points (e.g., wells, drive-points, screened augers) have zones of influence in excess of a few feet. Therefore, the spatial frequency of sampling points should be carefully selected and designed.

2) Flexibility of Sampling Point Design

In most cases *well-point* diameters in excess of 1 7/8 inches will permit the use of most types of submersible pumping devices for low-flow (minimal drawdown) sampling. It is suggested that *short* (e.g., less than 1.6 m) screens be incorporated into the monitoring design where possible so that comparable results from one device to another might be expected. *Short*, of course, is relative to the degree of vertical water quality variability expected at a site.

3) Equilibration of Sampling Point

Time should be allowed for equilibration of the well or sampling point with the formation after installation. Placement of well or sampling points in the subsurface produces some disturbance of ambient conditions. Drilling techniques (e.g., auger, rotary, etc.) are generally considered to cause more disturbance than *direct-push* technologies. In either case, there may be a period (i.e., days to months) during which water quality near the point may be distinctly different from that in the formation. Proper development of the sampling point and adjacent formation to remove fines created during emplacement will shorten this water quality *recovery* period.

III. Definition of Low-Flow Purging and Sampling

It is generally accepted that water in the well casing is non-representative of the formation water and needs to be purged prior to collection of ground-water samples. However, the water in the screened interval may indeed be representative of the formation, depending upon well construction and site hydrogeology. Wells are purged to some extent for the following reasons: the presence of the air interface at the top of the water column resulting in an oxygen concentration gradient with depth, loss of volatiles up the water column, leaching from or sorption to the casing or filter pack, chemical changes due to clay seals or backfill, and surface infiltration.

Low-flow purging, whether using portable or dedicated systems, should be done using pump-intake located in the middle or slightly above the middle of the screened interval. Placement of the pump too close to the bottom of the well will cause increased entrainment of solids which have collected in the well over time. These particles are present as a result of well development, prior purging and sampling events, and natural colloidal transport and deposition. Therefore, placement of the pump in the middle or toward the top of the screened interval is suggested. Placement of the pump at the top of the water column for sampling is only recommended in unconfined aquifers, screened across the water table, where this is the desired sampling point. Low-

flow purging has the advantage of minimizing mixing between the overlying stagnant casing water and water within the screened interval.

A. Low-Flow Purging and Sampling

Low-flow refers to the velocity with which water enters the pump intake and that is imparted to the formation pore water in the immediate vicinity of the well screen. It does not necessarily refer to the flow rate of water discharged at the surface which can be affected by flow regulators or restrictions. Water level drawdown provides the best indication of the stress imparted by a given flow-rate for a given hydrological situation. The objective is to pump in a manner that minimizes stress (drawdown) to the system to the extent practical taking into account established site sampling objectives. Typically, flow rates on the order of 0.1 - 0.5 L/min are used, however this is dependent on site-specific hydrogeology. Some extremely coarse-textured formations have been successfully sampled in this manner at flow rates to 1 L/min. The effectiveness of using low-flow purging is intimately linked with proper screen location, screen length, and well construction and development techniques. The reestablishment of natural flow paths in both the vertical and horizontal directions is important for correct interpretation of the data. For high resolution sampling needs, screens less than 1 m should be used. Most of the need for purging has been found to be due to passing the sampling device through the overlying casing water which causes mixing of these stagnant waters and the dynamic waters within the screened interval. Additionally, there is disturbance to suspended sediment collected in the bottom of the casing and the displacement of water out into the formation immediately adjacent to the well screen. These disturbances and impacts can be avoided using dedicated sampling equipment, which precludes the need to insert the sampling device prior to purging and sampling.

Isolation of the screened interval water from the overlying stagnant casing water may be accomplished using low-flow minimal drawdown techniques. If the pump intake is located within the screened interval, most of the water pumped will be drawn in directly from the formation with little mixing of casing water or disturbance to the sampling zone. However, if the wells are not constructed and developed properly, zones other than those intended may be sampled. At some sites where geologic heterogeneities are sufficiently different within the screened interval, higher conductivity zones may be preferentially sampled. This is another reason to use shorter screened intervals, especially where high spatial resolution is a sampling objective.

B. Water Quality Indicator Parameters

It is recommended that water quality indicator parameters be used to determine purging needs prior to sample collection in each well. Stabilization of parameters such as pH, specific conductance, dissolved oxygen, oxidation-reduction potential, temperature and turbidity should be used to determine when formation water is accessed during purging. In general, the order of stabilization is pH, temperature, and specific conductance, followed by oxidation-reduction potential, dissolved oxygen and turbidity. Temperature and pH, while commonly used as purging indicators, are actually quite insensitive in distinguishing between formation water and stagnant casing water; nevertheless, these are important parameters for data interpretation purposes and should also be measured. Performance criteria for determination of stabilization should be based on water-level drawdown, pumping rate and equipment specifications for measuring indicator parameters. Instruments are available which utilize in-line flow cells to continuously measure the above parameters.

It is important to establish specific well stabilization criteria and then consistently follow the same methods thereafter, particularly with respect to drawdown, flow rate and sampling device. Generally, the time or purge volume required for parameter stabilization is independent of well depth or well volumes. Dependent variables are well diameter, sampling device, hydrogeochemistry, pump flow rate, and whether the devices are used in a portable or dedicated manner. If the sampling device is already in place (i.e., dedicated sampling systems), then the time and purge volume needed for stabilization is much shorter. Other advantages of dedicated equipment include less purge water for waste disposal, much less decontamination of equipment, less time spent in preparation of sampling as well as time in the field, and more consistency in the sampling approach which probably will translate into less variability in sampling results. The use of dedicated equipment is strongly recommended at wells which will undergo routine sampling over time.

If parameter stabilization criteria are too stringent, then minor oscillations in indicator parameters may cause purging operations to become unnecessarily protracted. It should also be noted that turbidity is a very conservative parameter in terms of stabilization. Turbidity is always the last parameter to stabilize. Excessive purge times are invariably related to the establishment of too stringent turbidity stabilization criteria. It should be noted that natural turbidity levels in ground water may exceed 10 nephelometric turbidity units (NTU).

C. Advantages and Disadvantages of Low-Flow (Minimum Drawdown) Purging

In general, the advantages of low-flow purging include:

- samples which are representative of the *mobile* load of contaminants present (dissolved and colloid-associated);
- minimal disturbance of the sampling point thereby minimizing sampling artifacts;
- less operator variability, greater operator control;

- reduced stress on the formation (minimal drawdown);
- less mixing of stagnant casing water with formation water;
- reduced need for filtration and, therefore, less time required for sampling;
- smaller purging volume which decreases waste disposal costs and sampling time;
- better sample consistency; reduced artificial sample variability.

Some disadvantages of low-flow purging are:

- higher initial capital costs,
- greater set-up time in the field,
- need to transport additional equipment to and from the site,
- increased training needs,
- resistance to change on the part of sampling practitioners,
- concern that new data will indicate a *change in conditions* and trigger an *action*.

IV. Low-Flow (Minimal Drawdown) Sampling Protocols

The following ground-water sampling procedure has evolved over many years of experience in ground-water sampling for organic and inorganic compound determinations and as such summarizes the authors' (and others) experiences to date (Barcelona et al., 1984, 1994; Barcelona and Helfrich, 1986; Puls and Barcelona, 1989; Puls et. al. 1990, 1992; Puls and Powell, 1992; Puls and Paul, 1995). High-quality chemical data collection is essential in ground-water monitoring and site characterization. The primary limitations to the collection of *representative* ground-water samples include: mixing of the stagnant casing and *fresh* screen waters during insertion of the sampling device or ground-water level measurement device; disturbance and resuspension of settled solids at the bottom of the well when using high pumping rates or raising and lowering a pump or bailer; introduction of atmospheric gases or degassing from the water during sample handling and transfer, or inappropriate use of vacuum sampling device, etc.

A. Sampling Recommendations

Water samples should not be taken immediately following well development. Sufficient time should be allowed for the ground-water flow regime in the vicinity of the monitoring well to stabilize and to approach chemical equilibrium with the well construction materials. This lag time will depend on site conditions and methods of installation but often exceeds one week.

Well purging is nearly always necessary to obtain samples of water flowing through the geologic formations in the screened interval. Rather than using a general but arbitrary guideline of purging three casing volumes prior to sampling, it is recommended that an in-line water quality measurement device (e.g., flow-through cell) be used to establish the stabilization time for several parameters (e.g. , pH, specific conductance, redox, dissolved oxygen, turbidity) on a well-specific basis. Data on pumping rate, drawdown, and volume required for parameter stabilization can be used as a guide for conducting subsequent sampling activities.

The following are recommendations to be considered before, during and after sampling:

- use low-flow rates (<0.5 L/min), during both purging and sampling to maintain minimal drawdown in the well;
- maximize tubing wall thickness, minimize tubing length;
- place the sampling device intake at the desired sampling point;
- minimize disturbances of the stagnant water column above the screened interval during water level measurement and sampling device insertion;
- make proper adjustments to stabilize the flow rate as soon as possible;
- monitor water quality indicators during purging;
- collect unfiltered samples to estimate contaminant loading and transport potential in the subsurface system.

B. Equipment Calibration

Prior to sampling, all sampling device and monitoring equipment should be calibrated according to manufacturer's recommendations and the site Quality Assurance Project Plan (QAPP) and Field Sampling Plan (FSP). Calibration of pH should be performed with at least two buffers which bracket the expected range. Dissolved oxygen calibration must be corrected for local barometric pressure readings and elevation.

C. Water Level Measurement and Monitoring

It is recommended that a device be used which will least disturb the water surface in the casing. Well depth should be obtained from the well logs. Measuring to the bottom of the well casing will only cause resuspension of settled solids from the formation and require longer purging times for turbidity equilibration. Measure well depth after sampling is completed. The water level measurement should be taken from a permanent reference point which is surveyed relative to ground elevation.

D. Pump Type

The use of low-flow (e.g., 0.1-0.5 L/min) pumps is suggested for purging and sampling all types of analytes. All pumps have some limitation and these should be investigated with respect to application at a particular site. Bailers are inappropriate devices for low-flow sampling.

1) General Considerations

There are no unusual requirements for ground-water sampling devices when using low-flow, minimal drawdown techniques. The major concern is that the device give consistent results and minimal disturbance of the sample across a range of *low* flow rates (i.e., < 0.5 L/min). Clearly, pumping rates that cause minimal to no drawdown in one well could easily cause *significant* drawdown in another well finished in a less transmissive formation. In this sense, the pump should not cause undue pressure or temperature changes or physical disturbance on the water sample over a reasonable sampling range. Consistency in operation is critical to meet accuracy and precision goals.

2) Advantages and Disadvantages of Sampling Devices

A variety of sampling devices are available for low-flow (minimal drawdown) purging and sampling and include peristaltic pumps, bladder pumps, electrical submersible pumps, and gas-driven pumps. Devices which lend themselves to both dedication and consistent operation at definable low-flow rates are preferred. It is desirable that the pump be easily adjustable and operate reliably at these lower flow rates. The peristaltic pump is limited to shallow applications and can cause degassing resulting in alteration of pH, alkalinity, and some volatiles loss. Gas-driven pumps should be of a type that does not allow the gas to be in direct contact with the sampled fluid.

Clearly, bailers and other *grab* type samplers are ill-suited for low-flow sampling since they will cause repeated disturbance and mixing of *stagnant* water in the casing and the *dynamic* water in the screened interval. Similarly, the use of inertial lift foot-valve type samplers may cause too much disturbance at the point of sampling. Use of these devices also tends to introduce uncontrolled and unacceptable operator variability.

Summaries of advantages and disadvantages of various sampling devices are listed in Herzog et al. (1991), U. S. EPA (1992), Parker (1994) and Thurnblad (1994).

E. Pump Installation

Dedicated sampling devices (left in the well) capable of pumping and sampling are preferred over <u>any</u> other type of device. Any portable sampling device should be slowly and carefully lowered to the middle of the screened interval or slightly above the middle (e.g., 1-1.5 m below the top of a 3 m screen). This is to minimize excessive mixing of the stagnant water in the casing above the screen with the screened interval zone water, and to minimize resuspension of solids which will have collected at the bottom of the well. These two disturbance effects have been shown to directly affect the time required for purging. There also appears to be a direct correlation between size of portable sampling devices relative to the well bore and resulting purge volumes and times. The key is to minimize disturbance of water and solids in the well casing.

F. Filtration

Decisions to filter samples should be dictated by sampling objectives rather than as a *fix* for poor sampling practices, and field-filtering of certain constituents should not be the default. Consideration should be given as to what the application of field-filtration is trying to accomplish. For assessment of truly dissolved (as opposed to operationally *dissolved* [i.e., samples filtered with 0.45 µm filters]) concentrations of major ions and trace metals, 0.1 µm filters are recommended although 0.45 µm filters are normally used for most regulatory programs. Alkalinity samples must also be filtered if significant particulate calcium carbonate is suspected, since this material is likely to impact alkalinity titration results (although filtration itself may alter the CO_2 composition of the sample and, therefore, affect the results).

Although filtration may be appropriate, filtration of a sample may cause a number of unintended changes to occur (e.g. oxidation, aeration) possibly leading to filtration-induced artifacts during sample analysis and uncertainty in the results. Some of these unintended changes may be unavoidable but the factors leading to them must be recognized. Deleterious effects can be minimized by consistent application of certain filtration guidelines. Guidelines should address selection of filter type, media, pore size, etc. in order to identify and minimize potential sources of uncertainty when filtering samples.

In-line filtration is recommended because it provides better consistency through less sample handling, and minimizes sample exposure to the atmosphere. In-line filters are available in both disposable (barrel filters) and non-disposable (in-line filter holder, flat membrane filters) formats and various filter pore sizes (0.1-5.0 µm). Disposable filter cartridges have the advantage of greater sediment handling capacity when compared to traditional membrane filters. Filters must be pre-rinsed following manufacturer's recommendations. If there are no recommendations for rinsing, pass through a minimum of 1 L of ground water following purging and prior to sampling. Once filtration has begun, a filter cake may develop as particles larger than the pore size accumulate on the filter membrane. The result is that the effective pore diameter of the membrane is reduced and particles smaller than the stated pore size are excluded from the filtrate. Possible corrective measures include prefiltering (with larger pore size filters), minimizing particle loads to begin with, and reducing sample volume.

G. Monitoring of Water Level and Water Quality Indicator Parameters

Check water level periodically to monitor drawdown in the well as a guide to flow rate adjustment. The goal is minimal drawdown (<0.1 m) during purging. This goal may be difficult to achieve under some circumstances due to geologic heterogeneities within the screened interval, and may require adjustment based on site-specific conditions and personal experience. In-line water quality indicator parameters should be continuously monitored during purging. The water quality

indicator parameters monitored can include pH, redox potential, conductivity, dissolved oxygen (DO) and turbidity. The last three parameters are often most sensitive. Pumping rate, drawdown, and the time or volume required to obtain stabilization of parameter readings can be used as a future guide to purge the well. Measurements should be taken every three to five minutes if the above suggested rates are used. Stabilization is achieved after all parameters have stabilized for three successive readings. In lieu of measuring all five parameters, a minimum subset would include pH, conductivity, and turbidity or DO. Three successive readings should be within ± 0.1 for pH, ± 3% for conductivity, ± 10 mv for redox potential, and ± 10% for turbidity and DO. Stabilized purge indicator parameter trends are generally obvious and follow either an exponential or asymptotic change to stable values during purging. Dissolved oxygen and turbidity usually require the longest time for stabilization. The above stabilization guidelines are provided for rough estimates based on experience.

H. Sampling, Sample Containers, Preservation and Decontamination

Upon parameter stabilization, sampling can be initiated. If an in-line device is used to monitor water quality parameters, it should be disconnected or bypassed during sample collection. Sampling flow rate may remain at established purge rate or may be adjusted slightly to minimize aeration, bubble formation, turbulent filling of sample bottles, or loss of volatiles due to extended residence time in tubing. Typically, flow rates less than 0.5 L/min are appropriate. The same device should be used for sampling as was used for purging. Sampling should occur in a progression from least to most contaminated well, if this is known. Generally, volatile (e.g., solvents and fuel constituents) and gas sensitive (e.g., Fe^{2+}, CH_4, H_2S/HS^-, alkalinity) parameters should be sampled first. The sequence in which samples for most inorganic parameters are collected is immaterial unless filtered (dissolved) samples are desired. Filtering should be done last and in-line filters should be used as discussed above. During both well purging and sampling, proper protective clothing and equipment must be used based upon the type and level of contaminants present.

The appropriate sample container will be prepared in advance of actual sample collection for the analytes of interest and include sample preservative where necessary. Water samples should be collected directly into this container from the pump tubing.

Immediately after a sample bottle has been filled, it must be preserved as specified in the site (QAPP). Sample preservation requirements are based on the analyses being performed (use site QAPP, FSP, RCRA guidance document [U. S. EPA, 1992] or EPA SW-846 [U. S. EPA, 1982]). It may be advisable to add preservatives to sample bottles in a controlled setting prior to entering the field in order to reduce the chances of improperly preserving sample bottles or introducing field contaminants into a sample bottle while adding the preservatives.

The preservatives should be transferred from the chemical bottle to the sample container using a disposable polyethylene pipet and the disposable pipet should be used only once and then discarded.

After a sample container has been filled with ground water, a Teflon™ (or tin)-lined cap is screwed on tightly to prevent the container from leaking. A sample label is filled out as specified in the FSP. The samples should be stored inverted at 4°C.

Specific decontamination protocols for sampling devices are dependent to some extent on the type of device used and the type of contaminants encountered. Refer to the site QAPP and FSP for specific requirements.

I. Blanks

The following blanks should be collected:

(1) field blank: one field blank should be collected from each source water (distilled/deionized water) used for sampling equipment decontamination or for assisting well development procedures.

(2) equipment blank: one equipment blank should be taken prior to the commencement of field work, from each set of sampling equipment to be used for that day. Refer to site QAPP or FSP for specific requirements.

(3) trip blank: a trip blank is required to accompany each volatile sample shipment. These blanks are prepared in the laboratory by filling a 40-mL volatile organic analysis (VOA) bottle with distilled/deionized water.

V. Low-Permeability Formations and Fractured Rock

The overall sampling program goals or sampling objectives will drive how the sampling points are located, installed, and choice of sampling device. Likewise, site-specific hydrogeologic factors will affect these decisions. Sites with very low permeability formations or fractures causing discrete flow channels may require a unique monitoring approach. Unlike water supply wells, wells installed for ground-water quality assessment and restoration programs are often installed in low water-yielding settings (e.g., clays, silts). Alternative types of sampling points and sampling methods are often needed in these types of environments, because low-permeability settings may require extremely low-flow purging (<0.1 L/min) and may be technology-limited. Where devices are not readily available to pump at such low flow rates, the primary consideration is to avoid dewatering of

the well screen. This may require repeated recovery of the water during purging while leaving the pump in place within the well screen.

Use of low-flow techniques may be impractical in these settings, depending upon the water recharge rates. The sampler and the end-user of data collected from such wells need to understand the limitations of the data collected; i.e., a strong potential for underestimation of actual contaminant concentrations for volatile organics, potential false negatives for filtered metals and potential false positives for unfiltered metals. It is suggested that comparisons be made between samples recovered using low-flow purging techniques and samples recovered using passive sampling techniques (i.e., two sets of samples). Passive sample collection would essentially entail acquisition of the sample with no or very little purging using a dedicated sampling system installed within the screened interval or a passive sample collection device.

A. Low-Permeability Formations (<0.1 L/min recharge)

1. Low-Flow Purging and Sampling with Pumps

a. "portable or non-dedicated mode" - Lower the pump (one capable of pumping at <0.1 L/min) to mid-screen or slightly above and set in place for minimum of 48 hours (to lessen purge volume requirements). After 48 hours, use procedures listed in Part IV above regarding monitoring water quality parameters for stabilization, etc., but do not dewater the screen. If excessive drawdown and slow recovery is a problem, then alternate approaches such as those listed below may be better.

b. "dedicated mode" - Set the pump as above at least a week prior to sampling; that is, operate in a dedicated pump mode. With this approach significant reductions in purge volume should be realized. Water quality parameters should stabilize quite rapidly due to less disturbance of the sampling zone.

2. Passive Sample Collection

Passive sampling collection requires insertion of the device into the screened interval for a sufficient time period to allow flow and sample equilibration before extraction for analysis. Conceptually, the extraction of water from low yielding formations seems more akin to the collection of water from the unsaturated zone and passive sampling techniques may be more appropriate in terms of obtaining "representative" samples. Satisfying usual sample volume requirements is typically a problem with this approach and some latitude will be needed on the part of regulatory entities to achieve sampling objectives.

B. Fractured Rock

In fractured rock formations, a low-flow to zero purging approach using pumps in conjunction with packers to isolate the sampling zone in the borehole is suggested. Passive multi-layer sampling devices may also provide the most "representative" samples. It is imperative in these settings to identify flow paths or water-producing fractures prior to sampling using tools such as borehole flowmeters and/or other geophysical tools.

After identification of water-bearing fractures, install packer(s) and pump assembly for sample collection using low-flow sampling in "dedicated mode" or use a passive sampling device which can isolate the identified water-bearing fractures.

VI. Documentation

The usual practices for documenting the sampling event should be used for low-flow purging and sampling techniques. This should include, at a minimum: information on the conduct of purging operations (flow-rate, drawdown, water-quality parameter values, volumes extracted and times for measurements), field instrument calibration data, water sampling forms and chain of custody forms. See Figures 2 and 3 and "Ground Water Sampling Workshop -- A Workshop Summary" (U. S. EPA, 1995) for example forms and other documentation suggestions and information. This information coupled with laboratory analytical data and validation data are needed to judge the "useability" of the sampling data.

VII. Notice

The U.S. Environmental Protection Agency through its Office of Research and Development funded and managed the research described herein as part of its in-house research program and under Contract No. 68-C4-0031 to Dynamac Corporation. It has been subjected to the Agency's peer and administrative review and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Figure 2. **Ground Water Sampling Log**

Project _____ **Site** _____ **Well No.** _____ **Date** _____

Well Depth _____ **Screen Length** _____ **Well Diameter** _____ **Casing Type** _____

Sampling Device _____ **Tubing type** _____ **Water Level** _____

Measuring Point _____ **Other Infor** _____

_____

Sampling Personnel _____

Time	pH	Temp	Cond.	Dis.O_2	Turb.	[ ]Conc			Notes

Type of Samples Collected

_____

Information: 2 in = 617 ml/ft, 4 in = 2470 ml/ft: $Vol_{cyl} = \pi r^2 h$, $Vol_{sphere} = 4/3\pi r^3$

Figure 3. **Ground Water Sampling Log** (with automatic data logging for most water quality parameters)

Project _____ **Site** _____ **Well No.** _____ **Date** _____

Well Depth _____ **Screen Length** _____ **Well Diameter** _____ **Casing Type** _____

Sampling Device _____ **Tubing type** _____ **Water Level** _____

Measuring Point _____ **Other Infor** _____

_____

Sampling Personnel _____

Time	Pump Rate	Turbidity	Alkalinity	[ ] Conc	Notes

Type of Samples Collected

_____

Information: 2 in = 617 ml/ft, 4 in = 2470 ml/ft: $Vol_{cyl} = \pi r^2 h$, $Vol_{sphere} = 4/3\pi r^3$

EHS Support

LOW FLOW GROUNDWATER SAMPLING FORM

Project Name: _____

Project Number: _____

Time (Initial): _____

Initial Water Level: _____ ft

Depth to Product: _____ ft

Total Well Depth: _____ ft

Well Identification: _____

Sample Date: _____

Field Technician(s): _____

Inner Casing Diameter (in): _____

Pump and Tubing Type: _____

Start Purge Time: _____

Time	Flow Rate	Water Level	Temp.	pH	Conductivity	Turbidity	DO	ORP	Odor	Color	Comments
	__L/min	ft	°C / °F	S.U.	__S/cm	NTU	mg/L	mV			

Comments: _____

End Purge Time: _____

Final Water Level: _____ ft

Total Volume Purged: _____ gal

One Well Volume (prior to purging, if applicable): _____ gal

Well Purged Dry? ☐ Yes ☐ No

Tubing Inlet Depth: _____

SAMPLE ID	TIME	ANALYSES	QA/QC SAMPLE	REMARKS

Gas Concentration in Well: _____ ppm

Formula for Calculating Well Casing Volume

$$[A] = \frac{\pi D^2 L}{4} * 7.48 \frac{gal}{ft^3}$$

D = Well casing inner diameter *(converted to feet)*

L = Height of water column (ft)

Parameter	Stabilization Criteria*
Temperature	± 3% of reading (minimum of ± 0.2 C)
pH	+/- 0.1
Specific Conductance	+/- 3%
ORP	+/- 10 millivolts
Dissolved Oxygen	+/- 0.3 milligrams per liter
Turbidity	Not a stabilization criteria; however, the lower the turbidity the better

* - USEPA, 1996 (Puls and Barcelona) Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures

Signature: _____

United States Environmental Protection Agency | Office of Research and Development | Office of Solid Waste and Emergency Response | EPA/540/S-95/504 April 1996

Ground Water Issue

LOW-FLOW (MINIMAL DRAWDOWN) GROUND-WATER SAMPLING PROCEDURES

by Robert W. Puls[1] and Michael J. Barcelona[2]

Background

The Regional Superfund Ground Water Forum is a group of ground-water scientists, representing EPA's Regional Superfund Offices, organized to exchange information related to ground-water remediation at Superfund sites. One of the major concerns of the Forum is the sampling of ground water to support site assessment and remedial performance monitoring objectives. This paper is intended to provide background information on the development of low-flow sampling procedures and its application under a variety of hydrogeologic settings. It is hoped that the paper will support the production of standard operating procedures for use by EPA Regional personnel and other environmental professionals engaged in ground-water sampling.

For further information contact: Robert Puls, 405-436-8543, Subsurface Remediation and Protection Division, NRMRL, Ada, Oklahoma.

I. Introduction

The methods and objectives of ground-water sampling to assess water quality have evolved over time. Initially the emphasis was on the assessment of water quality of aquifers as sources of drinking water. Large water-bearing units were identified and sampled in keeping with that objective. These were highly productive aquifers that supplied drinking water via private wells or through public water supply systems. Gradually, with the increasing awareness of subsurface pollution of these water resources, the understanding of complex hydrogeochemical processes which govern the fate and transport of contaminants in the subsurface increased. This increase in understanding was also due to advances in a number of scientific disciplines and improvements in tools used for site characterization and ground-water sampling. Ground-water quality investigations where pollution was detected initially borrowed ideas, methods, and materials for site characterization from the water supply field and water analysis from public health practices. This included the materials and manner in which monitoring wells were installed and the way in which water was brought to the surface, treated, preserved and analyzed. The prevailing conceptual ideas included convenient generalizations of ground-water resources in terms of large and relatively homogeneous hydrologic *units*. With time it became apparent that conventional water supply generalizations of *homogeneity* did not adequately represent field data regarding pollution of these subsurface resources. The important role of *heterogeneity* became increasingly clear not only in geologic terms, but also in terms of complex physical,

[1]National Risk Management Research Laboratory, U.S. EPA
[2]University of Michigan

Superfund Technology Support Center for Ground Water

National Risk Management Research Laboratory
Subsurface Protection and Remediation Division
Robert S. Kerr Environmental Research Center
Ada, Oklahoma

Technology Innovation Office
Office of Solid Waste and Emergency Response, US EPA, Washington, DC

Walter W. Kovalick, Jr., Ph.D.
Director

chemical and biological subsurface processes. With greater appreciation of the role of heterogeneity, it became evident that subsurface pollution was ubiquitous and encompassed the unsaturated zone to the deep subsurface and included unconsolidated sediments, fractured rock, and *aquitards* or low-yielding or impermeable formations. Small-scale processes and heterogeneities were shown to be important in identifying contaminant distributions and in controlling water and contaminant flow paths.

It is beyond the scope of this paper to summarize all the advances in the field of ground-water quality investigations and remediation, but two particular issues have bearing on ground-water sampling today: aquifer heterogeneity and colloidal transport. Aquifer heterogeneities affect contaminant flow paths and include variations in geology, geochemistry, hydrology and microbiology. As methods and the tools available for subsurface investigations have become increasingly sophisticated and understanding of the subsurface environment has advanced, there is an awareness that in most cases a primary concern for site investigations is characterization of contaminant flow paths rather than entire aquifers. In fact, in many cases, plume thickness can be less than well screen lengths (e.g., 3-6 m) typically installed at hazardous waste sites to detect and monitor plume movement over time. Small-scale differences have increasingly been shown to be important and there is a general trend toward smaller diameter wells and shorter screens.

The hydrogeochemical significance of colloidal-size particles in subsurface systems has been realized during the past several years (Gschwend and Reynolds, 1987; McCarthy and Zachara, 1989; Puls, 1990; Ryan and Gschwend, 1990). This realization resulted from both field and laboratory studies that showed faster contaminant migration over greater distances and at higher concentrations than flow and transport model predictions would suggest (Buddemeier and Hunt, 1988; Enfield and Bengtsson, 1988; Penrose et al., 1990). Such models typically account for interaction between the mobile aqueous and immobile solid phases, but do not allow for a mobile, reactive solid phase. It is recognition of this third *phase* as a possible means of contaminant transport that has brought increasing attention to the manner in which samples are collected and processed for analysis (Puls et al., 1990; McCarthy and Degueldre, 1993; Backhus et al., 1993; U. S. EPA, 1995). If such a phase is present in sufficient mass, possesses high sorption reactivity, large surface area, and remains stable in suspension, it can serve as an important mechanism to facilitate contaminant transport in many types of subsurface systems.

Colloids are particles that are sufficiently small so that the surface free energy of the particle dominates the bulk free energy. Typically, in ground water, this includes particles with diameters between 1 and 1000 nm. The most commonly observed mobile particles include: secondary clay minerals; hydrous iron, aluminum, and manganese oxides; dissolved and particulate organic materials, and viruses and bacteria. These reactive particles have been shown to be mobile under a variety of conditions in both field studies and laboratory column experiments, and as such need to be included in monitoring programs where identification of the *total* mobile contaminant loading (dissolved + naturally suspended particles) at a site is an objective. To that end, sampling methodologies must be used which do not artificially bias *naturally* suspended particle concentrations.

Currently the most common ground-water purging and sampling methodology is to purge a well using bailers or high speed pumps to remove 3 to 5 casing volumes followed by sample collection. This method can cause adverse impacts on sample quality through collection of samples with high levels of turbidity. This results in the inclusion of otherwise immobile artifactual particles which produce an overestimation of certain analytes of interest (e.g., metals or hydrophobic organic compounds). Numerous documented problems associated with filtration (Danielsson, 1982; Laxen and Chandler, 1982; Horowitz et al., 1992) make this an undesirable method of rectifying the turbidity problem, and include the removal of potentially mobile (contaminant-associated) particles during filtration, thus artificially biasing contaminant concentrations low. Sampling-induced turbidity problems can often be mitigated by using low-flow purging and sampling techniques.

Current subsurface conceptual models have undergone considerable refinement due to the recent development and increased use of field screening tools. So-called hydraulic *push* technologies (e.g., cone penetrometer, Geoprobe®, QED HydroPunch®) enable relatively fast screening site characterization which can then be used to design and install a monitoring well network. Indeed, alternatives to conventional monitoring wells are now being considered for some hydrogeologic settings. The ultimate design of any monitoring system should however be based upon adequate site characterization and be consistent with established monitoring objectives.

If the sampling program objectives include accurate assessment of the magnitude and extent of subsurface contamination over time and/or accurate assessment of subsequent remedial performance, then some information regarding plume delineation in three-dimensional space is necessary prior to monitoring well network design and installation. This can be accomplished with a variety of different tools and equipment ranging from hand-operated augers to screening tools mentioned above and large drilling rigs. Detailed information on ground-water flow velocity, direction, and horizontal and vertical variability are essential baseline data requirements. Detailed soil and geologic data are required prior to and during the installation of sampling points. This includes historical as well as detailed soil and geologic logs which accumulate during the site investigation. The use of borehole geophysical techniques is also recommended. With this information (together with other site characterization data) and a clear understanding of sampling

objectives, then appropriate location, screen length, well diameter, slot size, etc. for the monitoring well network can be decided. This is especially critical for new in situ remedial approaches or natural attenuation assessments at hazardous waste sites.

In general, the overall goal of any ground-water sampling program is to collect water samples with no alteration in water chemistry; analytical data thus obtained may be used for a variety of specific monitoring programs depending on the regulatory requirements. The sampling methodology described in this paper assumes that the monitoring goal is to sample monitoring wells for the presence of contaminants and it is applicable whether mobile colloids are a concern or not and whether the analytes of concern are metals (and metalloids) or organic compounds.

II. Monitoring Objectives and Design Considerations

The following issues are important to consider prior to the design and implementation of any ground-water monitoring program, including those which anticipate using low-flow purging and sampling procedures.

A. Data Quality Objectives (DQOs)

Monitoring objectives include four main types: detection, assessment, corrective-action evaluation and resource evaluation, along with *hybrid* variations such as site-assessments for property transfers and water availability investigations. Monitoring objectives may change as contamination or water quality problems are discovered. However, there are a number of common components of monitoring programs which should be recognized as important regardless of initial objectives. These components include:

1) Development of a conceptual model that incorporates elements of the regional geology to the local geologic framework. The conceptual model development also includes initial site characterization efforts to identify hydrostratigraphic units and likely flow-paths using a minimum number of borings and well completions;

2) Cost-effective and well documented collection of high quality data utilizing simple, accurate, and reproducible techniques; and

3) Refinement of the conceptual model based on supplementary data collection and analysis.

These fundamental components serve many types of monitoring programs and provide a basis for future efforts that evolve in complexity and level of spatial detail as purposes and objectives expand. High quality, reproducible data collection is a common goal regardless of program objectives.

High quality data collection implies data of sufficient accuracy, precision, and completeness (i.e., ratio of valid analytical results to the minimum sample number called for by the program design) to meet the program objectives. Accuracy depends on the correct choice of monitoring tools and procedures to minimize sample and subsurface disturbance from collection to analysis. Precision depends on the repeatability of sampling and analytical protocols. It can be assured or improved by replication of sample analyses including blanks, field/lab standards and reference standards.

B. Sample Representativeness

An important goal of any monitoring program is collection of data that is truly representative of conditions at the site. The term *representativeness* applies to chemical and hydrogeologic data collected via wells, borings, piezometers, geophysical and soil gas measurements, lysimeters, and temporary sampling points. It involves a recognition of the statistical variability of individual subsurface physical properties, and contaminant or major ion concentration levels, while explaining extreme values. Subsurface temporal and spatial variability are facts. Good professional practice seeks to maximize representativeness by using proven accurate and reproducible techniques to define limits on the distribution of measurements collected at a site. However, measures of representativeness are dynamic and are controlled by evolving site characterization and monitoring objectives. An evolutionary site characterization model, as shown in Figure 1, provides a systematic approach to the goal of consistent data collection.

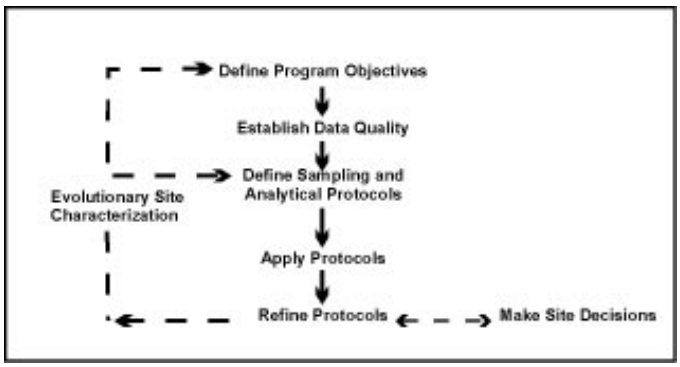

Figure 1. Evolutionary Site Characterization Model

The model emphasizes a recognition of the causes of the variability (e.g., use of inappropriate technology such as using bailers to purge wells; imprecise or operator-dependent methods) and the need to control avoidable errors.

1) Questions of Scale

A sampling plan designed to collect representative samples must take into account the potential scale of changes in site conditions through space and time as well as the chemical associations and behavior of the parameters that are targeted for investigation. In subsurface systems, physical (i.e., aquifer) and chemical properties over time or space are not statistically independent. In fact, samples taken in close proximity (i.e., within distances of a few meters) or within short time periods (i.e., more frequently than monthly) are highly auto-correlated. This means that designs employing high-sampling frequency (e.g., monthly) or dense spatial monitoring designs run the risk of redundant data collection and misleading inferences regarding trends in values that aren't statistically valid. In practice, contaminant detection and assessment monitoring programs rarely suffer these *over-sampling* concerns. In corrective-action evaluation programs, it is also possible that too little data may be collected over space or time. In these cases, false interpretation of the spatial extent of contamination or underestimation of temporal concentration variability may result.

2) Target Parameters

Parameter selection in monitoring program design is most often dictated by the regulatory status of the site. However, background water quality constituents, purging indicator parameters, and contaminants, all represent targets for data collection programs. The tools and procedures used in these programs should be equally rigorous and applicable to all categories of data, since all may be needed to determine or support regulatory action.

C. Sampling Point Design and Construction

Detailed site characterization is central to all decision-making purposes and the basis for this characterization resides in identification of the geologic framework and major hydro-stratigraphic units. Fundamental data for sample point location include: subsurface lithology, head-differences and background geochemical conditions. Each sampling point has a proper use or uses which should be documented at a level which is appropriate for the program's data quality objectives. Individual sampling points may not always be able to fulfill multiple monitoring objectives (e.g., detection, assessment, corrective action).

1) Compatibility with Monitoring Program and Data Quality Objectives

Specifics of sampling point location and design will be dictated by the complexity of subsurface lithology and variability in contaminant and/or geochemical conditions. It should be noted that, regardless of the ground-water sampling approach, few sampling points (e.g., wells, drive-points, screened augers) have zones of influence in excess of a few feet. Therefore, the spatial frequency of sampling points should be carefully selected and designed.

2) Flexibility of Sampling Point Design

In most cases *well-point* diameters in excess of 1 7/8 inches will permit the use of most types of submersible pumping devices for low-flow (minimal drawdown) sampling. It is suggested that *short* (e.g., less than 1.6 m) screens be incorporated into the monitoring design where possible so that comparable results from one device to another might be expected. *Short*, of course, is relative to the degree of vertical water quality variability expected at a site.

3) Equilibration of Sampling Point

Time should be allowed for equilibration of the well or sampling point with the formation after installation. Placement of well or sampling points in the subsurface produces some disturbance of ambient conditions. Drilling techniques (e.g., auger, rotary, etc.) are generally considered to cause more disturbance than *direct-push* technologies. In either case, there may be a period (i.e., days to months) during which water quality near the point may be distinctly different from that in the formation. Proper development of the sampling point and adjacent formation to remove fines created during emplacement will shorten this water quality *recovery* period.

III. Definition of Low-Flow Purging and Sampling

It is generally accepted that water in the well casing is non-representative of the formation water and needs to be purged prior to collection of ground-water samples. However, the water in the screened interval may indeed be representative of the formation, depending upon well construction and site hydrogeology. Wells are purged to some extent for the following reasons: the presence of the air interface at the top of the water column resulting in an oxygen concentration gradient with depth, loss of volatiles up the water column, leaching from or sorption to the casing or filter pack, chemical changes due to clay seals or backfill, and surface infiltration.

Low-flow purging, whether using portable or dedicated systems, should be done using pump-intake located in the middle or slightly above the middle of the screened interval. Placement of the pump too close to the bottom of the well will cause increased entrainment of solids which have collected in the well over time. These particles are present as a result of well development, prior purging and sampling events, and natural colloidal transport and deposition. Therefore, placement of the pump in the middle or toward the top of the screened interval is suggested. Placement of the pump at the top of the water column for sampling is only recommended in unconfined aquifers, screened across the water table, where this is the desired sampling point. Low-

flow purging has the advantage of minimizing mixing between the overlying stagnant casing water and water within the screened interval.

A. Low-Flow Purging and Sampling

Low-flow refers to the velocity with which water enters the pump intake and that is imparted to the formation pore water in the immediate vicinity of the well screen. It does not necessarily refer to the flow rate of water discharged at the surface which can be affected by flow regulators or restrictions. Water level drawdown provides the best indication of the stress imparted by a given flow-rate for a given hydrological situation. The objective is to pump in a manner that minimizes stress (drawdown) to the system to the extent practical taking into account established site sampling objectives. Typically, flow rates on the order of 0.1 - 0.5 L/min are used, however this is dependent on site-specific hydrogeology. Some extremely coarse-textured formations have been successfully sampled in this manner at flow rates to 1 L/min. The effectiveness of using low-flow purging is intimately linked with proper screen location, screen length, and well construction and development techniques. The reestablishment of natural flow paths in both the vertical and horizontal directions is important for correct interpretation of the data. For high resolution sampling needs, screens less than 1 m should be used. Most of the need for purging has been found to be due to passing the sampling device through the overlying casing water which causes mixing of these stagnant waters and the dynamic waters within the screened interval. Additionally, there is disturbance to suspended sediment collected in the bottom of the casing and the displacement of water out into the formation immediately adjacent to the well screen. These disturbances and impacts can be avoided using dedicated sampling equipment, which precludes the need to insert the sampling device prior to purging and sampling.

Isolation of the screened interval water from the overlying stagnant casing water may be accomplished using low-flow minimal drawdown techniques. If the pump intake is located within the screened interval, most of the water pumped will be drawn in directly from the formation with little mixing of casing water or disturbance to the sampling zone. However, if the wells are not constructed and developed properly, zones other than those intended may be sampled. At some sites where geologic heterogeneities are sufficiently different within the screened interval, higher conductivity zones may be preferentially sampled. This is another reason to use shorter screened intervals, especially where high spatial resolution is a sampling objective.

B. Water Quality Indicator Parameters

It is recommended that water quality indicator parameters be used to determine purging needs prior to sample collection in each well. Stabilization of parameters such as pH, specific conductance, dissolved oxygen, oxidation-reduction potential, temperature and turbidity should be used to determine when formation water is accessed during purging. In general, the order of stabilization is pH, temperature, and specific conductance, followed by oxidation-reduction potential, dissolved oxygen and turbidity. Temperature and pH, while commonly used as purging indicators, are actually quite insensitive in distinguishing between formation water and stagnant casing water; nevertheless, these are important parameters for data interpretation purposes and should also be measured. Performance criteria for determination of stabilization should be based on water-level drawdown, pumping rate and equipment specifications for measuring indicator parameters. Instruments are available which utilize in-line flow cells to continuously measure the above parameters.

It is important to establish specific well stabilization criteria and then consistently follow the same methods thereafter, particularly with respect to drawdown, flow rate and sampling device. Generally, the time or purge volume required for parameter stabilization is independent of well depth or well volumes. Dependent variables are well diameter, sampling device, hydrogeochemistry, pump flow rate, and whether the devices are used in a portable or dedicated manner. If the sampling device is already in place (i.e., dedicated sampling systems), then the time and purge volume needed for stabilization is much shorter. Other advantages of dedicated equipment include less purge water for waste disposal, much less decontamination of equipment, less time spent in preparation of sampling as well as time in the field, and more consistency in the sampling approach which probably will translate into less variability in sampling results. The use of dedicated equipment is strongly recommended at wells which will undergo routine sampling over time.

If parameter stabilization criteria are too stringent, then minor oscillations in indicator parameters may cause purging operations to become unnecessarily protracted. It should also be noted that turbidity is a very conservative parameter in terms of stabilization. Turbidity is always the last parameter to stabilize. Excessive purge times are invariably related to the establishment of too stringent turbidity stabilization criteria. It should be noted that natural turbidity levels in ground water may exceed 10 nephelometric turbidity units (NTU).

C. Advantages and Disadvantages of Low-Flow (Minimum Drawdown) Purging

In general, the advantages of low-flow purging include:

- samples which are representative of the *mobile* load of contaminants present (dissolved and colloid-associated);
- minimal disturbance of the sampling point thereby minimizing sampling artifacts;
- less operator variability, greater operator control;

- reduced stress on the formation (minimal drawdown);
- less mixing of stagnant casing water with formation water;
- reduced need for filtration and, therefore, less time required for sampling;
- smaller purging volume which decreases waste disposal costs and sampling time;
- better sample consistency; reduced artificial sample variability.

Some disadvantages of low-flow purging are:

- higher initial capital costs,
- greater set-up time in the field,
- need to transport additional equipment to and from the site,
- increased training needs,
- resistance to change on the part of sampling practitioners,
- concern that new data will indicate a *change in conditions* and trigger an *action*.

IV. Low-Flow (Minimal Drawdown) Sampling Protocols

The following ground-water sampling procedure has evolved over many years of experience in ground-water sampling for organic and inorganic compound determinations and as such summarizes the authors' (and others) experiences to date (Barcelona et al., 1984, 1994; Barcelona and Helfrich, 1986; Puls and Barcelona, 1989; Puls et. al. 1990, 1992; Puls and Powell, 1992; Puls and Paul, 1995). High-quality chemical data collection is essential in ground-water monitoring and site characterization. The primary limitations to the collection of *representative* ground-water samples include: mixing of the stagnant casing and *fresh* screen waters during insertion of the sampling device or ground-water level measurement device; disturbance and resuspension of settled solids at the bottom of the well when using high pumping rates or raising and lowering a pump or bailer; introduction of atmospheric gases or degassing from the water during sample handling and transfer, or inappropriate use of vacuum sampling device, etc.

A. Sampling Recommendations

Water samples should not be taken immediately following well development. Sufficient time should be allowed for the ground-water flow regime in the vicinity of the monitoring well to stabilize and to approach chemical equilibrium with the well construction materials. This lag time will depend on site conditions and methods of installation but often exceeds one week.

Well purging is nearly always necessary to obtain samples of water flowing through the geologic formations in the screened interval. Rather than using a general but arbitrary guideline of purging three casing volumes prior to sampling, it is recommended that an in-line water quality measurement device (e.g., flow-through cell) be used to establish the stabilization time for several parameters (e.g. , pH, specific conductance, redox, dissolved oxygen, turbidity) on a well-specific basis. Data on pumping rate, drawdown, and volume required for parameter stabilization can be used as a guide for conducting subsequent sampling activities.

The following are recommendations to be considered before, during and after sampling:

- use low-flow rates (<0.5 L/min), during both purging and sampling to maintain minimal drawdown in the well;
- maximize tubing wall thickness, minimize tubing length;
- place the sampling device intake at the desired sampling point;
- minimize disturbances of the stagnant water column above the screened interval during water level measurement and sampling device insertion;
- make proper adjustments to stabilize the flow rate as soon as possible;
- monitor water quality indicators during purging;
- collect unfiltered samples to estimate contaminant loading and transport potential in the subsurface system.

B. Equipment Calibration

Prior to sampling, all sampling device and monitoring equipment should be calibrated according to manufacturer's recommendations and the site Quality Assurance Project Plan (QAPP) and Field Sampling Plan (FSP). Calibration of pH should be performed with at least two buffers which bracket the expected range. Dissolved oxygen calibration must be corrected for local barometric pressure readings and elevation.

C. Water Level Measurement and Monitoring

It is recommended that a device be used which will least disturb the water surface in the casing. Well depth should be obtained from the well logs. Measuring to the bottom of the well casing will only cause resuspension of settled solids from the formation and require longer purging times for turbidity equilibration. Measure well depth after sampling is completed. The water level measurement should be taken from a permanent reference point which is surveyed relative to ground elevation.

D. Pump Type

The use of low-flow (e.g., 0.1-0.5 L/min) pumps is suggested for purging and sampling all types of analytes. All pumps have some limitation and these should be investigated with respect to application at a particular site. Bailers are inappropriate devices for low-flow sampling.

1) General Considerations

There are no unusual requirements for ground-water sampling devices when using low-flow, minimal drawdown techniques. The major concern is that the device give consistent results and minimal disturbance of the sample across a range of *low* flow rates (i.e., < 0.5 L/min). Clearly, pumping rates that cause minimal to no drawdown in one well could easily cause *significant* drawdown in another well finished in a less transmissive formation. In this sense, the pump should not cause undue pressure or temperature changes or physical disturbance on the water sample over a reasonable sampling range. Consistency in operation is critical to meet accuracy and precision goals.

2) Advantages and Disadvantages of Sampling Devices

A variety of sampling devices are available for low-flow (minimal drawdown) purging and sampling and include peristaltic pumps, bladder pumps, electrical submersible pumps, and gas-driven pumps. Devices which lend themselves to both dedication and consistent operation at definable low-flow rates are preferred. It is desirable that the pump be easily adjustable and operate reliably at these lower flow rates. The peristaltic pump is limited to shallow applications and can cause degassing resulting in alteration of pH, alkalinity, and some volatiles loss. Gas-driven pumps should be of a type that does not allow the gas to be in direct contact with the sampled fluid.

Clearly, bailers and other *grab* type samplers are ill-suited for low-flow sampling since they will cause repeated disturbance and mixing of *stagnant* water in the casing and the *dynamic* water in the screened interval. Similarly, the use of inertial lift foot-valve type samplers may cause too much disturbance at the point of sampling. Use of these devices also tends to introduce uncontrolled and unacceptable operator variability.

Summaries of advantages and disadvantages of various sampling devices are listed in Herzog et al. (1991), U. S. EPA (1992), Parker (1994) and Thurnblad (1994).

E. Pump Installation

Dedicated sampling devices (left in the well) capable of pumping and sampling are preferred over <u>any</u> other type of device. Any portable sampling device should be slowly and carefully lowered to the middle of the screened interval or slightly above the middle (e.g., 1-1.5 m below the top of a 3 m screen). This is to minimize excessive mixing of the stagnant water in the casing above the screen with the screened interval zone water, and to minimize resuspension of solids which will have collected at the bottom of the well. These two disturbance effects have been shown to directly affect the time required for purging. There also appears to be a direct correlation between size of portable sampling devices relative to the well bore and resulting purge volumes and times. The key is to minimize disturbance of water and solids in the well casing.

F. Filtration

Decisions to filter samples should be dictated by sampling objectives rather than as a *fix* for poor sampling practices, and field-filtering of certain constituents should not be the default. Consideration should be given as to what the application of field-filtration is trying to accomplish. For assessment of truly dissolved (as opposed to operationally *dissolved* [i.e., samples filtered with 0.45 µm filters]) concentrations of major ions and trace metals, 0.1 µm filters are recommended although 0.45 µm filters are normally used for most regulatory programs. Alkalinity samples must also be filtered if significant particulate calcium carbonate is suspected, since this material is likely to impact alkalinity titration results (although filtration itself may alter the CO_2 composition of the sample and, therefore, affect the results).

Although filtration may be appropriate, filtration of a sample may cause a number of unintended changes to occur (e.g. oxidation, aeration) possibly leading to filtration-induced artifacts during sample analysis and uncertainty in the results. Some of these unintended changes may be unavoidable but the factors leading to them must be recognized. Deleterious effects can be minimized by consistent application of certain filtration guidelines. Guidelines should address selection of filter type, media, pore size, etc. in order to identify and minimize potential sources of uncertainty when filtering samples.

In-line filtration is recommended because it provides better consistency through less sample handling, and minimizes sample exposure to the atmosphere. In-line filters are available in both disposable (barrel filters) and non-disposable (in-line filter holder, flat membrane filters) formats and various filter pore sizes (0.1-5.0 µm). Disposable filter cartridges have the advantage of greater sediment handling capacity when compared to traditional membrane filters. Filters must be pre-rinsed following manufacturer's recommendations. If there are no recommendations for rinsing, pass through a minimum of 1 L of ground water following purging and prior to sampling. Once filtration has begun, a filter cake may develop as particles larger than the pore size accumulate on the filter membrane. The result is that the effective pore diameter of the membrane is reduced and particles smaller than the stated pore size are excluded from the filtrate. Possible corrective measures include prefiltering (with larger pore size filters), minimizing particle loads to begin with, and reducing sample volume.

G. Monitoring of Water Level and Water Quality Indicator Parameters

Check water level periodically to monitor drawdown in the well as a guide to flow rate adjustment. The goal is minimal drawdown (<0.1 m) during purging. This goal may be difficult to achieve under some circumstances due to geologic heterogeneities within the screened interval, and may require adjustment based on site-specific conditions and personal experience. In-line water quality indicator parameters should be continuously monitored during purging. The water quality

indicator parameters monitored can include pH, redox potential, conductivity, dissolved oxygen (DO) and turbidity. The last three parameters are often most sensitive. Pumping rate, drawdown, and the time or volume required to obtain stabilization of parameter readings can be used as a future guide to purge the well. Measurements should be taken every three to five minutes if the above suggested rates are used. Stabilization is achieved after all parameters have stabilized for three successive readings. In lieu of measuring all five parameters, a minimum subset would include pH, conductivity, and turbidity or DO. Three successive readings should be within ± 0.1 for pH, ± 3% for conductivity, ± 10 mv for redox potential, and ± 10% for turbidity and DO. Stabilized purge indicator parameter trends are generally obvious and follow either an exponential or asymptotic change to stable values during purging. Dissolved oxygen and turbidity usually require the longest time for stabilization. The above stabilization guidelines are provided for rough estimates based on experience.

H. Sampling, Sample Containers, Preservation and Decontamination

Upon parameter stabilization, sampling can be initiated. If an in-line device is used to monitor water quality parameters, it should be disconnected or bypassed during sample collection. Sampling flow rate may remain at established purge rate or may be adjusted slightly to minimize aeration, bubble formation, turbulent filling of sample bottles, or loss of volatiles due to extended residence time in tubing. Typically, flow rates less than 0.5 L/min are appropriate. The same device should be used for sampling as was used for purging. Sampling should occur in a progression from least to most contaminated well, if this is known. Generally, volatile (e.g., solvents and fuel constituents) and gas sensitive (e.g., Fe^{2+}, CH_4, H_2S/HS^-, alkalinity) parameters should be sampled first. The sequence in which samples for most inorganic parameters are collected is immaterial unless filtered (dissolved) samples are desired. Filtering should be done last and in-line filters should be used as discussed above. During both well purging and sampling, proper protective clothing and equipment must be used based upon the type and level of contaminants present.

The appropriate sample container will be prepared in advance of actual sample collection for the analytes of interest and include sample preservative where necessary. Water samples should be collected directly into this container from the pump tubing.

Immediately after a sample bottle has been filled, it must be preserved as specified in the site (QAPP). Sample preservation requirements are based on the analyses being performed (use site QAPP, FSP, RCRA guidance document [U. S. EPA, 1992] or EPA SW-846 [U. S. EPA, 1982]). It may be advisable to add preservatives to sample bottles in a controlled setting prior to entering the field in order to reduce the chances of improperly preserving sample bottles or introducing field contaminants into a sample bottle while adding the preservatives.

The preservatives should be transferred from the chemical bottle to the sample container using a disposable polyethylene pipet and the disposable pipet should be used only once and then discarded.

After a sample container has been filled with ground water, a Teflon™ (or tin)-lined cap is screwed on tightly to prevent the container from leaking. A sample label is filled out as specified in the FSP. The samples should be stored inverted at 4°C.

Specific decontamination protocols for sampling devices are dependent to some extent on the type of device used and the type of contaminants encountered. Refer to the site QAPP and FSP for specific requirements.

I. Blanks

The following blanks should be collected:

(1) field blank: one field blank should be collected from each source water (distilled/deionized water) used for sampling equipment decontamination or for assisting well development procedures.

(2) equipment blank: one equipment blank should be taken prior to the commencement of field work, from each set of sampling equipment to be used for that day. Refer to site QAPP or FSP for specific requirements.

(3) trip blank: a trip blank is required to accompany each volatile sample shipment. These blanks are prepared in the laboratory by filling a 40-mL volatile organic analysis (VOA) bottle with distilled/deionized water.

V. Low-Permeability Formations and Fractured Rock

The overall sampling program goals or sampling objectives will drive how the sampling points are located, installed, and choice of sampling device. Likewise, site-specific hydrogeologic factors will affect these decisions. Sites with very low permeability formations or fractures causing discrete flow channels may require a unique monitoring approach. Unlike water supply wells, wells installed for ground-water quality assessment and restoration programs are often installed in low water-yielding settings (e.g., clays, silts). Alternative types of sampling points and sampling methods are often needed in these types of environments, because low-permeability settings may require extremely low-flow purging (<0.1 L/min) and may be technology-limited. Where devices are not readily available to pump at such low flow rates, the primary consideration is to avoid dewatering of

the well screen. This may require repeated recovery of the water during purging while leaving the pump in place within the well screen.

Use of low-flow techniques may be impractical in these settings, depending upon the water recharge rates. The sampler and the end-user of data collected from such wells need to understand the limitations of the data collected; i.e., a strong potential for underestimation of actual contaminant concentrations for volatile organics, potential false negatives for filtered metals and potential false positives for unfiltered metals. It is suggested that comparisons be made between samples recovered using low-flow purging techniques and samples recovered using passive sampling techniques (i.e., two sets of samples). Passive sample collection would essentially entail acquisition of the sample with no or very little purging using a dedicated sampling system installed within the screened interval or a passive sample collection device.

A. Low-Permeability Formations (<0.1 L/min recharge)

1. Low-Flow Purging and Sampling with Pumps

a. "portable or non-dedicated mode" - Lower the pump (one capable of pumping at <0.1 L/min) to mid-screen or slightly above and set in place for minimum of 48 hours (to lessen purge volume requirements). After 48 hours, use procedures listed in Part IV above regarding monitoring water quality parameters for stabilization, etc., but do not dewater the screen. If excessive drawdown and slow recovery is a problem, then alternate approaches such as those listed below may be better.

b. "dedicated mode" - Set the pump as above at least a week prior to sampling; that is, operate in a dedicated pump mode. With this approach significant reductions in purge volume should be realized. Water quality parameters should stabilize quite rapidly due to less disturbance of the sampling zone.

2. Passive Sample Collection

Passive sampling collection requires insertion of the device into the screened interval for a sufficient time period to allow flow and sample equilibration before extraction for analysis. Conceptually, the extraction of water from low yielding formations seems more akin to the collection of water from the unsaturated zone and passive sampling techniques may be more appropriate in terms of obtaining "representative" samples. Satisfying usual sample volume requirements is typically a problem with this approach and some latitude will be needed on the part of regulatory entities to achieve sampling objectives.

B. Fractured Rock

In fractured rock formations, a low-flow to zero purging approach using pumps in conjunction with packers to isolate the sampling zone in the borehole is suggested. Passive multi-layer sampling devices may also provide the most "representative" samples. It is imperative in these settings to identify flow paths or water-producing fractures prior to sampling using tools such as borehole flowmeters and/or other geophysical tools.

After identification of water-bearing fractures, install packer(s) and pump assembly for sample collection using low-flow sampling in "dedicated mode" or use a passive sampling device which can isolate the identified water-bearing fractures.

VI. Documentation

The usual practices for documenting the sampling event should be used for low-flow purging and sampling techniques. This should include, at a minimum: information on the conduct of purging operations (flow-rate, drawdown, water-quality parameter values, volumes extracted and times for measurements), field instrument calibration data, water sampling forms and chain of custody forms. See Figures 2 and 3 and "Ground Water Sampling Workshop -- A Workshop Summary" (U. S. EPA, 1995) for example forms and other documentation suggestions and information. This information coupled with laboratory analytical data and validation data are needed to judge the "useability" of the sampling data.

VII. Notice

The U.S. Environmental Protection Agency through its Office of Research and Development funded and managed the research described herein as part of its in-house research program and under Contract No. 68-C4-0031 to Dynamac Corporation. It has been subjected to the Agency's peer and administrative review and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Figure 2. **Ground Water Sampling Log**

Project _____ **Site** _____ **Well No.** _____ **Date** _____

Well Depth _____ **Screen Length** _____ **Well Diameter** _____ **Casing Type** _____

Sampling Device _____ **Tubing type** _____ **Water Level** _____

Measuring Point _____ **Other Infor** _____

_____

Sampling Personnel _____

Time	pH	Temp	Cond.	Dis.O_2	Turb.	[ ]Conc			Notes

Type of Samples Collected

_____

Information: 2 in = 617 ml/ft, 4 in = 2470 ml/ft: $Vol_{cyl} = \pi r^2 h$, $Vol_{sphere} = 4/3\pi r^3$

Figure 3. **Ground Water Sampling Log** (with automatic data logging for most water quality parameters)

Project _____ **Site** _____ **Well No.** _____ **Date** _____

Well Depth _____ **Screen Length** _____ **Well Diameter** _____ **Casing Type** _____

Sampling Device _____ **Tubing type** _____ **Water Level** _____

Measuring Point _____ **Other Infor** _____

_____

Sampling Personnel _____

Time	Pump Rate	Turbidity	Alkalinity	[ ] Conc	Notes

Type of Samples Collected

_____

Information: 2 in = 617 ml/ft, 4 in = 2470 ml/ft: $Vol_{cyl} = \pi r^2 h$, $Vol_{sphere} = 4/3\pi r^3$

SOP-44 VOLUME-PURGE METHOD FOR GROUNDWATER SAMPLING

Purpose

The purpose of this standard operating procedure (SOP) is to describe groundwater purging and collection procedures from wells using well-volume purging and sampling techniques. This SOP includes calculation of a well volume for specific well volume removal and high or unknown volume purging for wells containing in-place pumps (e.g., municipal, water treatment facility). The objective of purging wells with in-place pumps or without in-place pump is to collect a groundwater sample representative of aquifer conditions.

The well-volume approach method is based on purging three to five well volumes before sampling. This method is generally conducted with a bailer or pump. This method may be the selected sample method if groundwater parameter stabilization cannot be achieved using low-flow sampling techniques (SOP-43 Low-Flow Groundwater Sampling) or low-flow sampling techniques are not appropriate.

Relevant EHS Support SOPs

- SOP-04 Field Documentation
- SOP-05 Sample Management and Shipping
- SOP-06 Pre-Field Mobilization
- SOP-07 Investigation Derived Waste
- SOP-08 Field Equipment Operation and Calibration
- SOP-09 Equipment Decontamination
- SOP-41 Fluid Measurement
- SOP-46 Water Sampling for Chemical Analysis.

Attachments

- **Attachment A** EHS Support Groundwater Sampling Form

Required Materials

- Air monitoring instrumentation (e.g., photoionization detector [PID]) and supplies, if required
- Water quality meters (e.g., temperature, pH, conductance, dissolved oxygen [DO], oxidation-reduction potential [ORP], turbidity)
- Field logbook and field documentation
- Site plan showing well or water bore locations
- Health and Safety Plan (HASP)
- Personal protective equipment
- Indelible ink pens and waterproof marking pen

- Bailer, bailer string or rope, as appropriate
- Pump, controller, and power source—generator or battery, as appropriate
- Teflon or polyethylene tubing, as appropriate
- Decontamination equipment and supplies
- Bucket, drums, or other large container for storing and/or transporting purged water
- Measuring equipment (tape, water level indicator)
- Camera
- Appropriate sample containers, sampling forms, shipping equipment, wrapping tape.

1 Volume Purging Method

The well-volume method is a traditional technique where a pre-determined volume or fixed volume of water is removed from the well including any stagnant water located above the well screen. Stabilization groundwater field-measured parameters are not specific to the volume purging method; however, field-measured parameters may be part of the project work plan and is highly recommended.

Two common well-volume purging methods are outlined in this SOP—using a bailer and using a pump. The advantages and disadvantages of each purging equipment is outlined in **Table 1**.

Table 1 Groundwater Technique Considerations

Advantages	Disadvantages
Bailing method: • Represents water as a composite across the well screen • Standard and accepted method • Easy to understand and implement • Less mixing of the stagnant casing water with the formation water • Bailers are inexpensive, portable, and easy to operate	• Generates more investigative derived waste • Small scale heterogeneities are not possible • Method can mobilize solids • Little concern is given to how purging protocols and devices (e.g., bailers) affect the chemistry of groundwater samples • Can cause underestimation of maximum contaminant concentrations due to dilution • Can cause overestimation due to contaminant mobilization, degassing, or increased sample turbidity • Dewatering lower-yield wells causes losses of volatile organic compounds (VOCs), affects dissolved oxygen (DO) and carbon dioxide (CO2) concentrations / levels • Excessive drawdown can cause overestimation from soil gas or mobilization of soil-bound contaminants in the overlying formation or “smear zone”
Volume-purging is generally most effective in: • Soils with low to high hydraulic conductivities • Monitoring wells with any screen length	• Generates more investigative-derived waste • Is not a good method in low-yield formation groundwater, fractured bedrock, or very turbid water • Can cause underestimation of maximum contaminant concentrations due to dilution • Can cause overestimation due to contaminant mobilization, degassing, or increased sample turbidity • May affect some field-measured parameters (DO, oxidation reduction potential (ORP)) • Long-screened intervals (e.g., >9 m) or open-hole wells where the hydraulic flow pathways are unknown • Use where the aquifer is contaminated by non-aqueous phase liquids; however, a bailer can be a preferable method for collection of non-aqueous phase liquid

Note: Both bailer and pump method can contain equipment which require decontamination. Decontamination will be conducted with the accordance of SOP-09 Field Decontamination or the manufacturer’s recommendations.

Equipment Cautions: Factors to consider include: the analytes being evaluated, the type and location of the well being sampled, physical characteristics of the well (diameter and total depth), depth to water, geology adjacent to the screened interval and the groundwater chemistry.

1.1 Calculating the Well Volume

The volume of water in the well will be calculated based on the height of the water column in the well and the well diameter.

1. Open the well. If required, use a photoionization detector or equivalent to measure for the presence of volatile organic compounds. Record the results of the photoionization detector measurement in field logbook or approved field documentation.
2. Measure the depth to water and total depth of the well using a water level indicator. Fluid level and total depth will be measured in accordance with the guidelines provided in SOP-41 Fluid Measurements. Record the measurements in the field logbook or approved field documentation.
3. If NAPL is present, use an interface probe for depth measurements.
4. If NAPL is present, collection or removal of NAPL should be conducted in accordance with the project work plan.
5. Measure the nominal inside diameter of the well casing.
6. Calculate the volume of water in the well using one of the following equations:
   a. Calculation of 1 well volume using the formula:

      $V = \pi r^2 L$ (cf)

   Where:
   V = well volume (gallons or litres)
   π = pi (3.14)
   r = radius of monitoring well in feet or meters (L)
   L = height of the water column in feet or meters (the height of the water column is determined by subtracting the depth to water from the total depth of the well).
   cf = conversion factor (V/L^3)
   US Customary Units = 7.48 gal/ft^3
   Metric Units = 1,000 L/m^3

   b. Column height and known volume.
   Locate the casing diameter using **Table 2** below. Multiply the corresponding Volume of 1 length (foot or meter) per water column (H1) times the height of the water column (L).
   V = L (H1)

Table 2 Approximate Casing Volumes for Common Casing Sizes

US Customary Units		Metric Units	
Casing Inner Diameter (inches)	***Volume of 1 foot per water column (H1) (gal)***	***Casing Diameter (mm)***	***Volume of 1 meter per water column (H1) (Liter)***
1	0.04	50	2
2	0.16	80	5
3	0.35	100	8
4	0.67	125	12.5
6	1.47	150	17.7

7. Record the calculated well volume in the field logbook or field documentation.

1.2 Groundwater Sampling Procedures using a Bailer

1.2.1 Equipment Considerations

- Bailers vary in construction and type (single-check or double-check valve, metal, polyvinyl chloride, polyethylene, or Teflon material, diameter, lengths,) and shall be selected based on chemical of interest and sample depth.
- If additional weights are needed for a bailer, the weights and any attaching materials for the weights shall be non-reactive.
- The bailer line (e.g., nylon, cotton, wire) type shall consider the chemical of interest and be non-reactive.

1.2.2 *Bailer Method Procedure*

Note: The procedures below incorporate measurement of groundwater field-measured parameters. If these parameters are not necessary, the project work plan will note the deviation.

1. Measure and record the fluid depth and total well depth. Calculate the volume of water in the well and volume of water to remove.
2. Don a new pair of disposable nitrile or surgical gloves.
3. Open the plastic wrap of a new disposable bailer or decontaminated bailer exposing the bailer hanger.
4. Securely tie the line to the bailer hanger. A slip knot is preferred. The knot should be checked periodically throughout the bailing process to ensure the knot stays secure (i.e., the bailer is not lost down the well).
5. Remove the plastic wrap from the bailer.
6. Slowly lower the bailer through the well and into the water column until the bailer is fully submerged.
7. Carefully remove the bailer from the well. Do not allow the bailer line to come into contact with the ground. If the bailer line must be placed on the ground, a clean, plastic sheet shall be placed on the ground below the line.

8. Empty the water from the bailer into a bucket, pail, or container. It is recommended the volume of the bailer or bucket be known to estimate the volume of water removed during purging.
9. Continue to remove groundwater via the bailer until one well volume or a known volume has been removed. Collect and record groundwater field-measured parameters. Generally, field-measured parameters should include temperature, pH, conductivity, DO, ORP, and turbidity. Note and record any physical observations, such as color, odor, visual turbidity, effervescence, or presence of particulates. Field instruments shall be calibrated in accordance with SOP-08 Field Equipment Calibration and Operation.
10. Continue to bail groundwater from the well at a constant rate until another well volume or known volume is removed and the groundwater field-measured parameters are collected and recorded.
11. Continue alternating bailing and recording groundwater field-measured parameters until the required well volumes are removed.
12. Collect a final groundwater measurement after the well volumes have been removed.
13. If the well is purged dry, attempt to remove 3 well volumes prior to sampling. Groundwater field-measured parameters and final depth to groundwater should be recorded to the best extent practicable.
14. If 3 well volumes cannot be removed, purge the well dry and allow the well to recover until at least one of the following is met:
    - A minimum of 2 hours has elapsed since purging.
    - There is sufficient water volume present to obtain the sample.
    - The water in the well has recovered to 80% of the initial pre-well volume.
15. The well will be re-purged if more than 24 hours has elapsed since the well went dry and sampling begins.
16. Place representative groundwater directly into the sample bottles or sample container.
17. Follow the project work plan for sampling and in accordance with SOP-05 Sample Management and Shipping, and SOP-46 Water Sampling for Chemical Analysis.
18. Discard purge water and disposable equipment or supplies in accordance with the project work plan or SOP-07 Investigation Derived Waste.

1.3 Groundwater Sampling Procedures using a Pump

1.3.1 Wells with In-Place Pumps and Plumbing

Procedural Caution: Be aware of the site or well requirements for working with in-place pumps. Generally, wells with in-place pumps are positioned in large diameter wells and can produce large volumes of groundwater. The wells are commonly under the guidance or jurisdiction of a public or private entity with intended purposes (e.g., public water supply, water treatment, water cooling) . Safety considerations can include electrical, mechanical, or other equipment components, flow and flow control, splashes, chemicals used as part processing stream.

Wells with in-place plumbing are commonly found at municipal water treatment plants, industrial water supplies, private residences, etc. General limitations of in-place pump are:

- the pump is suspended in the well at a pre-selected depth (hard mounted) and cannot be moved up or down during purging and sampling.

- not enough is generally known about the construction aspects of the wells to apply the same criteria as used for monitoring wells (i.e., 3 to 5 well volumes).

Generally, when collecting a groundwater sample from these wells, removal of three to five well volumes of groundwater may not be practical or required. The purge volume may depend on factors such as if the pumps are running continuously, intermittently, or haven't been operating for a length of time, layout of the pumping system (e.g., if storage/pressure tanks are located between the sampling point and the pump), equipment operability. This SOP assumes the in-place pump and plumbing function properly.

1. Record details about sample location, equipment, or conditions.
2. Don a new pair of nitrile or surgical gloves.
3. If the pump runs continuously:

    a. No purging is necessary other than opening a valve or spigot and allowing groundwater to purge into a bucket or container for a few minutes.
    b. If a storage tank is present between the pump and the discharge point, a spigot, valve, or other sampling point should be located between the pump and the storage tank. If a spigot, valve or other sampling point cannot be located, use a valve or spigot closest to the storage tank or container, if present. Once located, open the valve or spot and allow the water to purge into a bucket or container for a few minutes.
    c. Measure and record pH, specific conductance, temperature, and turbidity and any observations about the water (clarity, odor, color, sheen). DO and ORP is recommended; however, both may be biased due to pumping or storage conditions.

4. If the pumps run intermittently or infrequently, the pump should be energized.

    d. Best judgment should be used to remove enough water from the plumbing to flush standing water from the piping and any storage tanks which may be present. The pumping flow rate should be taken into consideration when determining time to operate pump and purge groundwater. Generally, 15 to 30 minutes may be adequate.
    e. Measure and record at 3- to 5-minute intervals pH, specific conductance, temperature, and turbidity and any observations about the water (clarity, odor, color, sheen). DO and ORP is recommended; however, both may be biased due to pumping or storage conditions.

5. Place the representative groundwater directly into the sample bottles or sample container.
6. Follow the project work plan for sampling and in accordance with SOP-05 Sample Management and Shipping, and SOP-46 Water Sampling for Chemical Analysis.
7. Discard purge water and disposable equipment or supplies in accordance with the project work plan or SOP-07 Investigation Derived Waste.

1.3.2 Wells without In-Place Pumps

1.3.2.1 Equipment Considerations

- Tubing type (e.g., polyethylene, Teflon, etc.) shall consider the chemical of interest and be non-reactive.
- The pump shall be deep enough, so purging does not evacuate groundwater below the pump. Running the pump without water may cause damage.
- The pumping speed is not relative to the method; however, the discharge should not be operated at a rate which causes the well to go dry.
- Dedicated pumps are preferable to portable pumps.
- If a portable pump is used, the pump shall be decontaminated between purging.
- If a portable pump is used, new or dedicated tubing must be used at each sampling location.
- If a petroleum-powered generator is used to run the sampling pump, the power source must be located downwind of the wellhead and any sampling apparatus.

1.3.2.2 Pump Purging Procedures

Note: This procedure incorporates measurement of groundwater field-measured parameters. If these parameters are not necessary, the project work plan will note the deviation.

1. Measure and record the fluid depth and total well depth. Calculate the volume of water in the well and volume of water to remove.
2. The pump intake must be in an appropriate location with respect to well screen, saturated portion of well, targeted contamination zone, or formation. If the project work plan does not specify pump intake depth, the pump intake should be positioned at the midpoint of the well screen length or midpoint of the saturated portion of the well if the well screen is not fully submerged. If details about the well are not available, the pump intake should be placed about 5 feet (1.5 meters) above the bottom of the well or based on professional judgement.
3. Place any plastic sheeting, if necessary, on the ground to avoid equipment contact with the ground.
4. Don a new pair of disposable nitrile or surgical gloves.
5. Connect the tubing to pump.
6. Slowly lower the pump and tubing to the pump intake depth. In some situations, safety cables, hooks, or safety ties may be required. Ensure the equipment is decontaminated and is non-reactive.
7. Attach power supply to pump.
8. Begin pumping at a slow rate and then gradually increase the rate.
9. Discharge the water into a bucket, pail, or container. It is recommended the volume of bucket or container be known to estimate the volume of water removed during purging.
10. Routinely measure and record the depth to water and groundwater field-measured parameters generally including temperature, pH, conductivity, DO, ORP, and turbidity during the purging cycle. Note and record any physical observations, such as color, odor, visual turbidity, effervescence, or presence of particulates.
11. Continue purging groundwater until the calculated well volume is removed.

   a. The pump generally should not be moved but can be lowered if the water level drops below the pump intake.
   b. The pump rate can be decreased for sample collection in order to allow filling of sampling containers (this is often necessary to fill VOC sampling vials).
   c. As in all groundwater sampling, make sure the flow-through cell, if used, is bypassed during sample collection.
12. Collect and record a final groundwater measurement after the well volumes have been removed.
13. If the well is purged dry, attempt to remove 3 well volumes prior to sampling. Groundwater field-measured parameters and final depth to groundwater should be recorded to the best extent practicable.
14. If 3 well volumes cannot be removed, purge the well dry and allow the well to recover until at least one of the following is met:
    - A minimum of 2 hours has elapsed since purging.
    - There is sufficient water volume present to obtain the sample.
    - The water in the well has recovered to 80% of the initial pre-well volume.
15. The well will be re-purged if more than 24 hours has elapsed since the well went dry and sampling begins.
16. Place the representative groundwater directly into the sample bottles or sample container.
17. Follow the project work plan for sampling and in accordance with SOP-05 Sample Management and Shipping, and SOP-46 Water Sampling for Chemical Analysis.
18. Discard purge water and disposable equipment or supplies in accordance with the project work plan or SOP-07 Investigation Derived Waste.

2 Records

Field notes will be kept in a bound field logbook or approved field documentation following the format specified in SOP-04 Field Documentation. A Groundwater Sample Sheet is contained as **Attachment A**. Documentation of the sampling event should include (at a minimum):

- Well identification and location
- Type of equipment and supplies
- Well construction details including well screen length
- Air monitoring readings, if required
- Water level and total depth measurements
- Groundwater Sampling Form details
  - Physical water observation
  - Containment and volume of water removed
  - Name of the sample collector/s
  - Pump intake depth
  - Pumping rates, drawdown, indicator parameters values, calculated or measured total volume pumped, and clock time of each set of measurements.
  - Times (start, finish, sample time)
  - Laboratory information (sample ID, preservative, QA/QC)
  - Purge water disposal location and date of disposal
- Field observations
- Weather conditions
- Any problems encountered
- Equipment rental company pre-calibration sheet.

Attachment A EHS Support Groundwater Sampling Form

EHS Support

GROUNDWATER SAMPLING FORM

Project Name:_____

Project Number:_____

Casing Inner Diameter:_____ in

Water Level (Initial):_____ ft

Depth to Product:_____ ft

Total Well Depth:_____ ft

Height of Water Column (L):_____ ft

One Well Volume:_____ x 3 (min) _____ x 5 (max) _____ gals

Well Identification: _____

Sample Date: _____

Field Technician(s):_____

Purge Method: ☐ Bailer ☐ Pump ☐ Jet

☐ Other: _____

Pump / Bailer Type: _____

Tubing Inner Diameter (in):_____

Start Purge Time:_____

Time	Volume Removed	Water Level	Temp.	pH	Conductivity	Turbidity	DO	ORP	Odor	Color	Comments
	gal	feet	°C / °F	S.U.	__S/cm	NTU	mg/L	mV			

Comments:_____

End Purge Time:_____

Final Water Level: _____ ft

Well Purged Dry? Yes ☐ No ☐

Total Volume Purged:_____ gal

SAMPLE ID	TIME	ANALYSES	QA/QC SAMPLE	REMARKS

Formulas for Calculating Well Casing Volume

Standard Inner Diameter Casing	Non-Standard Inner Diameter Casing
$V = L * H1$ V = Volume (gal) L = Height of water column (ft) H1 = Conversion factor (see below)	$V = \frac{\pi D^2 L}{4} * 7.48 \frac{gal}{ft^3}$ V = Volume (gal) D = Well inner casing diameter (converted to ft) L = Height of water column (ft)

Measure inner diameter (ID) of well

ID (in.),	H1 = (gal/ft)
1	= 0.04
1.25	= 0.06
2	= 0.16
4	= 0.66
6	= 1.47

Gas Concentration in Well:_____ ppm

Purge Water Containerized? ☐ Yes ☐ No

Disposal Location: _____

Disposal Date: _____

Signature: _____

EHS Support

GROUNDWATER SAMPLING FORM

Project Name:_____

Project Number:_____

Casing Inner Diameter:_____ in

Water Level (Initial):_____ ft

Depth to Product:_____ ft

Total Well Depth:_____ ft

Height of Water Column (L):_____ ft

One Well Volume:_____ x 3 (min) _____ x 5 (max) _____ gals

Well Identification: _____

Sample Date: _____

Field Technician(s):_____

Purge Method: ☐ Bailer ☐ Pump ☐ Jet

☐ Other: _____

Pump / Bailer Type: _____

Tubing Inner Diameter (in):_____

Start Purge Time:_____

Time	Volume Removed	Water Level	Temp.	pH	Conductivity	Turbidity	DO	ORP	Odor	Color	Comments
	gal	feet	°C / °F	S.U.	__S/cm	NTU	mg/L	mV			

Comments:_____

End Purge Time:_____

Final Water Level: _____ ft

Well Purged Dry? Yes ☐ No ☐

Total Volume Purged:_____ gal

SAMPLE ID	TIME	ANALYSES	QA/QC SAMPLE	REMARKS

Formulas for Calculating Well Casing Volume

Standard Inner Diameter Casing	Non-Standard Inner Diameter Casing
$V = L * H1$ V = Volume (gal) L = Height of water column (ft) H1 = Conversion factor (see below)	$V = \frac{\pi D^2 L}{4} * 7.48 \frac{gal}{ft^3}$ V = Volume (gal) D = Well inner casing diameter (converted to ft) L = Height of water column (ft)

Measure inner diameter (ID) of well

ID (in.),	H1 = (gal/ft)
1	= 0.04
1.25	= 0.06
2	= 0.16
4	= 0.66
6	= 1.47

Gas Concentration in Well:_____ ppm

Purge Water Containerized? ☐ Yes ☐ No

Disposal Location: _____

Disposal Date: _____

Signature: _____

SOP-46 Water Sampling for Chemical Analysis

Purpose

The purpose of this standard operating procedure (SOP) is to provide general procedures for the preparation of water samples for chemical analysis during field investigations. This SOP focuses on the requirements for accurate sample collection and preservation of water samples for representative quality analysis. For this SOP, water sampling refers to those samples whose main constituent is water such as samples collected from surface water, groundwater, and/or waste water. In addition, this SOP assumes bottle sets received from the laboratory will contain the required preservative (i.e., the bottles are pre-preserved by the laboratory, and preservative will not be required in the field).

Relevant EHS Support SOPs

- SOP-04: Field Documentation
- SOP-05 Sample Management and Shipping
- SOP-08 Field Equipment Operation and Calibration
- SOP-09 Equipment Decontamination

Attachments

- No attachments

Required Materials

- Field logbook and field documentation
- Site maps, site layouts, site plans
- Health and Safety Plan (HASP)
- Appropriate personal protective equipment (PPE)
- Black waterproof and/or indelible ink pens
- Chain-of-custody form, sample labels, custody seals
- Material Safety Data Sheets (from the laboratory, for each preservative type)
- Filters, if applicable
- Laboratory-supplied bottle set, with preservative as needed
- Other approved sample storage containers, if applicable
- Labels, custody seals, coolers, ice, Chain of Custody forms, tape, plastic baggies
- Equipment required, if applicable, to monitor the water sample parameters

1 Water Sampling for Chemical Analysis

Water samples are collected and analyzed to evaluate the chemical quality of the water. The chemical characteristics of the water aid in understanding the groundwater or surface water system of interest, or is used as a monitoring control for waste water treatment facilities or meeting criteria to discharge treated water.

There are two types of samples that can be collected during a sample event: grab samples or composite samples. Grab samples (or discrete samples) are discrete samples collected at a specific location and time. Composite samples (or homogenized samples) are samples composited from two or more locations at the time of sampling. Composite samples usually represent an averaged concentration for a period of time. Samples collected for VOC analysis are generally not composited or homogenized, unless specified.

Accurate sample collection and preservation is crucial in acquiring representative data. The project work plan or quality assurance project plan (QAPP) should be reference to understand the project needs and sample requirements. The project work plan or QAPP should provide a clear understanding to sample locations, sample identification, analytical testing, number and type of quality control samples, or other project-related needs (objective, equipment, laboratory supplier, purging method-if required, etc.).

1.1 General Water Sampling Considerations

Although the procedures used to fill sample bottles may seem a minor consideration, filling them improperly can jeopardize the careful work that may have gone into properly purging a well to produce minimally-disturbed, representative sample. Improper sampling techniques can cause changes in sample composition due to agitation and exposure to air which can result in the loss of contaminants by volatilization or degassing. The following are general considerations when preparing for collection of water samples:

- The specific order of sample collection, processing and preservation for specific analytes should be adhered to consistently throughout the project. The recommended sequence for sample collection and processing is often based on logistics for maintaining sample integrity and based on the analytes' sensitivity to change. The sequence can be modified, depending on the types of samples to be collected and on data objectives.
- Volatile organic compound (VOC) samples (and other organic-sensitive analytes) are typically collected first if collecting samples for multiple analytes. The more sensitive the analytical parameters being collected (e.g., VOCs and redox-sensitive metals), the more cautious the filling procedures should be. A suggested sample order, if not specified in the project work plan or QAPP may include:
    - VOCs
    - Semi VOCs (SVOCs)
    - Herbicides/Pesticides/Polychloride Biphenyls (PCBs)
    - Total Petroleum Hydrocarbons (TPH)

  - Metals, Cyanide, or Radionuclides
  - Other water-quality parameters (microbiological, anion/cation, ammonia, sulfides/sulfates, nitrates/nitrites, etc.)
  - Nutrients (e.g., phosphorous)
  - Filtered samples (e.g., dissolved metals, ultra-trace metals, etc,).
  - Additional sample order consideration might include a sulfate sample collected before samples preserved with sulfuric acid (e.g., nitrogen series, phenolics).
- If questions exists pertaining to sampling or laboratory concerns check with the laboratory(s) or laboratory-project manager to ensure the sample containers, required sample volume, preservation, and holding times are understood prior to the project start. Several analytes in a sample suite may be grouped together in one (or more) bottle based on the preservation method and analytical testing method.
- Laboratory quality assurance and control procedures should be referenced prior to field sampling to ensure accurate the project work plan and chain of custody procedures are followed. Sample management and shipping can be referenced in SOP-05. A laboratory example of holding times can be reference as an attachment to SOP-05.
- Ensure field equipment is properly decontaminated in accordance with the guidelines provided in SOP-09 and is calibrated with the guidelines provided in SOP-08 or the instrument's manual.
- During purging and/or sample collection the flow should be a smooth, solid stream of water with no air or gas bubbles in the tubing or flow cell. Gradually adjust the pumping rate to eliminate bubbles, if present.
- Prepare sample containers. Keep sample containers capped until it is time to fill them to avoid possible container contamination.
- If water samples are collected via bailer, it is recommended to use a bottom emptying devise to slow/control the release of the water sample into the laboratory bottles.
- Any equipment (e.g., flow through cell, multi-parameter quality meter) used to monitor water quality parameters will be disconnected to allow the sample to be collected directly from the discharge tubing.
- Groundwater samples from a purged well will be collected in a continual process following the purge cycle.
- For groundwater samples collected by using low-flow sampling techniques, the pumping/discharge rate should:
  - Be high enough to fill sample bottles efficiently and with minimal exposure to atmospheric conditions, but low enough to minimize sample alteration or aeration.
  - Allow for a smooth and uniform flow, preferably about 250 millimeters per minute.
  - Remain unchanged from the purging cycle to the sampling cycle.

1.2 Water Sample Procedures

Water samples are generally collected

- Directly from a sample port, faucet, or spigot at the sample point location.
- Directly or indirectly at a surface water location (refer to SOP-61) at the sample point location or via an intermediate container or drop-down tube.

- Directly or indirectly from a well that has been purged of groundwater (SOP-43 and SOP-44) using down-hole tubing or via an intermediate container (i.e., bailer).

Do not use a bottles containing preservative to directly collect the water sample from a surface water body, pond, or lagoon. Instead employ an intermediate container for sample collection and transfer the sample to the bottle containing preservative.

Ensure sample tubing has been disconnected from any inline equipment (e.g., flow-through cell) prior to filling sample jars.

Assuming all pre-sample activities (e.g., purging, stabilization of water quality parameters, bottle labeling) are completed

1. For water samples from a port, faucet, or spigot, disinfect the port, faucet, or spigot with an alcohol swab or approved-cleaning detergeant. Open the sampling port and allow the water to flow (about 250 ml/min) for 2 to 3 minutes. Collect the discharged water into a bucket.
2. If sampling for VOCs, fill the volatile organic analyte (VOA) vials first.
   a. Slowly fill each 40 ml VOA vial with water taking care not to let it over flow and lose preservative.
   b. Completely fill the VOA vial with water so a meniscus is formed at the top of the container.
   c. Place the cap with Teflon septum on the vial top and secure.
   d. Turn the VOA vial upside down and check for the presence of air bubbles. Tap the bottom of the VOA vials to dislodge any bubbles that may have formed around the cap or sides.
   e. If no bubbles are present, the sample is considered to have “No Headspace” and the sampling for that vial is complete. Move onto the next VOA vial or sample container.
   f. If bubbles are present, remove the cap and fill the VOA vial with additional sample water to completely fill the vial and form a meniscus. Replace the cap and reconfirm there are no bubbles in vial. If air bubbles are still present after three attempts, discard the sample jar and obtain a new VOA vial for sample collection.
   g. If the purge water has observable entrained gas bubbles in the effluent, or if the sample effervesces or fizzes during collection of the water sampling into the (HCl) pre-preserved VOA, the collected sample and/or vial will be discarded. Instead, use a new VOA vial containing no preservative, or rinse the VOA vial with the representative purge water to completely remove the HCl preservative, to collect the sample. The sample will be contained in the VOA vial with the “No Headspace” procedures d) to f) and the chain of custody will note the sample is unpreserved. It is recommended to inform the laboratory of the unpreserved sample and holding time change.
      Notes:
      - A sample that is off-gassing in a sealed container may cause a potential eruption hazard.
      - The hold time of an unpreserved sample is reduced from 14 days to 7 days.
3. Fill remaining sample containers for other analytes, and seal sample containers. Ensure sufficient volume is available to fill the bottle set or testing method criteria (“No Headspace” for other analytes) is achieved. Consult with the project manager, project work plan, QAPP, or laboratory representative if potential concerns arise to assess possible corrective actions.

4. If water samples require filtration (further discussed in the next section):
   - Attach the in-line disposable filter to the sample tubing or hose. Using the water pressure from the pump, press the water through the filter. Allow (and discard) a minimum of 100 milliliters of water to pass through the filter cartridge before filling the appropriate sample containers with the sufficient container volume. Discard any filters that become clogged and attach a new filter as appropriate. Discard filter between sample locations.
   - Set up the filtration assembly, positive vacuum system, or syringe. Transfer the representative water into the appropriate holding chamber. Push or press the sample across the filter. The filtered sample will be placed directly into the appropriate sample jar, or transferred from the filtered-water chamber and into the appropriate sample jar. Discard any filters that become clogged and attach a new filter as appropriate. Discard filter between sample locations.
5. Complete the chain of custody noting sample identification, time, date, analytical testing required, quality control samples, and any other notes that would be useful to a laboratory. (For instance, if a sheen is observed in the sample, note on the chain of custody. This may assist the laboratory in preventing potential instrument issues.)
6. Place, package, and ship the appropriately labeled sample containers to the subcontracted laboratory following the guidelines provided in SOP-04 Field Documentation and SOP-05 Sample Management and Shipping.
7. Discard purged water in accordance with the project work plan and in accordance with SOP-07 Investigative Derived Waste.

1.3 Field Filtration Guidelines

Filtration is the physical process used to separate the particulate and aqueous fractions of a water sample. Samples are filtered for several purposes; for example, to remove microorganisms in order to help preserve ambient analyte concentrations, to remove suspended materials that interfere with specified analytical procedures, and to determine chemical speciation and fractionation of trace elements for geochemical studies.

Field filtration may be required for dissolved metals, alkalinity, hexavalent chromium, ultra-trace metals, total organic content (TOC), dissolved organic content (DOC), and speciated analytes such as ferrous iron, arsenic and selenium. In some of these analytes, zero headspace is required in the bottle. Be sure to check with the project work plan, QAPP, and laboratory for sample collection and containment requirements.

Accomplish in-line filtration through the use of disposable, high capacity filter cartridges (barrel-type) or membrane filters in an in-line filter apparatus. The high capacity, barrel-type filter is preferred due to the higher surface area associated with this configuration. If a membrane filter is utilized, a minimum diameter of 142 mm is suggested. The filter size and material should be appropriate for the expected quality of the water sample, the volume of water to be filtered, the analyte(s) to be measured, and the method of filtration. The filtration technique should minimize the sample exposure to air.

A generally accepted filter size is 0.45 microns, however, 0.2 micron filters can be used if the removal of bacteria or metal colloids is required. The most commonly used field filtration techniques are:

- In-line disposable filters (filter during sample collection)

Examples of a field filters including barrel-type filter cartridge or membrane filter.

- Hand-held and operated positive vacuum pump or syringe filters (filter after collection)

Examples of a hand-help positive vacuum pump and syringe-type filter.

2 Records

Field notes will be kept in a bound field logbook or approved field documentation following the format specified in SOP-04 Field Documentation. Field notebooks and field documentation should be used to record:

- Sample Identification
- Sample time and date
- Media collected
- Sample location
- Sample testing method
- Location and identification of quality control samples and types
- Chain of Custody forms

Appendix D Draft Quality Assurance Project Plan

LNAPL Natural Source Zone Depletion Quality Assurance Project Plan (QAPP)

St. Croix, U.S. Virgin Islands

Prepared for:

St. Croix Alumina Site

Prepared by:

EHS Support

April 2021

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Acronyms

A	analytical error
bgs	below ground surface
BTEX	benzene, toluene, ethylbenzene, and xylene
CA	corrective action
CCV	Continuing Calibration Verification
cm	centimeters
COC	contaminant of concern
COPC	contaminant of potential concern
CSMS	computerized sample management system
DNAPL	Dense Non-Aqueous Phase Liquid
DOC	dissolved organic carbon
DQI	data quality indicators
DQO	data quality objectives
DS	Diamond Shamrock Tributary
E	external
EB	equipment blank
EDD	electronic data delivery
EDMS	Enterprise Database Management System
EPA	Ohio Environmental Protection Agency
ESD	Explanation of Significant Differences
FB	field blank
FM	Field Manager
ft	feet
GC	Gas Chromatography
GWIT	Groundwater Interceptor Trench
HASP	Health and Safety Plan
HAZWOPER	Hazardous Waste Operations and Emergency Response
HDPE	high density polyethylene
HOVIC	Hess Oil Virgin Islands Corp
I	internal

ICV	Initial Calibration Verification
ID	client sample identification
IS	Internal Standard
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
LIMS	Laboratory Information Management System
LOQ	Limit of quantification
MCL	maximum contaminant level
MDL	method detection limit
MDRU	Mobile DNAPL Recovery Unit
MIM	Metal injection molding
MIP	membrane interface probe
MS	matrix spike
MSD	matrix spike duplicate
NA	not applicable
ND	non detectable
NPDES	National Pollutant Discharge Elimination System
OA	Organic Acid
OM&M	Operation, Maintenance and Monitoring
OU-5	Operable Unit 5
PID	Photo Ionization Device
PM	Project Manager
PQO	project quality objectives
PVC	polyvinyl chloride
QA	quality assurance
QA Manager	Quality Assurance Manager
QAPP	Quality Assurance Project Plan
QC	quality control
RL	reporting limit
ROD	1997 Record of Decision
RPD	relative percent difference
RSD	Relative Standard Deviation

S	sampling error
S&A	sampling and analytical error
SOP	Standard Operating Procedure
SOW	Scope of Work
SVOC	semi- volatile organic compounds
TB	trip blank
TCL	Target Compound List
TPH	total petroleum hydrocarbon
USEPA	United States Environmental Protection Agency
VOA	Volatile Organic Analysis
VOC	volatile organic compounds

Trademarks, trade names, company, or product names referenced herein are used for identification purposes only and are the property of their respective owners.

1 Introduction

This Quality Assurance Project Plan (QAPP) details the planning processes for collecting data and describes the implementation of the Quality Assurance (QA) and Quality Control (QC) activities developed for the assessment of natural source zone depletion (NSZD) at the St. Croix Alumina facility in St. Croix, U.S. Virgin Islands (Site). The objectives of this QAPP are to generate data that are technically valid, legally defensible, and support meeting the project goals for the Light Non-Aqueous Phase Liquid (LNAPL) Natural Source Zone Depletion Work Plan. The objective of the proposed work is to identify the presence and magnitude of LNAPL mass loss due to NSZD processes. This QAPP consists of four main components:

- Project Management
- Measurement and Data Acquisition
- Assessment and Oversight
- Data Validation and Usability

The above components will incorporate QA/QC requirements cited within the following guidance documents:

- USEPA Requirements for Quality Assurance Project Plans, USEPA QA/R-5, March 2001
- USEPA Guidance for the Data Quality Objectives (DQOs) Process, QA/G-4, February 2006
- Uniform Federal Policy for Quality Assurance Project Plans, Final Version March 2005

1.1 Project Background and History

The following parties entered into an Administrative Order on Consent (AOC), with the United States Environmental Protection Agency (USEPA), Region 2, on May 14, 2001 with an effective date of May 24, 2001:

- St. Croix Alumina, L.L.C. (referred to as SCA)
- ALCOA World Alumina, L.L.C. (formerly known as ALCOA Alumina and Chemical, L.L.C.) (referred to as ALCOA)
- Virgin Islands Alumina Company (referred to as VIALCO)
- Century Aluminum Company, Inc.
- Lockheed Martin Corporation (referred to as “Lockheed Martin”)
- Hess Oil Virgin Islands Corp. (referred to as HOVIC)
- HOVENSA L.L.C. (referred to as “HOVENSA”)

Pursuant to the AOC, these companies have agreed to work together to address Phase Separated Petroleum Hydrocarbon (PSPH) and Dissolved Phase Petroleum Hydrocarbon Constituents (DPPHC) located beneath the St. Croix Alumina facility in St. Croix, U.S. Virgin Islands. As per the AOC, a Project Operating Committee (POC) was formed to design, install, and operate a monitoring and remediation system for the Site.

A Draft PSPH Work Plan was submitted to the USEPA on July 23, 2001 (HOVIC, 2001). USEPA approved the PSPH Work Plan on August 8, 2001. Implementation of the PSPH Work Plan has been initiated and both PSPH and DPPHC recovery is underway. The initial Draft DPPHC Work Plan was submitted to USEPA

on September 21, 2001 (HOVIC, 2001a). The USEPA requested seven items be incorporated into a revised draft. This revised Draft DPPHC Work Plan was submitted to the USEPA on December 21, 2001 (HOVIC, 2001b). In a January 15, 2002 letter, the USEPA conditionally approved the work plan with proposed changes to timeline items (USEPA, 2002). An amended Draft was submitted to the USEPA on February 22, 2002 incorporating the requested USEPA timeline changes. The POC recommended that the quarterly status reports and the semiannual report be consolidated into one report submitted semiannually. The USEPA approved this recommendation in their March 3, 2005 letter.

The POC submitted a PSPH Pilot Study and DPPHC Sampling Plan Modification to USEPA on May 21, 2018. USEPA provided comments to the proposed plan, which were implemented by the POC, and a final PSPH Pilot Study (HOVIC, 2018) and DPPHC Sampling Plan Modification was submitted on June 11, 2018 (HOVIC, 2018). This recovery plan was implemented by the POC over 2018, 2019, and the first quarter of 2020.

Using historical data and the data collected from this modified LNAPL recovery program, a detailed assessment of LNAPL recovery/mobility and chemistry data was completed and reported in the July 2020 LNAPL Conceptual Site Model (CSM) and Remedial Action Work Plan (EHS Support LLC ["EHS Support"], 2020). This assessment demonstrated that the majority of LNAPL recovery wells have reached or are approaching a practicality endpoint. In addition, the July 2020 LNAPL CSM and Remedial Action Work Plan (EHS Support, 2020) proposed shutdown criteria for active recovery wells. However, due to uncertainties and data gaps, recovery operations are planned to continue through June 2021 (including well maintenance and semi-annual groundwater monitoring).

As a supplement to continued routine groundwater sampling activities and LNAPL recovery activities, it was proposed that additional analysis be conducted to support the assessment of NSZD processes in the aquifer. Based on the Site geohydrology and limited geochemical data, a combination of sulfate reduction and methanogenesis processes appear to be active and significant contributors to mass losses at the Site. A program of works was proposed to further define and quantify the processes contributing to such natural mass losses.

A NSZD Work Plan (2020) was developed and submitted to USEPA. The work plan outlines an iterative process of assessments utilizing existing monitoring wells for the Phase 1 assessments to collect temperature profile, geochemistry data and soil gas flux analysis in order to provide high resolution assessment of NSZD processes. This work will be supplemented by a Phase 2 program of works which uses high quality methods to quantify efflux. All assessments will be conducted in accordance with established NSZD and monitored natural attenuation (MNA) technical guidance (Interstate Technology & Regulatory Council [ITRC], 2009, 2014 and 2018; CRC Care, 2015 and 2018).

1.2 Site Setting and History

The Site consists of a former bauxite ore processing refinery that produced alumina, the raw material used to make aluminum. The facility was constructed in the mid-1960s. Historically, the refinery consisted of administrative offices, operations buildings, bulk storage containers (e.g., tanks, silos, and a bauxite ore shed), and various active bauxite processing operations including grinding, digestion, thickening, filtrations, precipitation, and calcination. Ancillary operations included oil-fired boilers, water desalination units, a warehouse, laboratories, maintenance facilities, and stormwater collection and

cooling ponds. Bauxite solid waste residue (e.g., red mud) disposal areas, a dock adjacent to the ship channel, and recreational areas were also located on-site.

Prior to the refinery being constructed, portions of the Site were used for production of sugar cane under various owners. Circa 1900 structures associated with the sugar cane are currently located on the western and northeastern portions of the property. The West Indian Sugar Factory, Inc. sold the Site to a private owner in 1937. The United States government assumed ownership of the Site in 1942, later transferring it to the Municipality of St. Croix in 1949. The Site was purchased by Harvey Aluminum, Inc. from the Government of the Virgin Islands in 1962, when construction of the refinery occurred. Martin Marietta Alumina, Virgin Islands Alumina Company, and SCA were owners of the refinery from 1968 through 1995. ALCOA took over the facility in 1998 and operated it until December 2000.

Currently, the facility remains generally inactive, and demolition of facility structures is ongoing. Former refinery bulk storage tanks (currently used for molasses storage by Diageo rum distillery since circa 2010) are located on the west side of the Site.

1.3 Geology and Hydrogeology

An in-depth evaluation of Site geology, hydrology, and geochemistry is provided in the LNAPL CSM and Remedial Action Work Plan (EHS Support, 2020), and is summarized below.

The Site is located on the south-central St. Croix coastline. The northern part of the Site is situated on the Kingshill Limestone, and the southern portion is overlain by younger alluvial deposits that fill erosional channels in the Kingshill Limestone and grade into recent (pre-Site development) reef and lagoon deposits principally of the former Krause Lagoon (Whetten, 1966). During Site development, areas of excavation and/or fill were established on the preexisting topography.

The Kingshill Limestone at the Site and vicinity is described as a buff- to white-colored soft marl (Graves, 1995). Deposits of the overlying Blessing Formation are reportedly absent at the Site, and the nearest occurrence was identified in test holes drilled in Barren Spot well field approximately 1-mile northeast of the Site (Graves, 1995). Deposits of the Jealously Formation that underlie the Kingshill Limestone are typically encountered between 85 to over 120 feet below ground surface (bgs) in the Site vicinity in south-central St. Croix and are considered the base of the freshwater aquifer (Graves, 1995). The Jealously Formation has not likely been encountered in Site borings for monitoring well installations.

An interval of gravels, sands, silt, and clay within the Kingshill Limestone is identified beneath the central portion of the Site that is broadly coincident with the location of the water table and intervals over which most Site wells are screened. Chert, caliche (calcium carbonate), and/or gypsum deposits are identified in the well screen intervals in Site borings logs in wells VW-13B, VW-33, VW-35, and VW-37. Conceivably, these minerals are more widespread within the lagoon clay identified in several Site borings but were not abundantly sampled due to the drilling techniques that were employed. The identified deposits appear to be contemporaneous with an interval of reef deposits containing coral and mollusk fossils within the Kingshill Limestone exposed in the quarry directly west of former well GM-12 and on the hillside north of GM-4 (Geraghty and Miller, 1982). The occurrence of reef and sediment deposits within the Kingshill Limestone likely coincide with the global sea level lowstand in the Middle to Late Miocene that is commonly observed within the Kingshill Limestone (Gill et al., 1999).

Following uplift and subaerial exposure of the Kingshill Limestone, several alluvial channels formed. The more recent alluvial channels are characterized by various proportions of soft or loosely consolidated sand, gravel, silt, and clay. The alluvial channels are now largely present in the subsurface beneath anthropogenic fill, although the channels are evident on a geologic map that was drafted prior to extensive Site development. It is not clear how the channels are hydraulically connected to lagoon deposits within the Kingshill Limestone; however, available data suggest that the channels are largely above the water table on the northern half of the Site.

South of the eroded edge of the Kingshill Limestone and on the southern portion of the Site, soft to very stiff organic clays, silty clays, and clayey silt deposits are present that formed in the historic Krause Lagoon. Krause Lagoon and the surrounding mangrove swamps were drastically altered after about the 1960s following the construction of industrial facilities and dredging of the shipping channel. The Krause lagoon deposits overlie a 4- to 10-foot-thick sand and gravel layer from about 10 to 30 feet below sea level that is derived from limestone and coral fragments that weathered from the Kingshill Limestone. The hydraulic connection between the Krause lagoon and Kingshill Limestone deposits is uncertain (Geraghty and Miller, 1982; Gill and Hubbard, 1987).

The general direction of groundwater flow beneath the Site is to the south-southwest and south towards the sea (GMS, 2020), consistent with groundwater equipotential in the broader region (Graves, 1995). The groundwater elevation at the Site typically ranges from about 0.5 to 3.5 feet above mean sea level (msl). Groundwater at the Site is largely present within the Kingshill Limestone. A notable groundwater elevation high is present at well GM-22, and the cause is presently unknown, but is conceivably a perched or isolated groundwater zone.

Original permeability of the Kingshill Limestone is in part related to the depositional environment; deeper water bathyal deposits and shallow lagoon deposits generally had low original porosity owing to a higher fraction of clay-sized carbonate particles (micrite), whereas shallower reef and washover deposits generally had a higher original porosity and permeability due to larger grain size and the presence of coral and shell fragments (Geraghty and Miller, Inc., 1982). Therefore, the distribution of the lagoon deposits in relation to sand pack/well screen intervals at the Site places a strong control on hydraulic properties of the groundwater saturated zone, specifically, large variations in hydraulic conductivity and storativity are expected.

In addition to variations in primary porosity of deposits at the Site, percolation of precipitation and groundwater seepage at the Site has re-precipitated sand-sized particles as micrite and filled pore spaces with secondary calcite (Geraghty and Miller, Inc., 1982). However, a review of Site borings logs has identified numerous poorly cemented and permeable layers within the Kingshill Limestone that consist of sand, gravel, sandstone, and sandstone-marl mixtures. Indeed, the frequently encountered no recovery- zones during drilling at the Site likely reflect zones of extremely loose sediment. Whereas these zones may have been attributed to void spaces, the associated changes in drilling resistance suggest that not all of those intervals were indeed voids.

1.4 Constituents of Concern

Hazardous substances have been identified at the site during previous investigations. The following list provides a summary of constituents detected.

- Volatile organic compounds (VOCs): BTEX (benzene, toluene, ethylbenzene, and xylenes):

- Semi-volatile organic compounds (SVOCs): Naphthalene; and
- Total petroleum hydrocarbons – diesel range organics (TPH-DRO).

2 QAPP Worksheet #1: Title and Approval Page

Site Name/Project Name:	St. Croix Alumina
Site Location:	St. Croix, U.S. Virgin Islands
Document Title:	Uniform Federal Policy – Quality Assurance Project Plan St. Croix Alumina
Lead Organization:	USEPA Region 2
Preparer's Name and Organizational Affiliation:	Danielle Sheheen, EHS Support LLC (EHS Support)
Preparer's Address, Telephone Number, and E-mail Address:	125 Bemis Street, Saraland, AL, 36571, (251) 591-9038, Danielle.sheheen@ehs-support.com
Preparation Date (Day/Month/Year):	April 9, 2021

Investigative Organization's Project Manager:

Signature Date:
Nigel Goulding, EHS Support

Investigative Organization's Project QA Officer:

Signature Date:
Amy Coats, EHS Support

Lead Organization's Project Manager:

Signature Date:
Carol Stein, USEPA Region 2

Approval Signature:

Signature Date:
Brian Epperson, HOVIC

Approval Signature:

Signature Date:
Brad Freeman, GeoMonitoring Services

3 QAPP Worksheet #2: QAPP Identifying Information

Site Name/Project Name: St. Croix Alumina

Site Location: St. Croix, U.S. Virgin Islands

Site Number/Code:

Operable Unit:

Contractor Name: EHS Support, LLC

Contractor Number: NA

Contract Title: NA

Work Assignment Number: NA

1. Identify guidance used to prepare QAPP: Uniform Federal Policy for Quality Assurance Project Plans, Manual V1 (2005)

2. Identify regulatory program: Comprehensive Environmental Response, Compensation, and Liability Act of 1980

3. Identify approval entity: USEPA Region 2

4. Indicate whether the QAPP is a generic or a project-specific QAPP. (circle one) This is a project-specific QAPP, which addresses the requirements of investigation activities. This QAPP may be amended, as required, for future work at the site.

5. List dates of scoping sessions that were held: None

6. List dates and titles of QAPP documents written for previous site work, if applicable: An earlier QAPP was submitted to USEPA Region 2 on June 24, 2002. The title was: Sampling and Analytical Quality Assurance Project Plan for the Dissolved Phase Petroleum Hydrocarbon Workplan for the St. Croix Alumina Site. This QAPP is being submitted to replace the earlier QAPP, which is outdated.

7. List organizational partners (stakeholders) and connection with lead organization:
   - St. Croix Alumina, L.L.C. (referred to as SCA)
   - ALCOA World Alumina, L.L.C. (formerly known as ALCOA Alumina and Chemical, L.L.C.) (referred to as ALCOA)
   - Virgin Islands Alumina Company (referred to as VIALCO)
   - Century Aluminum Company, Inc.
   - Lockheed Martin Corporation (referred to as “Lockheed Martin”)
   - Hess Oil Virgin Islands Corp. (referred to as HOVIC)
   - HOVENSA L.L.C. (referred to as “HOVENSA”)

8. List data users: USEPA Region 2, EHS Support, ad stakeholders listed above.

9. If any required QAPP elements and required information are not applicable to the project, then circle the omitted QAPP elements and required information on the attached table. Provide an explanation for their exclusion below:

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	Crosswalk to Related Documents
Project Management and Objectives		
2.1 Title and Approval Page	Title and Approval Page	Worksheet #1 – Title and Approval Page
2.2 Document Format and Table of Contents 2.2.1 Document Control Format 2.2.2 Document Control Numbering System 2.2.3 Table of Contents 2.2.4 QAPP Identifying Information	Table of Contents QAPP Identifying Information	The Table of Contents is provided following the QAPP cover page Worksheet #2 – QAPP Identifying Information
2.3 Distribution List and Project Personnel Sign-Off Sheet 2.3.1 Distribution List 2.3.2 Project Personnel Sign-Off Sheet	Distribution List Project Personnel Sign-Off Sheet	Worksheet #3 – Distribution List Worksheet #4 – Project Personnel Sign-Off
2.4 Project Organization 2.4.1 Project Organizational Chart 2.4.2 Communication Pathways 2.4.3 Personnel Responsibilities and Qualifications 2.4.4 Special Training Requirements and Certification	Project Organizational Chart Communication Pathways Personnel Responsibilities and Qualifications Table Special Personnel Training Requirements Table	Worksheet #5 – Project Organizational Chart Worksheet #6 – Communications Pathways Worksheet #7 – Personnel Responsibilities and Qualifications Worksheet #8 – Special Personnel Training Requirements
2.5 Project Planning/Problem Definition 2.5.1 Project Planning (Scoping) 2.5.2 Problem Definition, Site History, and Background	Project Planning Session Documentation (including Data Needs tables) Project Scoping Session Participants Sheet Problem Definition, Site History, and Background	Worksheet #9 – Project Team Planning Sessions Participants Sheet Worksheet #10 – Problem Definition

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	Crosswalk to Related Documents
	Site Maps (historical and present)	
2.6 Project Quality Objectives and Measurement Performance Criteria 2.6.1 Development of Project Quality Objectives Using the Systematic Planning Process 2.6.2 Measurement Performance Criteria	Site-Specific PQOs Measurement Performance Criteria Table	Worksheet #11 – Project Quality Objectives/Systematic Planning Process Statements Worksheets #12 – Measurement Performance Criteria for project analytes.
2.7 Secondary Data Evaluation	Sources of Secondary Data and Information Secondary Data Criteria and Limitations Table	Worksheet #13 – Secondary Data Criteria and Limitations
2.8 Project Overview and Schedule 2.8.1 Project Overview 2.8.2 Project Schedule	Summary of Project Tasks - Reference Limits and Evaluation Table Project Schedule/Timeline Table	Worksheet #14 – Summary of Project Tasks Worksheet #15 – Reference Limits and Evaluation Worksheet #16 – Project Schedule/Timeline
Measurement/Data Acquisition		
3.1 Sampling Tasks 3.1.1 Sampling Process Design and Rationale 3.1.2 Sampling Procedures and Requirements 3.1.2.1 Sampling Collection Procedures 3.1.2.2 Sample Containers, Volume, and Preservation 3.1.2.3 Equipment/Sample Containers Cleaning and Decontamination Procedures 3.1.2.4 Field Equipment Calibration, Maintenance, Testing, and Inspection Procedures 3.1.2.5 Supply Inspection and Acceptance Procedures	Sampling Design and Rationale Sample Location Map Sampling Locations and Methods/ SOP Requirements Table Analytical Methods/SOP Requirements Table Field Quality Control Sample Summary Table - Sampling SOPs Project Sampling SOP References Table Field Equipment Calibration, Maintenance, Testing, and Inspection Table	Worksheets #17 – Sampling Design Rationale Worksheet Worksheet #18 – Sampling Locations and Methods/SOP Requirements Worksheet #19 – Analytical SOP Requirements (Sample Containers Preservation and Holding Times) Worksheet #20 – Sample Quantities and Control Frequencies Worksheet #21 – Field Sampling SOP References Worksheet #22 – Field Equipment Calibration, Maintenance, Testing, and Inspection

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	Crosswalk to Related Documents
3.1.2.6 Field Documentation Procedures		The field sampling SOPs can be found in the Field Sampling Plan.
3.2 Analytical Tasks 3.2.1 Analytical SOPs 3.2.2 Analytical Instrument Calibration Procedures 3.2.3 Analytical Instrument and Equipment Maintenance, Testing, and Inspection Procedures 3.2.4 Analytical Supply Inspection and Acceptance Procedures	Analytical SOPs Analytical SOP References Table Analytical Instrument Calibration Table Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table	Worksheet #23 – Analytical SOP References Worksheet #24 – Analytical Instrument Calibration Worksheet #25 – Analytical Instrument and Equipment Maintenance, Testing, and Inspection The analytical SOPs can be found in **Appendix A**.
3.3 Sample Collection Documentation, Handling, Tracking, and Custody Procedures 3.3.1 Sample Collection Documentation 3.3.2 Sample Handling and Tracking System 3.3.3 Sample Custody	Sample Collection Documentation Handling, Tracking, and Custody SOPs Sample Container Identification Sample Handling Flow Diagram Example Chain-of-Custody Form and Seal	Worksheet #26 – Sample Handling System Worksheet #27 – Sample Custody Requirements An example of the COC form can be found in **Appendix A**
3.4 Quality Control Samples 3.4.1 Sampling Quality Control Samples 3.4.2 Analytical Quality Control Samples	QC Samples Table Screening/Confirmatory Analysis Decision Tree	Worksheets #28 present QC sample information for project analytes
3.5 Data Management Tasks 3.5.1 Project Documentation and Records 3.5.2 Data Package Deliverables 3.5.3 Data Reporting Formats 3.5.4 Data Handling and Management 3.5.5 Data Tracking and Control	Project Documents and Records Table Analytical Services Table - Data Management SOPs	Worksheet #29 – Project Documents and Records Worksheet #30 – Analytical Services
Assessment/Oversight		
4.1 Assessments and Response Actions 4.1.1 Planned Assessments	Assessments and Response Actions	Worksheet #31 – Planned Project Assessments

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	Crosswalk to Related Documents
4.1.2 Assessment Findings and Corrective Action Responses	Planned Project Assessments Table Audit Checklists Assessment Findings and Corrective Action Responses Table	Worksheet #32 – Assessment Findings and Corrective Action Responses
4.2 QA Management Reports	QA Management Reports Table	Worksheet #33 – QA Management Reports
4.3 Final Project Report		
Data Review		
5.1 Overview		
5.2 Data Review Steps 5.2.1 Step I: Verification 5.2.2 Step II: Validation 5.2.2.1 Step IIa Validation Activities 5.2.2.2 Step IIb Validation Activities 5.2.3 Step III: Usability Assessment 5.2.3.1 Data Limitations and Actions from Usability Assessment 5.2.3.2 Activities	Verification (Step I) Process Table Validation (Steps IIa and IIb) Process Table Validation (Steps IIa and IIb) Summary Table Usability Assessment	Worksheet #34 – Verification (Step I) Process Worksheet #35 – Validation (Steps IIa and IIb) Process Worksheet #36 – Validation (Steps IIa and IIb) Summary Worksheet #37 – Usability Assessment
5.3 Streamlining Data Review 5.3.1 Data Review Steps to be Streamlined 5.3.2 Criteria for Streamlining Data Review 5.3.3 Amounts and Types of Data Appropriate for Streamlining		NA

4 QAPP Worksheet #3: Distribution List

QAPP Recipients	Title	Organization	Telephone Number	E-mail Address	Document Control Number
Carol Stein	Remedial Project Manager	USEPA Region 2	212 -637-4181	stein.carol@epa.gov	
Brian Epperson	Remediation Project Manager	HOVIC	713-496-7296	bepperson@hess.com	
Nigel Goulding	Project Manager	EHS Support	412-977-4474	nigel.goulding@ehs-support	
Bonnie Stadelmann	Laboratory Coordinator	EHS Support	312-914-7034	bonnie.stadelmann@ehs-support.com	
R.J. Modashia	Laboratory Project Manager	ALS Environmental	281-530-5656	rj.modashia@alsglobal.com	
Brad Freeman	Project Manager	GeoMonitoring Services	713-417-6141	brad@geomon.net	

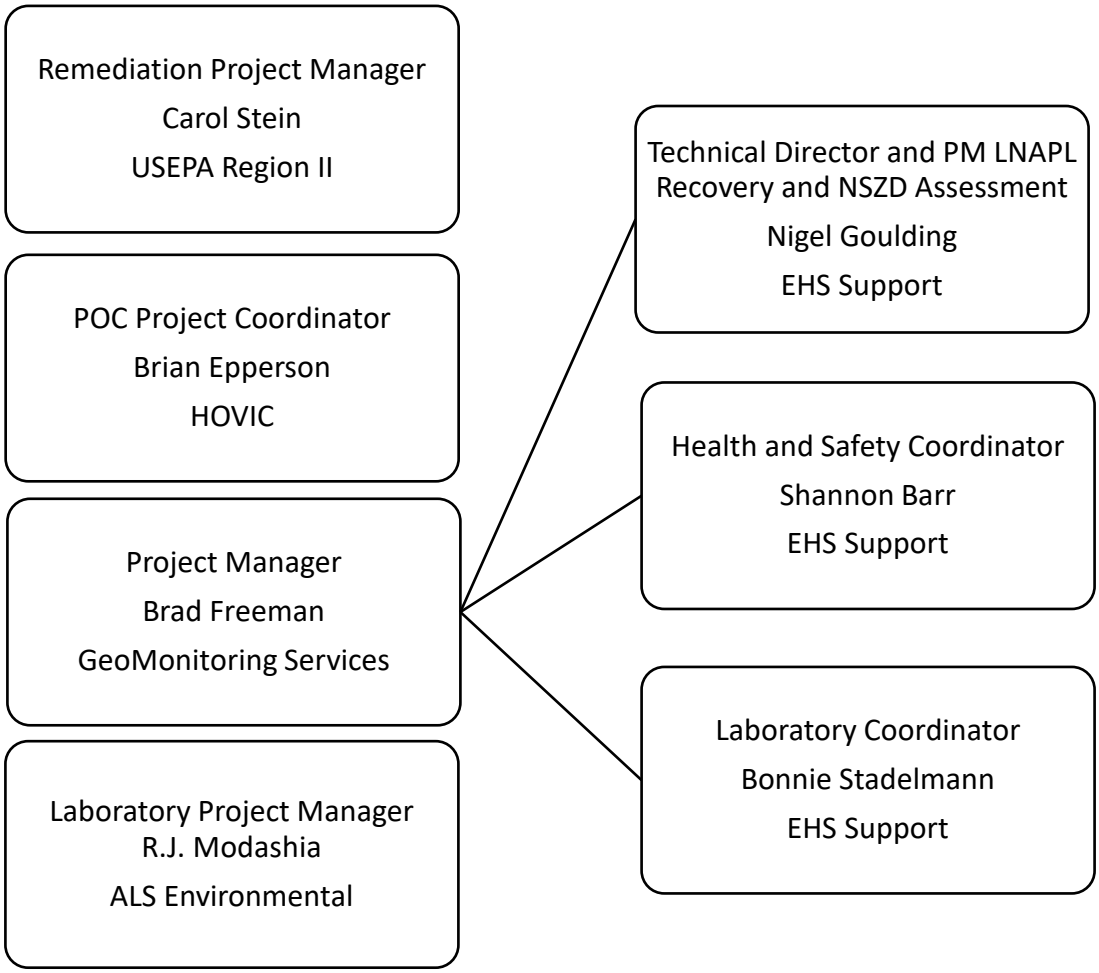
HOVIC = Hess Oil Virgin Islands Corp
USEPA = United States Environmental Protection Agency

5 QAPP Worksheet #4: Project Personnel Sign-Off Sheet

Project Personnel	Title	Organization	Telephone Number	Signature	Date QAPP Read
Nigel Goulding	Project Manager	EHS Support	412-977-4474		
Bonnie Stadelmann	Laboratory Coordinator	EHS Support	312-914-7034		
Brad Freeman	Project Manager	GeoMonitoring Services	713-417-6141		
R.J. Modashia	Laboratory Project Manager	ALS Environmental	281-530-5656		
Brian Epperson	Remediation Project Manager	HOVIC	713-496-7296		

Notes:
Project field team members, when assigned, will be required to sign that they have read applicable sections of this QAPP.
Field team members must read applicable sections of this QAPP and Standard Operating Procedures (SOPs) prior to participating in the project.
The project personnel sign-off table above documents key project personnel who have read the applicable sections of and will perform required activities in accordance with this QAPP.
HOVIC = Hess Oil Virgin Islands Corp
QAPP = Quality Assurance Project Plan
SOP = Standard Operating Procedure

6 QAPP Worksheet #5: Project Organizational Chart



7 QAPP Worksheet #6: Communication Pathways

Communication Drivers	Responsible Entity	Name	Phone Number	Procedure (Timing, Pathways, etc.)
Regulatory Liaison	HOVIC	Brian Epperson POC Project Coordinator	713-417-6141	Project Coordinator and key liaison with USEPA Region 2
Manage all project phases and Coordinates Field Work	GeoMonitoring	Brad Freeman, PM	713-417-6141	Will serve as the key liaison to USEPA Region 2 and POC.
Technical Director and PM for LNAPL and NSZD Assessment	EHS Support	Nigel Goulding, Technical Director and LNAPL/NSZD Lead	412-977-4474	Leads the scoping and technical assessment of data. Will lead project team in the development of major reports.
Stop work and initiation of corrective action	GeoMonitoring	Brad Freeman, PM	713-417-6141	The PM communicates within 24 hours of stop work to the project organization by phone, with confirmatory email.
Reporting of serious issues	GeoMonitoring	Brad Freeman, PM	713-417-6141	Report any serious issues to USEPA Region 2, Project Coordinator, and POC within 24 hours by telephone or email.
Approval of amendments to the QAPP	EHS Support	Amy Coats, Analytical QC Manager	941-356-1030	Obtain initial approval from the EHS Support PM and submit document amendments within 10 business days to the POC and USEPA Region 2 for approval.
Real time modifications to QAPP	EHS Support	Amy Coats, Analytical QC Manager (or designee)	941-356-1030	To be notified by EHS Support Field Manager of any changes to QAPP made in the field and reasons by phone or email within two business days. Will promptly notify the EHS Support PM of any such changes.
Reporting laboratory data quality issues	ALS Environmental	R.J. Modashia, Laboratory PM	281-530-5656	Will report all QA/QC issues with project field samples to PM and Analytical QC Manager within two business days.
Corrective actions	EHS Support	Amy Coats, Analytical QC Manager (or designee)	941-356-1030	Will evaluate the need for corrective action for field and analytical issues in conjunction with the PM, the Field Manager, or the Laboratory QA Manager, as appropriate.

Communication Drivers	Responsible Entity	Name	Phone Number	Procedure (Timing, Pathways, etc.)
Release of analytical data	EHS Support	Amy Coats, Analytical QC Manager (or designee)	941-356-1030	Will approve release of final analytical data following completion of validation.

HVOIC = Hess Oil Virgin Islands Corp
LNAPL = light non-aqueous phased liquid
NSZD = natural source zone depletion
PM = Project Manager
POC =
QAPP = quality assurance project plan
QC = quality control
USEPA = United States Environmental Protection Agency

8 QAPP Worksheet #7: Personnel Responsibilities and Qualification Table

Name	Title	Organizational Affiliation	Responsibilities	Education and Experience Qualifications
Nigel Goulding	PM	EHS Support	See below	M. Phil, Environmental Science, Auckland University, 1993 B.S. Geography, Auckland University, 1990
Brad Freeman	PM and Field Manager	GeoMonitoring	See below	B.A., Business Administration, Texas A&M University, 2007 Registered Environmental Manager
Bonnie Stadelmann	Laboratory Coordinator	EHS Support	See below	M.S., Natural Resource Management, University of Illinois, 1997 B.A., Communications/Photography, Columbia College, 1990
Amy Coats	Analytical QC Manager	EHS Support	See below	B.A., Chemistry, New College of Florida
Shannon Barr	Health and Safety Manager	EHS Support	See below	B.S., Safety Science, Indiana University of Pennsylvania, 2010
R.J. Modashia	Project Manager	ALS Environmental	See below	B.S., Chemistry, University of Houston, 2013

This section identifies key individuals involved in all major aspects of the project, including project management, health and safety, field mobilization, sampling, sample analysis, Quality Assurance (QA) activities (including field and laboratory assessments), data review, and data use. In addition, this section describes the roles and responsibilities of key individuals and the details related to the chain of command.

Communication pathways for resolving sampling and analysis issues, data distribution, and modification of the Quality Assurance Project Plan (QAPP) also described.

Nigel Goulding, Technical Director (TD), is directly responsible for the development, implementation, and management of the QAPP. Mr. Goulding's responsibilities include ensuring that the field implementation team and PM is aware of the QAPP and is implementing its provisions.

Brad Freeman is the Project Manager and Field Manager (PM/FM) and serves as field point of contact for TD and the Field Technicians implementing the project. As Project Manager, Mr. Freeman's responsibilities will be to ensure that the scope is executed in accordance with the QAPP and the technical requirements provided by the TD. In his secondary role as Field Manager he must also:

- Identify site-specific resource requirements.

- Oversee the management and execution of the project in compliance with Scopes of Work (SOWs), Health and Safety Plan (HASP), QAPP, and all applicable laws and regulations.
- Provide day-to-day coordination on technical issues in specific areas of expertise.
- Develop and implement field-related work plans with the facility, ensure schedule compliance, and adhere to management-developed study requirements.
- Assure QC of sampling, sample management, field-testing, and laboratories.
- Assure timeliness and quality of required sampling related site submittals.
- Control laboratory services requests.
- Coordinate laboratory and field sampling activities.
- Manage laboratory data reports.
- Implement QC for technical data provided by the field staff including field measurement data.

Amy Coats has been appointed by Mr. Goulding to be the Quality Assurance Manager (QA Manager), responsible for the development, implementation, and oversight of the QAPP. Mr. Goulding will assign periodic QAPP review to Ms. Coats or to another person who is acceptable to the agency. Any revisions will be submitted to USEPA Region 2.

The PM will have the assistance of the QA Manager, as needed. The PM is directly responsible for ensuring that the performance of assigned tasks adhere to all quality assurance, quality control, and chain-of-custody procedures specified in the QAPP.

Field Manager and Field Technician are responsible for implementing designated QA/QC procedures and for reporting all QC data to the QA Manager for review. They are responsible for implementing corrective actions as required and ordered by the QA Manager. Field Technician must verify proper completion of sample tracking forms and related analytical and QC forms and review sample documentation to ensure sampling is performed in accordance with procedures. They are responsible for reviewing and implementing the QAPP as it is applicable to the task they are performing and reporting all concerns to the FM and QA Manager.

The Laboratory PM, R.J. Modashia with ALS Environmental, is responsible for ensuring that the analysis is performed as specified in the project QAPP and for the reporting and disposition of laboratory nonconformance's that pertain to the subject project.

The Laboratory QA Director, with ALS Environmental, provides deliverables that meet the project-specific plans, communicates with QA Manager, as necessary and maintains current distribution lists for laboratory-specific attachments, project-specific manuals, and standard operating procedures. The Laboratory QA Director will assist in performing QA and QC audits, periodically determine the effectiveness of the QA program in the laboratory and verify completion of corrective actions cited in audits. They will resolve nonconformance and perform statistical analyses using results of QC sample analyses. In addition, the Laboratory QA Director will resolve ongoing and recurring nonconformance within the laboratory, recommend corrective actions for resolution of nonconformance, review statistical data to verify the laboratory is meeting stated QC goals. The Laboratory QA Director has the authority to stop production of data in a laboratory area where the review of QC data or procedures shows significant problems.

9 QAPP Worksheet #8: Special Personnel Training Requirement Table

Project Function	Specialized Training – Title or Description of Course	Training Provider	Training Date	Personnel/Groups Receiving Training	Personnel Titles/ Organizational Affiliation	Location of Training Records/Certificates
Field Activities	Occupational Safety and Health Administration 40-hour Hazardous Waste Operations and Emergency Response (i.e., HAZWOPER) training and medical monitoring, and any other project-specific training as specified in the Health and Safety Plan (HASP)	Brad Freeman, GeoMonitoring Services	40-hour HAZWOPER – January 27, 2014 8-hour HAZWOPER refresher – June7, 2020	All field team members working on-site	All GeoMonitoring, facility, and subcontractor personnel working on-site	GeoMonitoring Services project files Subcontractor and facility project files will be provided to EHS Support prior to commencement of field activities
Analytical Chemistry	Laboratory-specific training and proficiency testing	Project Laboratory	Training dates kept in company training records	All personnel analyzing project samples	Laboratory personnel	Laboratory project files

10 QAPP Worksheet #9 Project Scoping Session Participants Sheet

Project Name: St. Croix Alumina

Site Name: St. Croix Alumina

Site Location: St. Croix, U.S. Virgin Islands

Projected Date(s) of Sampling: TBD, 2021

Project Manager: Nigel Goulding/Brad Freeman (Technical Director/Project Manager)

Name	Title	Affiliation	Phone #	E-mail Address
Nigel Goulding	Technical Director	EHS Support	412-977-4474	Nigel.goulding@ehs-support.com
Brad Freeman	Project Manager/Field Manager	GeoMonitoring Services	713- 417-6141	Brad@geomon.net
Danielle Sheheen	QAPP Preparer	EHS Support	251-591-9038	Danielle.sheheen@ehs-support.com
Andrew Fowler	QAPP Reviewer	EHS Support	442-287-9357	Andrew.fowler@ehs-support.com
Bonnie Stadelmann	Laboratory Manager	EHS Support	312-914-7034	Bonnie.stadelmann@ehs-support.com

QAPP = quality assurance project plan

The internal QAPP scoping discussion was conducted to discuss preparation of the document for upcoming investigation activities for multiple media including soil, sediment, groundwater, and surface water. Schedule of activities will be based on document approvals. Kick off calls will be conducted prior to the start of work and project personnel will review required sections of the QAPP.

11 QAPP Worksheet #10: Problem Definition

This worksheet outlines the data quality objectives (DQOs) and has been prepared in accordance and compliance with U.S. EPA's Data Quality Objective Process (U.S. EPA-QA/G-4) document. The DQO Process is a series of logical steps that provides guidance for designing a plan for collecting data of sufficient quality and quantity to support the goals of a study. It is both flexible and iterative and applies to both decision-making and estimation. The DQO Process is intended to:

- clarify the study objective;
- define the appropriate type of data;
- determine the most appropriate conditions from which to collect the data; and
- specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of the data.

The DQO Process consists of seven iterative steps which include:

- Step 1: State the problem
- Step 2: Identify the goal of the study
- Step 3: Identify the information inputs
- Step 4: Define the boundaries of the study
- Step 5: Develop the analytic approach (develop a decision rule)
- Step 6: Specify performance or acceptance criteria (specify tolerable limits on decision errors)
- Step 7: Develop the plan for obtaining data

The DQO Process allows one or more of these steps to be revisited as more information on the problem is obtained.

Step 1: State the Problem

Historical operations at the St. Croix Alumina site have resulted in the presence of hazardous constituents that may present a threat to human health and the environment. Environmental monitoring of groundwater is required as described below.

Step 2: Identify the Goals of the Study

A geohydrology and geochemistry assessment to facilitate a better understanding of and quantify the natural source zone processes for LNAPL (phase separated impacts), evaluate the stability of LNAPL and dissolved phase plumes and evaluate natural attenuation processes of dissolved phase constituents in groundwater downgradient of the LNAPL.

Step 3: Identify Information Inputs

- Implement a comprehensive sampling program for groundwater that meet the data requirements for groundwater monitoring program.
- Confirm analytical methods used to achieve laboratory method detection limits (MDLs) and reporting limits (RLs) are suitable for reporting to USEPA Region 2.

Step 4: Define the Boundaries of the Study

The spatial boundaries of the study area in the Site include the undeveloped property and the Anguilla Landfill to the west, residential developments to the north, industrial developments and several well fields to the east, and the Caribbean Sea to the south.

Step 5 – Develop the Analytical Approach (Develop a Decision Rule)

Volatile Organic Compound (VOC) and Naphthalene samples results will be compared to USEPA Maximum Contaminant Levels (MCLs). The comparison to MCLs will only be used for reporting purposes. It should be noted that the Work Plan does not contain a provision for groundwater remediation. In conjunction with the routine groundwater sampling, the objective of the proposed supplemental LNAPL and NSZD work is to define the mobility/recoverability of the LNAPL and identify the presence and magnitude of NSZD processes and mass losses.

Step 6 – Performance or Acceptance Criteria (Specify Tolerable Limits on Decision Errors)

Data will be deemed acceptable for use if it meets the laboratory methods performance metrics, as described in Worksheet #12. In addition, data validation will be performed in accordance with the program outlined in Worksheets #35 and #36 to ensure data usability and reliability.

Analytical data are subject to random and systemic errors at different stages of the collection process – from field collection to sample analysis. The combination of all these errors is called "total study error". There are typically two contributors to the total study error:

- *Sampling error* – constituent concentrations may vary over time and space. Limited sampling may miss sampling some features of the natural variation because it is usually impractical to measure an entire population. Sampling design error occurs when the data collection design does not capture the complete variability of the environment.
- *Measurement error* – influenced by imperfections in the physical sample collection, measurement, and analysis system. Measurement errors is a combination of random and system errors that are introduced at various steps of the measurement process.

Decision-making problems are generally addressed by performing statistical hypothesis tests on the collected data which are then used to select between one condition (a baseline condition or null hypothesis) and another (the alternative condition or alternative hypothesis). The null hypothesis is presumed to be the true (unknown) value in the absence of contradicting evidence.

In the context of analytical data collected for the St. Croix site, the following hypotheses have been developed:

- Null Hypothesis: Analytes are equal to or below the applicable screening level for the various environmental media sampled.
- Alternative Hypothesis: Analytes are greater than the applicable screening level for the various environmental media sampled.

It is noted that for analytes where the reporting limit is greater than the screening level, the reporting limit will be used as the screening level.

There are two possible decision error limits to be considered when evaluating these hypotheses:

1. A false rejection decision error, or a Type I decision error, is the type of error made when the null hypothesis is rejected when it is actually true. For example, this type of error would result in deciding that the site is contaminated above the screening levels when it is not.

2. A false acceptance decision error, or a Type II decision error, is the type of error made when the null hypothesis is not rejected when it is actually false. For example, this type of error would result in deciding that the site is not contaminated above the screening levels when it is.

The closer the reported value is to the specified action level, the higher the probability that an incorrect decision will be made. At sites where a large number of samples are collected spatially or temporarily to test the null and alternative hypotheses (such as what is proposed for this site), summary statistics are often developed for a population of samples (e.g., mean or median are calculated for a group of soil samples collected from a particular area of a site). To reduce the probability of making an incorrect decision based on the statistical value, a “gray region” is often identified around the action level where the decision error is considered to be tolerable. In turn, tolerable decision limits are established outside the “gray region”. The gray region is bounded on one side by the Action Level and on the other by that value where the consequences of making a false acceptance decision error becomes serious, i.e., the consequences of committing a false acceptance decision error would be significant.

There are no project-specific Action Levels, groundwater sample results are compared to the EPA-approved Minimum Action Levels. Given the focused scope of this investigation, the specific DQO conditions for the project cited in Step 5, the extremely conservative nature of the proposed screening criteria, and the sampling plan design that incorporates both systematic and judgmental sampling, no gray region will be applied and the hypotheses will be tested directly against the reported value. Therefore, if the reported value for an analyte for a given media exceeds the screening level, the alternative hypothesis is satisfied. Conversely, if the reported value for an analyte for a given media is equal to or lower than the screening level, the null hypothesis is satisfied.

Step 7 – Develop the Plan for Obtaining Data

The detailed plan for obtaining data is provided in the LNAPL NSZD Work Plan. A summary of project tasks are provided in QAPP Worksheet #14.

12 QAPP Worksheet #11: Project Quality Objectives/Systematic Planning Process Statements

Who will use the data?

USEPA – Region 2 and its consultants, the Project Operating Committee for St. Croix Alumina, and EHS Support.

What will the Data be used for?

Data will be used to monitor existing conditions and concentrations of VOCs, SVOCs and TPH-DRO in groundwater downgradient of the source area, as well as to facilitate a better understanding of and quantify the natural attenuation degradation of the historical dissolved and phase-separated impacts in the groundwater at the Site.

What types of data are needed?

Laboratory analytical data will be needed to evaluate concentrations of contaminants of potential concern (COPCs) (see **Section 1.4**) in groundwater samples.

How "good" does the data need to be in order to support the environmental decision?

Data must be of sufficient quality and quantity to support monitoring of conditions and concentrations of VOCs in groundwater downgradient of the source area, in accordance with USEPA guidance.

How much data are needed?

The proposed number of samples is summarized in Worksheet #18.

Where, when, and how should the data be collected/generated?

Proposed sample location and schedule for routine groundwater sampling will be in accordance with the groundwater sampling and analysis plan and associated revisions that are proposed as part of the Annual Groundwater Monitoring Report. Proposed sample locations and schedule for field work implementation for the supplemental NSZD assessments are provided in the LNAPL Natural Source Zone Depletion Work Plan, dated November 2020. SOPs for field sample collection are summarized in Worksheet #21.

Who will collect and generate the data?

GeoMonitoring personnel will collect analytical samples. Samples will be shipped to ALS Environmental for analysis.

How will the data be reported?

Data will be reported by ALS Environmental to EHS Support via electronic data delivery (EDD) that is compatible with EHS Support's Environmental Quality Information System (EQiUS) database. A full data package, including raw data, will also be provided by the laboratory in electronic PDF format. Summary tables of data results accompanied by the PDF data reports will be provided to USEPA in applicable reports.

How will the data be archived?

Electronic data will be archived in EHS Support's EQiUS system and is available into infinity. PDF laboratory reports will be archived by EHS Support in servers equipped with backup systems.

13 QAPP Worksheet #12: Measurement Performance Criteria Table

Matrix	Water
Analytical Group	VOCs (BTEX) SW-846 8260C/ HS-MSV001

BTEX = benzene, toluene, ethylbenzene, and xylene
VOC = volatile organic compound

QC Sample	Data Quality Indicators (DQIs)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/Measurement Performance Criteria	Corrective Action
Method Blank (MB)	Accuracy/Bias/ Contamination	One per batch of 20 analytical samples	Analyte concentrations <1/2 LOQ	Analyte concentrations <1/2 LOQ	Correct problem. If required, re-prep and reanalyze Method Blank and all QC samples and field samples processed with the contaminated blank. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control Sample (LCS)	Accuracy/Bias	One per batch of 20 analytical samples	Benzene: 74-120% Toluene: 77-118% Ethylbenzene: 77-117% Xylenes, Total: 75-122%	Benzene: 74-120% Toluene: 77-118% Ethylbenzene: 77-117% Xylenes, Total: 75-122%	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Matrix Spike (MS)	Accuracy/Bias	One per batch of 20 analytical samples	Benzene: 70-127% Toluene: 70-123% Ethylbenzene: 70-124%	Benzene: 70-127% Toluene: 70-123% Ethylbenzene: 70-124%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the

QC Sample	Data Quality Indicators (DQIs)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/Measurement Performance Criteria	Corrective Action
			Xylenes, Total: 70-130%	Xylenes, Total: 70-130%	specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.
Matrix Spike Duplicate (MSD)	Precision	One per batch of 20 analytical samples	RPD ≤ 20%	RPD ≤ 20%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.
Surrogates	Accuracy/ Bias	Each QC and Field Sample	Lab Samples (MB, LCS): 1,2-Dichloroethane-d4 70-123% 4-Bromofluorobenzene 82-115% Dibromofluoromethane 73-126% Toluene-d8 81-120% Field Samples (including MS/MSD): 1,2-Dichloroethane-d4 70-126% 4-Bromofluorobenzene 81-113% Dibromofluoromethane 77-123% Toluene-d8 82-127%	Lab Samples (MB, LCS): 1,2-Dichloroethane-d4 70-123% 4-Bromofluorobenzene 82-115% Dibromofluoromethane 73-126% Toluene-d8 81-120% Field Samples (including MS/MSD): 1,2-Dichloroethane-d4 70-126% 4-Bromofluorobenzene 81-113% Dibromofluoromethane 77-123% Toluene-d8 82-127%	Correct problem, then re-prep and reanalyze all failed samples for all surrogates in the associated preparatory batch if sufficient sample material is available and within holding time. If obvious chromatographic interference is present, reanalysis may not be necessary, but the failures must be discussed in the Case Narrative.

DQI = data quality indicator
LCS = laboratory control sample
LOQ = limit of quantification
MB = method blank
MS = matrix spike
MSD = matrix spike duplicate
QC = quality control
RPD = relative percent difference
SOP = standard operating procedure

Matrix	Water
Analytical Group	Naphthalene SW-846 8270D/ HS-MSSV003

QC Sample	Data Quality Indicators (DQIs)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/Measurement Performance Criteria	Corrective Action
Method Blank (MB)	Accuracy/Bias/ Contamination	One per batch of 20 analytical samples	Analyte concentrations <1/2 LOQ	Analyte concentrations <1/2 LOQ	Correct problem. If required, re-prep and reanalyze Method Blank and all QC samples and field samples processed with the contaminated blank. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control Sample (LCS)	Accuracy/Bias	One per batch of 20 analytical samples	45-120%	45-120%	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Matrix Spike (MS)	Accuracy/Bias	One per batch of 20 analytical samples	45-120%	45-120%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.

QC Sample	Data Quality Indicators (DQIs)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/Measurement Performance Criteria	Corrective Action
Matrix Spike Duplicate (MSD)	Precision	One per batch of 20 analytical samples	RPD ≤ 20%	RPD ≤ 20%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.
Surrogates	Accuracy/ Bias	Each QC and Field Sample	2-Fluorobiphenyl: 40-125% 4-Terphenyl-d14: 40-135% Nitrobenzene-d5: 41-120%	2-Fluorobiphenyl: 40-125% 4-Terphenyl-d14: 40-135% Nitrobenzene-d5: 41-120%	Correct problem, then re-prep and reanalyze all failed samples for all surrogates in the associated preparatory batch if sufficient sample material is available and within holding time. If obvious chromatographic interference is present, reanalysis may not be necessary, but the failures must be discussed in the Case Narrative.

DQI = data quality indicator
LCS = laboratory control sample
LOQ = limit of quantification
MB = method blank
MS = matrix spike
MSD = matrix spike duplicate
QC = quality control
RPD = relative percent difference
SOP = standard operating procedure

Matrix	Water
Analytical Group	TPH-DRO SW-846 8015C/ HS-GCFID003

TPH = total petroleum hydrocarbon

QC Sample	Data Quality Indicators (DQIs)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/Measurement Performance Criteria	Corrective Action
Method Blank (MB)	Accuracy/Bias/ Contamination	One per batch of 20 analytical samples	Analyte concentrations <1/2 LOQ	Analyte concentrations <1/2 LOQ	Correct problem. If required, re-prep and reanalyze Method Blank and all QC samples and field samples processed with the contaminated blank. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control Sample (LCS)	Accuracy/Bias	One per batch of 20 analytical samples	70-130%	70-130%	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Matrix Spike (MS)	Accuracy/Bias	One per batch of 20 analytical samples	70-130%	70-130%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.

QC Sample	Data Quality Indicators (DQIs)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/Measurement Performance Criteria	Corrective Action
Matrix Spike Duplicate (MSD)	Precision	One per batch of 20 analytical samples	RPD ≤ 20%	RPD ≤ 20%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.
Surrogates	Accuracy/ Bias	Each QC and Field Sample	60-135%	60-135%	Correct problem, then re-prep and reanalyze all failed samples for all surrogates in the associated preparatory batch if sufficient sample material is available and within holding time. If obvious chromatographic interference is present, reanalysis may not be necessary, but the failures must be discussed in the Case Narrative.

DQI = data quality indicator
LCS = laboratory control sample
LOQ = limit of quantification
MB = method blank
MS = matrix spike
MSD = matrix spike duplicate
QC = quality control
RPD = relative percent difference
SOP = standard operating procedure

Matrix	Water
Analytical Group	Methane RSK-175/ HS-GCFID010

QC Sample	Data Quality Indicators (DQIs)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/Measurement Performance Criteria	Corrective Action
Method Blank (MB)	Accuracy/Bias/ Contamination	One per batch of 20 analytical samples	Analyte concentrations <1/2 LOQ	Analyte concentrations <1/2 LOQ	Correct problem. If required, re-prep and reanalyze Method Blank and all QC samples and field samples processed with the contaminated blank. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control Sample (LCS)	Accuracy/Bias	One per batch of 20 analytical samples	75-125%	75-125%	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Matrix Spike (MS)	Accuracy/Bias	One per batch of 20 analytical samples	75-125%	75-125%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not

QC Sample	Data Quality Indicators (DQIs)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/Measurement Performance Criteria	Corrective Action
					met and explain in the Case Narrative.
Matrix Spike Duplicate (MSD)	Precision	One per batch of 20 analytical samples	RPD ≤ 30%	RPD ≤ 30%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.

DQI = data quality indicator
LCS = laboratory control sample
LOQ = limit of quantification
MB = method blank
MS = matrix spike
MSD = matrix spike duplicate
QC = quality control
RPD = relative percent difference
SOP = standard operating procedure

Matrix	Water
Analytical Group	Metals and Cations SW-846 6020A/ HS-MET003

QC Sample	Data Quality Indicators (DQIs)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/Measurement Performance Criteria	Corrective Action
Method Blank (MB)	Accuracy/Bias/ Contamination	One per batch of 20 analytical samples	Analyte concentrations <1/2 LOQ	Analyte concentrations <1/2 LOQ	Correct problem. If required, re-prep and reanalyze Method Blank and all QC samples and field samples processed with the contaminated blank. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control Sample (LCS)	Accuracy/Bias	One per batch of 20 analytical samples	All Analytes 80-120% Iron Manganese Calcium Magnesium Potassium Sodium	All Analytes 80-120% Iron Manganese Calcium Magnesium Potassium Sodium	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Matrix Spike (MS)	Accuracy/Bias	One per batch of 20 analytical samples	All Analytes 80-120% Iron Manganese Calcium Magnesium	All Analytes 80-120% Iron Manganese Calcium Magnesium	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.

QC Sample	Data Quality Indicators (DQIs)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/Measurement Performance Criteria	Corrective Action
			Potassium Sodium	Potassium Sodium	
Matrix Spike Duplicate (MSD)	Precision	One per batch of 20 analytical samples	RPD ≤ 20%	RPD ≤ 20%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.
Post Digestion Spike (PDS)	Accuracy/Bias	As needed for MS/MSD criteria failures	80-120% of true value	80-120% of true value	Unacceptable results indicate a possible matrix effect. Perform dilution test.
Serial Dilution Test Check (SD)	Accuracy/Bias	As needed for PDS criteria failures	Dilution must agree within ±10% of the original determination for analytes present >10 times the MQL.	Dilution must agree within ±10% of the original determination for analytes present >10 times the MQL.	Results indicate possible matrix effect. Narrate.

DQI = data quality indicator
LCS = laboratory control sample
LOQ = limit of quantification
MB = method blank
MS = matrix spike
MSD = matrix spike duplicate
PDS = post digestion spike
QC = quality control
RPD = relative percent difference
SD = serial dilution test check
SOP = standard operating procedure

Matrix	Water
Analytical Group	Anions EPA 300.0/ HS-IC001

QC Sample	Data Quality Indicators (DQIs)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/Measurement Performance Criteria	Corrective Action
Method Blank (MB)	Accuracy/Bias/ Contamination	One per batch of 20 analytical samples	Analyte concentrations <1/2 LOQ	Analyte concentrations <1/2 LOQ	Correct problem. If required, re-prep and reanalyze Method Blank and all QC samples and field samples processed with the contaminated blank. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control Sample (LCS)	Accuracy/Bias	One per batch of 20 analytical samples	All Analytes 90-110% Chloride Sulfate Nitrate Nitrite	All Analytes 90-110% Chloride Sulfate Nitrate Nitrite	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Matrix Spike (MS)	Accuracy/Bias	One per batch of 20 analytical samples	All Analytes 80-120% Chloride Sulfate	All Analytes 80-120% Chloride Sulfate	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze

QC Sample	Data Quality Indicators (DQIs)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/Measurement Performance Criteria	Corrective Action
			Nitrate Nitrite	Nitrate Nitrite	MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.
Matrix Spike Duplicate (MSD)	Precision	One per batch of 20 analytical samples	RPD ≤ 20%	RPD ≤ 20%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.

DQI = data quality indicator
LCS = laboratory control sample
LOQ = limit of quantification
MB = method blank
MS = matrix spike
MSD = matrix spike duplicate
QC = quality control
RPD = relative percent difference
SOP = standard operating procedure

Matrix	Water
Analytical Group	Dissolved Organic Carbon (DOC) SW-846 9060A/ HS-WC021

DOC = dissolved organic carbon

QC Sample	Data Quality Indicators (DQIs)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/Measurement Performance Criteria	Corrective Action
Method Blank (MB)	Accuracy/Bias/ Contamination	One per batch of 20 analytical samples	Analyte concentrations <1/2 LOQ	Analyte concentrations <1/2 LOQ	Correct problem. If required, re-prep and reanalyze Method Blank and all QC samples and field samples processed with the contaminated blank. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control Sample (LCS)	Accuracy/Bias	One per batch of 20 analytical samples	85-115%	85-115%	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Matrix Spike (MS)	Accuracy/Bias	One per batch of 20 analytical samples	80-120%	80-120%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not

QC Sample	Data Quality Indicators (DQIs)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/Measurement Performance Criteria	Corrective Action
					met and explain in the Case Narrative.
Matrix Spike Duplicate (MSD)	Precision	One per batch of 20 analytical samples	RPD ≤ 20%	RPD ≤ 20%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.

DQI = data quality indicator
LCS = laboratory control sample
LOQ = limit of quantification
MB = method blank
MS = matrix spike
MSD = matrix spike duplicate
QC = quality control
RPD = relative percent difference
SOP = standard operating procedure

Matrix	Water
Analytical Group	Ammonia SM 4500 NH3+B&F/ HS-WC026

QC Sample	Data Quality Indicators (DQIs)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/Measurement Performance Criteria	Corrective Action
Method Blank (MB)	Accuracy/Bias/ Contamination	One per batch of 20 analytical samples	Analyte concentrations <1/2 LOQ	Analyte concentrations <1/2 LOQ	Correct problem. If required, re-prep and reanalyze Method Blank and all QC samples and field samples processed with the contaminated blank. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control Sample (LCS)	Accuracy/Bias	One per batch of 20 analytical samples	85-115%	85-115%	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Matrix Spike (MS)	Accuracy/Bias	One per batch of 20 analytical samples	80-120%	80-120%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.

QC Sample	Data Quality Indicators (DQIs)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/Measurement Performance Criteria	Corrective Action
Matrix Spike Duplicate (MSD)	Precision	One per batch of 20 analytical samples	RPD ≤ 20%	RPD ≤ 20%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.

DQI = data quality indicator
LCS = laboratory control sample
LOQ = limit of quantification
MB = method blank
MS = matrix spike
MSD = matrix spike duplicate
QC = quality control
RPD = relative percent difference
SOP = standard operating procedure

Matrix	Water
Analytical Group	Sulfide SM 4500S2-D/ HS-WC035

QC Sample	Data Quality Indicators (DQIs)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/Measurement Performance Criteria	Corrective Action
Method Blank (MB)	Accuracy/Bias/ Contamination	One per batch of 10 analytical samples	Analyte concentrations <LOQ	Analyte concentrations <LOQ	Correct problem. If required, re-prep and reanalyze Method Blank and all QC samples and field samples processed with the contaminated blank. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control Sample (LCS)	Accuracy/Bias	One per batch of 10 analytical samples	85-115%	85-115%	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Matrix Spike (MS)	Accuracy/Bias	One per batch of 10 analytical samples	77-124%	77-124%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.

QC Sample	Data Quality Indicators (DQIs)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/Measurement Performance Criteria	Corrective Action
Matrix Spike Duplicate (MSD)	Precision	One per batch of 10 analytical samples	RPD ≤ 20%	RPD ≤ 20%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.

DQI = data quality indicator
LCS = laboratory control sample
LOQ = limit of quantification
MB = method blank
MS = matrix spike
MSD = matrix spike duplicate
QC = quality control
RPD = relative percent difference
SOP = standard operating procedure

Matrix	Water
Analytical Group	Alkalinity SM 2320B/ HS-WC001

QC Sample	Data Quality Indicators (DQIs)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/Measurement Performance Criteria	Corrective Action
Method Blank (MB)	Accuracy/Bias/ Contamination	One per batch of 20 analytical samples	Analyte concentrations < LOQ	Analyte concentrations < LOQ	Correct problem. If required, re-prep and reanalyze Method Blank and all QC samples and field samples processed with the contaminated blank. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control Sample (LCS)	Accuracy/Bias	One per batch of 20 analytical samples	85-115%	85-115%	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Sample Duplicate (DUP)	Precision	One per batch of 20 analytical samples	RPD ≤ 20%	RPD ≤ 20%	MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.

DQI = data quality indicator

DUP = duplicate
LCS = laboratory control sample
MB = method blank
QC = quality control
RPD = relative percent difference
SOP = standard operating procedure

Matrix	Water
Analytical Group	Total Kjeldahl Nitrogen (TKN) for Total N Calculation SM 4500 NH3+D/ HS-WC033

TKN = total Kjeldahl nitrogen

QC Sample	Data Quality Indicators (DQIs)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/Measurement Performance Criteria	Corrective Action
Method Blank (MB)	Accuracy/Bias/ Contamination	One per batch of 20 analytical samples	Analyte concentrations < LOQ	Analyte concentrations < LOQ	Correct problem. If required, re-prep and reanalyze Method Blank and all QC samples and field samples processed with the contaminated blank. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control Sample (LCS)	Accuracy/Bias	One per batch of 20 analytical samples	75-125%	75-125%	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Sample Duplicate (DUP)	Precision	One per batch of 20 analytical samples	RPD ≤ 20%	RPD ≤ 20%	MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.

DUP = sample duplicate

DQI = data quality indicator
LCS = laboratory control sample
LOQ = limit of quantification
MB = method blank
QC = quality control
RPD = relative percent difference
SOP = standard operating procedure

Matrix	Soil Gas
Analytical Group	Carbon Dioxide RSK-175/ VOA-DISGAS ALS Simi Valley

QC Sample	Data Quality Indicators (DQIs)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/Measurement Performance Criteria	Corrective Action
Method Blank (MB)	Accuracy/Bias/ Contamination	One per batch of 20 analytical samples	Analyte concentrations <LOQ	Analyte concentrations <LOQ	Correct problem. If required, re-prep and reanalyze Method Blank and all QC samples and field samples processed with the contaminated blank. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control Sample (LCS)	Accuracy/Bias	One per batch of 20 analytical samples	59-113%	59-113%	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control Sample Duplicate (LCSD)	Precision	One per batch of 20 analytical samples	RPD ≤ 12%	RPD ≤ 12%	If RPD indicates obvious analysis difficulties, sample volume available and reanalyze batch. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.

QC Sample	Data Quality Indicators (DQIs)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/Measurement Performance Criteria	Corrective Action
Matrix Spike (MS)	Accuracy/Bias	One per batch of 20 analytical samples	50-150%	50-150%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.
Matrix Spike Duplicate (MSD)	Precision	One per batch of 20 analytical samples	RPD ≤ 30%	RPD ≤ 30%	If RPD indicates obvious analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.

Refer to Worksheet #37 for Completeness goal
DQI = data quality indicator
LCS = laboratory control sample
LOQ = limit of quantification
MB = method blank
MS = matrix spike
MSD = matrix spike duplicate
QC = quality control
RPD = relative percent difference
SOP = standard operating procedure

14 QAPP Worksheet #13: Secondary Data Criteria and Limitations Table

Secondary Data	Data Source (Originating Organization, Report Title, and Date)	Data Generator(s) (Originating Org., Data Types, Data Generation/Collection Dates)	How Data Will Be Used	Limitations on Data Use
Historical Data	Semiannual Groundwater Monitoring and Status Report. St. Croix Alumina, U.S. Virgin Islands, March 5, 2021.	GeoMonitoring Services	Support additional data investigation activities.	The historical data are considered to be valid data.

15 QAPP Worksheet #14: Summary of Project Tasks

Sampling Tasks:

Phase 1:

- Routine semi-annual groundwater sampling will be collected from the monitoring wells (VW1, VW25, VW16, VW27, GM11, GM14, MMX, VW34, and VW37) and analyzed for Benzene, Toluene, Ethylbenzene, Total Xylenes (BTEX) by method 8260C, Naphthalene by method 8270D, and Total Petroleum Hydrocarbons Diesel Range Organics (TPH-DRO) by Method 8015C.
- Sampling and analysis of groundwater for petroleum hydrocarbon and MNA parameters in 17 wells located beneath the LNAPL-impacted area (VW2, VW5, VW6, VW13, VW13B, VW14, VW20, VW20B, VW21B, VW23, VW24, VW29, VW30, VW31, VW32 and VW35), 4 upgradient wells (MMX, VW8, MM9 and VW11), and 7 downgradient wells (VW25, VW27, VW34, VW37, GM11, GM14 and GM-22). This sampling will be conducted in conjunction with the next semi-annual groundwater sampling event. Note: VW22 has been dry for several sampling events but will be checked and sampled if possible.
- **Temperature Profiling for NSZD** – Completion of a downhole temperature profiling assessment in the unsaturated and saturated zones to determine ΔT (temperature gradient for each well). This will comprise a minimum of five unsaturated zone temperature readings (2 feet from ground surface, 1 foot above groundwater, and three intervals equally spaced in between) and a minimum of three saturated zone temperature readings (1 foot below the groundwater interface, 5 feet below the groundwater surface, and 10 feet bgs; where wells are deeper additional temperature readings will be collected). In addition to the wells in which groundwater sampling is being conducted, temperature profiles will also be obtained from wells VW3, VW9R, VW10, and GM22 to aid with defining background conditions and wells VW4, VW7, VW15, and VW18 to capture spatial variability in and around the source area.
- **Well Head Space Soil Gas** – Measurement of deep vadose methane (CH_4), carbon dioxide (CO_2), and hydrogen sulfide (H_2S) gas concentrations will be completed in all wells where temperature profiles are to be measured. This will consist of covering the well annulus and measuring the headspace gas concentration 1 foot above the water level in the well casing following the technique of Sweeney et al. (2017).

Phase 2: The Phase 2 work involves the use of advanced methods to quantify mass depletion rates and does not consist of traditional laboratory analyses. The Standard Operating Procedures (SOPs) for the Phase 2 work are included as **Appendix D**. At this time, the preliminary scope of the Phase 2 Comprehensive Grid Soil Sampling Assessment will include the following:

- Advance up to 25 grid soil gas sampling locations and collect associated monitoring wellhead space readings immediately above the water table.
- LI-COR 7810, E-Flux, CO-2 (or other equivalent) field instrument/collection.
- Carbon-13 (^{13}C) and carbon-14 (^{14}C) laboratory analysis, as required.

Analysis Tasks:

Analytical samples will be submitted to ALS Environmental Laboratory for analysis in accordance with the procedures detailed in the QAPP. Sample analyses per media type are as follows:

Groundwater:

Sampling analyses and methods are further detailed in Worksheet #18.

Quality Control Tasks:

The samples will be collected as documented in the SOPs and Worksheet #17. The QA samples are described in Worksheet #20.

Secondary Data:

See Worksheet #13 for the Secondary Data Criteria and Limitations table.

Data Management Tasks:

The overall data quality objective is to develop and implement procedures for field sampling, chain-of-custody, laboratory analysis, and reporting which will provide results that are scientifically valid, and the levels of which are sufficient to meet quality objectives. Specific procedures for sampling, chain-of-custody, laboratory and field instruments calibration, laboratory analysis, reporting of data, internal quality control, preventative maintenance of field and laboratory equipment, and corrective action are described in other sections of this QAPP. The specific, required QA objectives for accuracy, precision, representativeness, completeness, sensitivity, selectivity, and comparability are described in this section.

Measurement performance criteria for precision, accuracy/bias, representativeness, completeness, sensitivity, quantitation limits, selectivity, and comparability have been established for each matrix and parameter. These measures of performance are also referred to as Data Quality Indicators (DQIs) and are discussed in detail in the following sections.

Precision is the agreement among a set of replicate measurements without consideration of the “true” or accurate value: i.e., variability between measurements of the same material for the same analyte. Precision is measured statistically, such as calculating variance or standard deviation.

Field precision is assessed through the collection and measurement of field duplicates (one extra sample in addition to the original field sample). Field duplicates will be collected at a frequency of one per 20 investigative samples per matrix per analytical parameter. Precision will be measured through the calculation of relative percent difference (RPD). The resulting information will be used to assess sample homogeneity, spatial variability at the site, sample collection reproducibility, and analytical variability. Field duplicate RPDs must be <30% for aqueous samples. Field precision will be improved by following SOPs, utilizing experienced/trained sampling crews, and conducting field audits.

Precision in the laboratory is assessed through the calculation of RPD for laboratory duplicate samples (two samples from the same container). Laboratory precision measures both sample preparation and analysis reproducibility.

For organic analyses, laboratory precision will be assessed through the analysis of matrix spike/matrix spike duplicate (MS/MSD) samples and/or field duplicates. MS/MSD samples will be performed at a frequency of one per sampling event. Laboratory duplicate samples, equipment blanks, and trip blanks will be performed at a frequency of one per sampling event.

Accuracy is the degree of agreement of a measured value with its true value. It should be noted that precise data may not be accurate data. Accuracy can be expressed as a percent recovery or percent deviation of the measurement with respect to its known or true value.

The following QA/QC samples will be collected unless noted otherwise:

- Equipment blanks for analytical laboratory analyses (volatile organic compounds [VOCs]) are collected at a frequency of one per parameter per twenty samples collected. Equipment blanks are not required if the samples are collected using dedicated sampling equipment. Blind equipment blanks will be collected (i.e., it will be labeled so it is not evident to the laboratory that it is a blank sample).
    - Equipment blanks will be collected by passing laboratory-supplied deionized water over and/or through the respective decontaminated sampling equipment utilized during each sampling effort.
- Trip Blanks (TB) for VOCs will be provided by the laboratory and are submitted for analysis with site samples at a frequency of one trip blank per cooler containing VOC samples.
    - Trip blank samples will be analyzed for the same VOCs for which the associated media are being analyzed.
- The equipment and trip blanks will indicate any adverse effects of sample contamination from an outside source (i.e., sample collection) and could result in a positive or negative bias. Bias is minimized by following the SOPs for equipment decontamination, utilizing an experienced/trained sampling crew, conducting field audits, and ensuring the purity of any materials used for decontamination.
- MS/MSD for analytical laboratory analysis are collected at a frequency of one sample per 20 samples per matrix submitted for analysis. If less than 10 samples are collected, batch MS/MSD shall be used for QA/QC evaluations.
- Field Duplicates for analytical laboratory analysis are collected at a frequency of one sample per 20 samples per matrix submitted for analysis. If less than 20 samples are collected batch duplicates such as MS/MSD and Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD) shall be used as a precision evaluation for the laboratory data. Blind duplicates will be collected (i.e., it will be labeled so it is not evident to the laboratory that it is a blank sample).

Documentation and Records:

Project-related documentation will include, but not be limited to, the following information and records:

- Sample collection records, field logs, sample preparation and analysis logs, instrument printouts, and results of calibration and QC checks
- Environmental monitoring real-time data collection activities

- Chain-of-Custody forms
- Off-site laboratory data reports, may include:
  - Preliminary Report/Deliverables – pdf emailed or fax
  - Sample Identification
  - Sample Receipt information (date of receipt at laboratory, date of extraction & analysis)
  - Sample results
  - Surrogate Recovery and applicable limits
  - QC Summary for method blanks, LCS, MS/MSD to include results and applicable limits
  - EDD (cvs or xml file) emailed as specified for the requested turnaround time.
  - Final Report Deliverables due within specified turnaround time. Final report will be delivered via electronic copy. This report must include:
    - Standard report with sample result summary;
    - Case narrative;
    - Method references;
    - Analysis and extraction dates; Sample identification information (including client sample identification (ID) and laboratory ID);
    - Data Package Checklist;
    - Chain-of-custody (including internal chain-of-custody); and
    - QA/QC signoff
- QC sample records
- General field procedures
- Corrective Action Reports
- Site Records, including Visitor Logs and Daily Safety Meetings

All original records generated for on-site activities will be kept on site during field activities. Copies of documents may be maintained in the SharePoint electronic project file. After field activities have been completed, the original files will be maintained by the PM or QA Manager until the project is completed. Original reports for laboratory analysis will be obtained electronically and saved in the SharePoint project file.

Document control is the process of ensuring that documents are reviewed for adequacy, approved for release, and used at the location where the prescribed activity is performed. A document is defined as information in any medium that describes, defines, specifies, reports, certifies, requires, or provides data or results pertaining to environmental programs.

Records control is the process of providing ready retrieval, storage, protection, and disposition of records. A record is defined as a completed and valid document and/or other material that provides objective evidence pertaining to the quality of an item or process. Records typically include but are not limited to:

- Work Plan and other project specific documents
- Electronic records
- Technical proposals
- Chain-of-custody records
- Other project planning documents
- On-site data reports/results
- Project reports

- Field logbooks
- SOPs

Procedures for records control are necessary for meeting project requirements, access of sensitive information, and retention and availability of files during and after the project's period of performance.

The TD and PM will establish the project file requirements, including definition of records, in accordance with this QAPP. A file coordinator will maintain a file structure to facilitate retrieval of any desired document or record. Documents will be uniquely identified and filed according to chronological order and document type.

Retention and ultimate disposition of records will be completed in accordance with project specifications. Disposition includes transferring all records to the client. At the completion of the project-required retention period, records will be transferred or discarded.

Records to be transferred will be inventoried before transfer, if required, under the direction of the PM. Upon transfer, the client representative should sign a receipt for records that references or includes the inventory list. The receipt and inventory will be maintained as evidence of the transfer. If required, records to be discarded will also be inventoried. The PM will review the inventory list and authorize in writing the disposition of those records. A copy of the discard authorization and associated inventory list will be maintained.

Quality-related documents define the objectives, policies, and procedures, which ensure the quality of items and services, provided by EHS Support. A system has been designed to revise, distribute, and control QA documents.

Quality-related documents have multiple levels of review and approval appropriate for the document. The signature of the reviewer on the document records these reviews. Quality-related documents are required to be periodically reviewed and, if necessary, revised. The frequency of this review depends on the type of document and on regulations and client requirements. In addition to periodic review and revision, quality-related documents must be revised when the activity, policy, or procedure they describe changes in a significant manner. The QAPP will be revised, as necessary.

Document control is necessary to ensure that associates have access to current policies and procedures at all times. Quality documents that are placed under a controlled distribution include this QAPP, Quality Policy Documents, and SOPs.

Quality-related documents are controlled by initially distributing them to the associates who need to be aware of or follow the contained information or procedures. The QA Manager is responsible for ensuring that revisions to the QAPP are distributed to necessary individuals. All subsequent revisions or updates to the document are also distributed to the associates. Records of distribution are maintained and demonstrate that current policies and procedures have been issued to all appropriate personnel.

Because many deliverable documents (work plans, final reports) will be produced for this project, consistency of style, organization, and format are important to overall quality, as are grammar, spelling, readability, and overall clarity. This person assists the TD and PM at the onset of the project, modifying as necessary the format and style guide for all deliverables. A style guide will be developed in

accordance with project requirements. The report coordinator will also function as an interface with the team's word processing and graphics staff as well as the records management staff.

Whenever possible, EHS Support establishes standard forms and content guidelines to ensure quality. Project plans, for example, will use common forms to ease preparation and review. For this task, the TD and PM will be responsible for the report quality.

During the preparation of a report, internal peer reviews are conducted on select areas and on select topics to evaluate performance, improve quality, and resolve professional differences of opinions. Peer reviews may be performed on program documents, implementation procedures, studies, and reports in highly specialized technical areas or in conjunction with special assignments. In general, each review is unique, has individual objectives, and requires that individual methodologies and technical skills be used.

Due to the unique nature of these reviews, the TD will evaluate the qualifications of potential reviewers to ensure only properly qualified peer reviewers are selected. Each peer review will be formally documented and signed by the reviewers.

Assessment/Audit Tasks:

The purpose of assessment is to ensure that the plan is implemented as prescribed. This section addresses tools and procedures for assessing the effectiveness of implementation of the project and associated QA/QC. The remainder of this section identifies the number, frequency, and type of assessments, including the approximate dates and names of responsible personnel. The assessments include but are not limited to peer reviews, management systems reviews, technical systems audits, performance evaluations, and audits of data quality.

Performance and system audits of both field and laboratory activities may be conducted to verify that sampling and analysis are performed in accordance with the procedures established in the plan. The audits of field and laboratory activities include two separate independent parts: Internal and external audits.

The EHS Support QA Manager and/or client representative may conduct internal audits of field activities (sampling and measurements). The audits would include examination of field sampling records; field instrument operating records; sample collection, handling, and packaging in compliance with the established procedures; maintenance of QA procedures; and chain of custody. These audits may occur at the onset of the project to verify that all established procedures are followed. Upon detection of a deficiency, the auditor has the authority to stop work being conducted and to notify the PM and/or Field Superintendent in order to determine and implement corrective action. Follow up audits may be conducted to correct deficiencies, and to verify that QA procedures are maintained throughout the project. The audits would involve review of field measurement records, instrumentation calibration records, and sample documentation. General considerations for field audits include information on:

- Sample Collection
- Sample Storage and Shipment
- Decontamination Equipment
- Safety
- Quality Control

Corrective actions may be required for two classes of problems: analytical and equipment problems and noncompliance problems. Analytical and equipment problems may occur during sampling and sample handling, sample preparation, laboratory instrumental analysis, and data review. Any nonconformance with the established QC procedures will be identified and corrected.

For noncompliance problems, a formal corrective action program will be determined and implemented at the time the problem is identified. The person who identifies the problem is responsible for completing a nonconformance report and notifying the Field Superintendent. The PM, FM, or his designee will issue a Nonconformance Report for each nonconformance condition. If the problem is analytical in nature, information on these problems will be promptly communicated to the QA Manager and documented in a laboratory nonconformance report. Implementation of corrective action will be documented by completing a Corrective Action Report.

Corrective actions will be implemented immediately, if possible, and documented in the field logbook. No staff member will initiate corrective action without prior communication of findings to the TD, PM, and appropriate project personnel. If corrective actions are insufficient, work may be stopped by the TD, PM, or QA Manager.

Technical staff and project personnel will be responsible for reporting all suspected technical or QA non-conformances or suspected deficiencies of any activity or issued document by reporting the situation to the PM or designee. The TD and/or PM will be responsible for assessing the suspected problems in consultation with the QA Manager in order to make a decision based on the potential for the situation to impact the quality of the data. If it is determined that the situation warrants a reportable nonconformance requiring corrective action, then a nonconformance report will be initiated by the PM.

The TD and PM will be responsible for ensuring that corrective actions for non-conformances are initiated by:

- Evaluating all reported non-conformances.
- Controlling additional work on nonconforming items.
- Determining disposition or action to be taken.
- Maintaining a log of non-conformances.
- Reviewing nonconformance reports and corrective actions taken.
- Ensuring nonconformance reports are included in the final site documentation in project files.

If appropriate, the TD and PM will ensure that no additional work dependent on the nonconforming activity is performed until the corrective actions are completed.

Corrective action for field measurements may include:

- Repeat the measurement to check the error.
- Check for all proper adjustments for ambient conditions (e.g., temperature).
- Check the batteries.
- Check the calibration.
- Re-calibrate.
- Replace the instrument or measurement devices.
- Stop work (if necessary).

The FM or his designee is responsible for all site activities. In this role, the FM at times is required to adjust the site programs to accommodate site-specific needs. When it becomes necessary to modify the sampling program, it will be noted in the project file.

The TD is responsible for controlling, tracking, and implementing the identified changes. Reports on all changes will be distributed to all affected parties.

Data Review Tasks:

This section describes the process for data review, verification, and validation per the Region III Modifications to National Functional Guidelines for Data Review. Data analysis will be reviewed by qualified individuals other than those performing the analysis. Preliminary or informal analysis or calculations may be performed by one or more originators and need not be completely checked but may be reviewed by the PM or his/her designee. Final calculations and summary data tables will be made on calculation sheets or spreadsheets, respectively, and will be peer reviewed. All data will be reviewed.

Data will be acceptable if they meet the following criteria:

- Field data sheets are complete;
- Laboratory data were reviewed/validated;
- Sample handling procedures documented on chain-of –custody forms;
- Sampling field activity reports are completed and follow outlined procedures;
- Field QC was conducted as planned and meets the acceptance criteria; and
- Laboratory QC was conducted and reported as outlined in this document.

Conclusions and/or recommendations will be reviewed by one or more peers to ensure their accuracy on the basis of the data that have been acquired and the analysis that has been conducted. Professionals who have the necessary knowledge and skill to perform the review and who are not directly involved in the activity being reviewed will perform technical reviews. Technical reviews will be documented, and this documentation will be retained in the project file. Any deviations from this QAPP in the field or laboratory data report are to be reported in the monthly progress report to USEPA.

16 QAPP Worksheet #15: Reference Limits and Evaluation Table

AQUEOUS SAMPLES

Analytical Method	Compound	Units	Quantitation Limit	Detection Limit	Minimum Screening Level
SW-846 8260C	Benzene	µg/L	1	0.2	5
SW-846 8260C	Toluene	µg/L	1	0.2	1000
SW-846 8260C	Ethylbenzene	µg/L	1	0.3	700
SW-846 8260C	o-Xylenes	µg/L	1	0.3	--
SW-846 8260C	m,p-Xylenes	µg/L	2	0.5	--
SW-846 8260C	Xylenes, Total	µg/L	1	0.3	10,000
SW-846 8270D	Naphthalene	µg/L	0.1	0.02	--
SW-846 8015C	TPH-DRO	µg/L	50	20	--
SM2320B	Alkalinity	µg/L	5000	5000	--
SW-846 6020B	Sodium	µg/L	200	14	--
SW-846 6020B	Potassium	µg/L	200	18	--
SW-846 6020B	Calcium	µg/L	500	34	--
SW-846 6020B	Magnesium	µg/L	200	10	--
SW-846 6020B	Iron (Total and Dissolved)	µg/L	200	12	--
SW-846 6020B	Manganese (Total and Dissolved)	µg/L	5	0.7	--
EPA 300.0	Chloride	µg/L	500	200	--
EPA 300.0	Sulfate	µg/L	500	200	--
EPA 300.0	Nitrate	µg/L	100	30	10,000
EPA 300.0	Nitrite	µg/L	100	30	1,000

Analytical Method	Compound	Units	Quantitation Limit	Detection Limit	Minimum Screening Level
SW-846 9060A	Dissolved Organic Carbon (DOC)	µg/L	1000	500	--
SM4500 S2-D	Sulfide	µg/L	50	11	--
SM4500 NH3-B-F	Ammonia	µg/L	50	25	--
Calculation (TKN/NO3/NO2)	Total Nitrogen	µg/L	500	107	--
RSK-175	Methane	µg/L	0.5	0.107	--
RSK-175 (ALS Simi Valley)	Carbon Dioxide	µg/L	1000	370	--

µg/L = microgram per liter
DOC = dissolved organic carbon
LOQ = limit of quantification
* MDL studies will be performed and updated annually by the laboratory
** Minimum screening levels = USEPA Maximum Contaminant Level

17 QAPP Worksheet #16: Project Schedule/Timeline Table

Activities	Organization	Dates (MM/DD/YY)		Deliverable	Deliverable Due Date
		Anticipated Date(s) of Initiation	Anticipated Date of Completion		
Pre-Field Work Mobilization Planning and Coordination	POC, GMS, USEPA, ALS Environmental, and EHS Support	May 2021	TBD, Long-term Monitoring	None – Coordination with contractors, laboratory, field personnel, etc.	N/A
Groundwater Monitoring Well Sampling	POC, GMS, USEPA, ALS Environmental, and EHS Support	May 2021	TBD, Long-term Monitoring	Semiannual Groundwater Sampling Reports	Within 30 days of receipt of Final Analytical Data Package
NSZD Evaluation	POC, GMS, USEPA, ALS Environmental, and EHS Support	04/01/2021	TBD	NSZD Evaluation Report	Within 60 days of receipt of Final Analytical Data Package

N/A = not applicable
NSZD = natural source zone depletion
TBD = to be determined
USEPA = United States Environmental Protection Agency

18 QAPP Worksheet #17: Sampling Design and Rationale

Groundwater sample locations were previously selected to sufficiently monitor existing conditions and concentrations of VOCs in groundwater downgradient of the source are at the St. Croix Alumina Site.

Four soil gas monitoring point clusters will be installed measure vadose gas concentration gradients. Soil gas monitoring clusters will be installed adjacent to a monitoring near the center of each LNAPL 'lobe' (VW-13B, VW-20B, and VW-31) and in one background location (MMX). In addition to being located in the center of each main LNAPL lobe, these locations represent different lithologies at the well screen (fine grained lagoon/evaporites, sandy/clastic material, and limestone.

COPCs are provided in **Section 1.4**.

19 QAPP Worksheet #18: Sampling Locations and Methods/SOP Requirement Table

Sampling Location/ID Number	Matrix	Depth (feet below top of casing)	Analytical Group	Concentration Level	Number of Samples (identify field duplicates)	Sampling SOP Reference	Rationale for Sampling Location
NZSD Assessment: LNAPL impacted area wells - VW2, VW5, VW6, VW13, VW13B, VW14, VW20, VW20B, VW21B, VW23, VW24, VW29, VW30, VW31, VW32 and VW35 Upgradient wells - MMX, VW8, MM9 and VW11 Downgradient wells - VW25, VW27, VW34, VW37, GM11, GM14 and GM-22	Groundwater	TBD	VOCs (BTEX), Naphthalene, TPH-DRO Alkalinity, Cations (Total Fe & Mn), Anions (Cl and SO_4), Nitrate and Nitrite, Dissolved Fe and Mn, Sulfide, Ammonia, TKN, Methane, Carbon Dioxide, and DOC	TBD	28, plus 2 field duplicates	SOP-43 and SOP-46	Monitor LNAPL and Groundwater Impacts
Semi-annual monitoring wells – VW1, VW25, VW16, VW27, VW34, VW37,	Groundwater	TBD	VOCs (BTEX), Naphthalene, TPH-DRO	TBD	7, plus 1 field duplicate	SOP-43 and SOP-46	Monitor Groundwater Impacts

Sampling Location/ID Number	Matrix	Depth (feet below top of casing)	Analytical Group	Concentration Level	Number of Samples (identify field duplicates)	Sampling SOP Reference	Rationale for Sampling Location
GM11, GM14, and MMX							
Based on the results of the Phase 1 Assessment, soil gas samples will be collected from potential locations ESG-1 through ESG-24	Soil Gas	TBD	Not applicable	TBD	TBD	EHS E-Flux Fossil Fuel Trap SOP, EHS LICOR LI-7810 Trap SOP, EHS Gas Gradient SOP, and EHS Temperature Gradient SOP	The specifics of the Phase 2 implementation will be based on the findings of the Phase 1 assessment (confirmation of active NSZD). The density of flux measurement locations and background areas will be determined based on the outcome of Phase 1 results, specifically the identification of NSZD loci and hydrological complexities. The method employed to measure vadose gas flux will be based on the outcome of Phase 1 results and may include a passive trap method or a DCC method. A key determinant will be the necessary grid spacing of the CO_2 monitoring network to capture representative hydrogeochemical variability in background and source area locations.

BTEX = benzene, toluene, ethylbenzene, and xylene
DRO = diesel range organics
LNAPL = liquid non-aqueous phase liquid
NSZD = natural source zone depletion
SOP = standard operating procedure
TBD = to be determined
TKN = total Kjeldahl nitrogen
TPH = total petroleum hydrocarbon
VOC = volatile organic compound

20 QAPP Worksheet #19: Analytical SOP Requirements Table

ALS Environmental
10450 Stancliff Road, Suite 210, Houston, TX 77099
R.J. Modashia, rj.modashia@alsglobal.com, 281-530-5656

Analyte/ Analyte Group	Analytical Method/SOP	Container (number, size/volume, type)	Preservation	Maximum Holding Time
BTEX	SW-846 8260C	3 x 40 mL VOA	HCL Kept at ≤6° C	14 Days 7 days if unpreserved
Naphthalene	SW-846 8270D	3 x 40 mL VOA	Kept at ≤6° C	Extract Water in 7 days, Analyzed 40 days after extraction
DRO	SW-846 8015C	3 x 40 mL VOA	Kept at ≤6° C With HCL	Analyze within 14 days if preserved with HCL, 7 days if unpreserved
Alkalinity	SM2320B	250 mL Plastic	Neat Kept at ≤6° C	14 days
Cations/Metals	SW-846 6020A	120 mL plastic	HNO3	180 days
Dissolved Metals	SW-846 6020A	125 mL plastic	Unpreserved or HNO3 if field filtered	180 days
Anions	EPA 300.0	125 mL Plastic Neat 125 mL /H2SO4	Cool to >0 to 6 º C H2SO4	48 if unpreserved 28 days
DOC	SW-846 9060A	40 mL VOA	Kept at ≤6° C	Kept at ≤6° C
Sulfate	EPA 300.0	125 mL Plastic Neat	Cool to >0 to 6 º C	28 days

Analyte/ Analyte Group	Analytical Method/SOP	Container (number, size/volume, type)	Preservation	Maximum Holding Time
Sulfide	SM4500 S2-D	500 mL Plastic	NAOH/ZN Kept at ≤6° C	7 days
Ammonia	SM4500 NH3 B-F	250 mL Plastic	H2SO4 Kept at ≤6° C	28 days
TKN	SM4500 NH3 -D	250 mL Plastic	H2SO4 Kept at ≤6° C	28 days
Methane	RSK-175	3 x 40mL HCl VOA	Kept at ≤6° C & HCL preserved	Analyze within 14 days if preserved with HCL, 7 days if unpreserved
Carbon Dioxide	RSK-175 (ALS Simi Valley)	3 x 40mL VOA	Kept at ≤6° C	No HT specified, recommended within 5 days of collection

BTEX = benzene, toluene, ethylbenzene, and xylene
DOC = dissolved organic carbon
DRO = diesel range organics
mL = milliliter
VOA =
VOC = volatile organic compound

21 QAPP Worksheet #20: Field Quality Control Sample Summary Table

Media	Analysis	Laboratory	Estimated Sample Quantity	Field QC Analyses			Laboratory QC Samples	
				Trip Blank	Equipment Blank	Field Duplicate	Matrix Spike	Matrix Spike Duplicate
Groundwater	VOCs (BTEX), Naphthalene, TPH-DRO Alkalinity, Cations (Total Fe & Mn), Anions (Cl and SO_4), Nitrate and Nitrite, Dissolved Fe and Mn, Sulfide, Ammonia, TKN, Methane, and DOC	ALS Environmental	35	1/ cooler	0	1/20 samples	1/20 samples	1/20 samples

Media	Analysis	Laboratory	Estimated Sample Quantity	Field QC Analyses			Laboratory QC Samples	
				Trip Blank	Equipment Blank	Field Duplicate	Matrix Spike	Matrix Spike Duplicate
Soil Gas	Carbon Dioxide	ALS Environmental	25	1	0	1	0	0

BTEX = benzene, toluene, ethylbenzene, and xylene
DRO = diesel range organics
QC = Quality Control
SOP = Standard Operating Procedure
TPH = total petroleum hydrocarbon
VOC = volatile organic compound
* Equipment blanks are not required if the samples are collected using dedicated sampling equipment. As stated in the OM&M Plan: Groundwater samples from each monitoring well will be collected using a disposable bailer dedicated to each monitoring well. The groundwater samples from each sump will be collected using a disposable bailer dedicated to each sump.

22 QAPP Worksheet #21: Project Sampling SOP Reference Table

Identification	Title of Standard Operating Procedure (SOP)	Preparer
SOP-04	Field Documentation	EHS Support LLC
SOP-05	Sample Management and Shipping	EHS Support LLC
SOP-08	Field Equipment Operation and Calibration	EHS Support LLC
SOP-09	Equipment Decontamination	EHS Support LLC
SOP-12	Quality Assurance/Quality Control Samples	EHS Support LLC
SOP-41	Fluid Measurement	EHS Support LLC
SOP-43	Low Flow Groundwater Sampling	EHS Support LLC
SOP-46	Water Sampling for Chemical Analysis	EHS Support LLC
N/A	Use of Passive CO_2 Traps	EHS Support LLC
N/A	Gas Gradient NSZD Rate Estimate	EHS Support LLC
N/A	Use of Dynamic Closed Chamber (LICOR meter)	EHS Support LLC
N/A	Temperature Gradient NSZD Rate Estimate	EHS Support LLC

N/A = not applicable
NSZD = natural source zone depletion
SOP = Standard Operating Procedure

23 QAPP Worksheet #22: Field Equipment Calibration, Maintenance, Testing, and Inspection Table

Field Equipment	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
PID	Daily by the field team	As required by manufacturer specification	VOCs in air	Check cable and battery charge	Daily prior to use	See SOP	Re-calibrate, troubleshoot according to manufacturer specifications, and replace instrument if necessary	Field personnel/ operator	43
Multi Water Quality Meter	Daily by the field team	Clean each probe and flow-through cell daily with deionized water and alconox. Replace probes as necessary. Replace batteries as necessary.	Attach groundwater sampling tubing to instrument's flow through cell.	Inspect instrument is clean, inspect for battery life, inspect for damage to cables or other parts of the instrument .	Daily prior to use	See equipment operation manual	Re-calibrate, troubleshoot according to manufacturer specifications, and replace instrument if necessary. Do not use if any parameter is not calibrated to within specified range of error.	Field personnel/ operator	43
Thermoprobe TP7-D thermocouple/reel instrument, or GEOKON Model 3810 thermistor string, or	Factory calibrated	As required by manufacturer specification	Temperature gradient	Inspect instrument is clean, inspect for battery life, inspect for	Daily prior to use	See equipment operation manual	N/A	Field personnel/ operator	Temp Gradient

Field Equipment	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
Thermochron Model DS1922L button logger				damage to cables or other parts of the instrument					
Landtec GEM™5000	Factory calibrated	As required by manufacturer specification	Soil gas gradient	Inspect instrument is clean, inspect for battery life, inspect for damage to cables or other parts of the instrument	Daily prior to use	See equipment operation manual	N/A	Field personnel/ operator	Gas Gradient
DCC soil flux system	No regular factory recalibration required. Calibration is recommende d based on QA/QC results and drift in replicate analyses over time	As required by manufacturer specification	Soil gas CO_2	Inspect instrument is clean, inspect for battery life, inspect for damage to cables or other parts of the instrument	Daily prior to use	See equipment operation manual	N/A	Field personnel/ operator	LICOR Trap

N/A = not applicable
PID = Photo Ionization Device
SOP = Standard Operating Procedure
VOC = volatile organic compound
[1]Specify the appropriate reference letter or number from the Project Sampling SOP References table (Worksheet #21).

24 QAPP Worksheet #23: Analytical SOP Reference Table

ALS Environmental
10450 Stancliff Road, Suite 210, Houston, TX 77099
R.J. Modashia, rj.modashia@alsglobal.com, 281-530-5656

SOP Number	Definitive or Screening Data	Instrument	Organization Performing Analysis
HS-MSV001, HS-MSSV003	BTEX by 8260C; Naphthalene by 8270D	Gas Chromatograph/ Mass Spectrometer	ALS Environmental
HS-GCFID003, HS-GCFID010	TPH-DRO by 8015C; Methane by RSK-175	Gas Chromatograph/Flame Ionization Detector	ALS Environmental
HS-MET003	Metals (Total and Diss.) and Cations by 6020A	Inductively Coupled Plasma Mass Spectrometer	ALS Environmental
HS-WC035, HS-WC026, HS-WC033	Sulfide, Ammonia, (for Total Nitrogen calc.) by SM 4500S2-D and SM4500 NH3-B-F	Spectro-photometer	ALS Environmental
HS-IC001	Anions	Ion Chromatograph	ALS Environmental
HS-WC021	Dissolved Organic Carbon (DOC)	Total Organic Carbon Analyzer	ALS Environmental
HS-WC001	Alkalinity by SM 2320B	Man Tech	ALS Environmental
HS-WC033	Total Kjeldahl Nitrogen (TKN) for Total Nitrogen Calc.by SM 4500 NH3+D	Ion Selective Electrode	ALS Environmental

SOP Number	Definitive or Screening Data	Instrument	Organization Performing Analysis
VOA-DISGAS	Carbon dioxide by RSK-175 (ALS Simi Valley)	Gas Chromatograph/ Flame Ionization Detector	ALS Environmental
HS-EQ001	Weighing samples and certified standards	Balances	ALS Environmental
HS-EQ003	Volumetric measurement of samples and certified standards	Mechanical Volumetric Pipettes	ALS Environmental

BTEX = benzene, toluene, ethylbenzene, and xylene
DRO = diesel range organics
GC = Gas Chromatography
MS = Matrix Spike
SOP = Standard Operating Procedure
TPH = total petroleum hydrocarbon
VOC = volatile organic compound

25 QAPP Worksheet #24: Analytical Instrument Calibration Table

ALS Environmental
10450 Stancliff Road, Suite 210, Houston, TX 77099
R.J. Modashia, rj.modashia@alsglobal.com, 281-530-5656

Instrument	Calibration Procedure/Range	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
BTEX GS/MS SW-846 8260C SOP HS-MSV001	BFB Tuning	Prior to ICAL; Every 12 hours during operation	HS-MSV001, Rev 11.6; Table 11.3	Retune instrument and verify. No samples shall be analyzed without a valid tune and tailing factor.	Analyst	HS-MSV001, Rev 11.6; Section 11.2 and Table 11.3, 11.13
	Initial Calibration (Minimum 5 levels for linear and 6 levels for quadratic) Aqueous - 0.5 ug/L to 200 ug/L Soil Reg Level – 2.5 ug/kg to 200 ug/kg Soil Med Level – 1.0 ug/L to 200ug/L	After ICV/CCV failure, After tune failure	Average RRF : see Table 11.4; RSD for Target analytes <20% (≤15% for DoD projects); or option below: Option 1 linear – least squares regression r > 0.995. Option 2 non-linear – r2 > 0.99 (must use 6 points at minimum). [Note: grand mean not allowed.]	Correct Problem and repeat initial calibration.	Analyst	HS-MSV001, Rev 11.6; Section 11.7-11.11
	ICV Standard	After each new calibration	All analytes within ±20% of expected value.	Reanalyze the ICV. If ICV fails again do system	Analyst	HS-MSV001, Rev 11.6;

Instrument	Calibration Procedure/Range	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
				maintenance and recalibrate.		Section 11.12
	CCV/CCB Standard	Daily, before sample analysis and every 12 hours during operation	All reported analytes and surrogates within ± 20% of true value. Blank with no compounds present greater than ½ LOQ and surrogate within ± 20% of true value.	Correct problem then repeat CCV/CCB. If second attempt fails, then repeat initial calibration.	Analyst	HS-MSV001, Rev 11.6; Section 11.14, Table 11.4
Naphthalene GS/MS SW-846 8270D SOP HS-MSSV003	DFTPP Tuning, DDT Breakdown, Benzidine/PCP Tailing Factors	Prior to ICAL; Every 12 hours during operation	Refer to DFTPP criteria listed in the Tables 11.2.1, 11.2.2 and 11.2.3. DDT breakdown must be <20% and benzidine & pentachlorophenol tailing factors <2.	Retune instrument and verify. No samples shall be analyzed without a valid tune and tailing factor.	Analyst	HS-MSSV003, Rev 7.1; Section 11.1-11.4, Table 11.2.1, Table 11.2.2, Table 11.2.3
	Initial Calibration (Minimum 5 levels for linear and 6 levels for quadratic) Aqueous- (nominally 0.1 for PAH only) 0.2-10 ug/L	Initial calibration prior to sample analysis.	Average RF meet and each level RF should meet min RF criteria in Table 22.1 and %RSD <20% (≤15% for DoD projects) or one option below: Option 1 linear – least squares regression, r > 0.995 or Option 2 non-linear – COD > 0.990, 6 points	Correct problem then repeat initial calibration.	Analyst	HS-MSSV003, Rev 7.1; Section 11.5-11.6

Instrument	Calibration Procedure/Range	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
			shall be used for 2nd order.			
	ICV Standard	Once per each new initial calibration.	All analytes within ±20% of expected value.	Correct problem then repeat initial calibration.	Analyst	HS-MSSV003, Rev 7.1; Section 11.7
	CCV Standard	Daily, before sample analysis and every 12 hours during operation	CCV RF meets min RF criteria in Table 22.1. CCV RF is ≤ 20% difference (when using RFs) or ≤ 20% drift (when using linear or non-linear calibration models). CCV IS RT±30 seconds from RT of the mid-point standard in the ICAL. EICP area within –50% to +100% of ICAL mid-point standard. All reported analytes within 20% of true values.	Correct problem then repeat CCV. If second attempt fails, then repeat initial calibration.	Analyst	HS-MSSV003, Rev 7.1; Section 11.8
DRO GC-FID SW-846 8015C SOP HS-GCFID003	Hydrocarbon Locator Standard	Prior to ICAL and before each 12-hour shift	Verify RT Windows, and set Absolute RT. Set range for DRO / ORO	N/A	Analyst	HS-GCFID003 Rev 7.3; Section 11.2
	Initial Calibration Curve (ICAL) Minimum 5 points; Range 50-200 ppm	Prior to sample analysis	Calibration Factor – mean RSD for all analytes ≤20%; or Linear – r > 0.995; or Quadratic – r2 > 0.99 (6	Correct problem and repeat initial calibration	Analyst	HS-GCFID003 Rev 7.3; Section 11.3

Instrument	Calibration Procedure/Range	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
			points shall be used for second order). Refit calibration against the newly created curve – all compounds for the lowest point must be within ±50% of true value and all other level within ±30% of true value for curve to be valid.			
	Initial Calibration Verification (ICV)	Separate source from ICAL; After multi-point initial calibration	All analytes within ±20% of expected value.	Correct problem and repeat initial calibration	Analyst	HS-GCFID003 Rev 7.3; Section 11.4
	Continuing Calibration verification (CCV)/ Continuing Calibration Blank (CCB)	Beginning of analytical sequence, after 10 samples and at the end of the analysis sequence	CCV- All analytes within ± 20% of expected value; CCB: no analytes greater than the ½ LOQ	Correct problem, then repeat initial calibration verification and reanalyze all samples since last successful calibration verification	Analyst	HS-GCFID003 Rev 7.3; Section 11.5
Methane GC-FID	Initial Calibration Curve (ICAL) Minimum 5 points	Prior to sample analysis	Linear – mean RSD for all analytes ±20%; or Linear – least squares regression, R > 0.995; or Non-linear – COD > 0.99 (6 points shall be used for	Correct problem and repeat initial calibration	Analyst	HS-GCFID010 Rev 6.4; Section 13.2

Instrument	Calibration Procedure/Range	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
RSK-175 SOP HS-GCFID010			second order). Linear calibration requires minimum of 5 point and quadratic requires 6 points.			
	Initial Calibration Verification (ICV)	Separate source from ICAL; After multi-point initial calibration	All analytes within ±20% of expected value.	Correct problem and repeat initial calibration	Analyst	HS-GCFID010 Rev 6.4; Section 13.3
	Continuing Calibration verification (CCV)/ Continuing Calibration Blank (CCB)	Beginning of analytical sequence, after 10 samples and at the end of the analysis sequence	CCV- All analytes within ± 20% of expected value; CCB: no analytes greater than the ½ LOQ	Correct problem, then repeat initial calibration verification and reanalyze all samples since last successful calibration verification	Analyst	HS-GCFID010 Rev 6.4; Section 18.6
Metals and Cations ICP-MS SW-846 6020A SOP HS-MET003	MS Tuning Sample	Prior to initial calibration and calibration verification	Meet criteria in SOP Section 11.4	Retune instrument then reanalyze tuning solution	Analyst	HS-MET003 Rev 8.5; Section 11.4
	Initial Calibration Curve (ICAL) Minimum 3 standards and a blank	Daily prior to sample analysis	r> 0.998	Prepare fresh standard and recalibrate	Analyst	HS-MET003 Rev 8.5; Section 11.5-11.6; 16.3

Instrument	Calibration Procedure/Range	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
	Initial Calibration Verification (ICV)	Once per each new initial calibration	All analytes within ±10% of expected value.	Correct problem and repeat ICAL	Analyst	HS-MET003 Rev 8.5; Section 11.7, 16.4
	Low-level ICV/CCV (LLICV/LLCCV)	Daily after initial calibration verification and continually at the end of every batch	All analytes within ±30% of expected value	Rinse system again and repeat LLICV/LLCCV. If reanalysis is unacceptable, any data at that level is questionable and must not be reported. Recalibrate the instrument and reanalyze affected samples	Analyst	HS-MET003 Rev 8.5; Section 16.6
	Calibration Blank, Initial and Continuing (ICB/CCB)	Initially after calibration verification and continuing after every 10 samples and at the end of the sequence	Analytes detected <MQL	Correct problem then reanalyze CCB and any previous samples with detections >MQL	Analyst	HS-MET003 Rev 8.5; Section 16.7
	Interference check solutions (ICSA and ICSAB)	Beginning of each daily analytical run and after 12 hours of operation as the run continues	ICS-A: All non-spiked trace analytes < MQL and others ±20% of true value. ICS-AB: trace analytes within ±20% of true value	Terminate analysis; locate and correct problem; reanalyze ICS; reanalyze all affected samples	Analyst	HS-MET003 Rev 8.5; Section 10.9.1 and 16.9

Instrument	Calibration Procedure/Range	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
	Calibration verification (CCV)	After every 10 samples and at the end of the sequence	All analyte(s) within ±10% of expected value	Correct problem then repeat calibration and reanalyze all samples since last successful CCV	Analyst	HS-MET003 Rev 8.5; Section 10.10 and 16.5
Anions Ion Chromatography EPA 300.0 SOP HS-IC001	Initial Calibration Curve (ICAL) Minimum 5 point Initial Calibration Blank (ICB)	Daily prior to sample analysis	r≥0.995 Analytes in ICB < ½ PQL	Correct problem, then repeat initial calibration	Analyst	HS-IC001 Rev 9.3; Section 10.10-10.11
	Retention Time window position establishment	Once per multi-point calibration	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used	N/A	Analyst	HS-IC001 Rev 9.3; Section 15.5
	Initial Calibration Verification (ICV)	Separate source from ICAL; After multi-point initial calibration	All analytes within ±10% of expected value.	Correct problem and/or prepare fresh ICV, then rerun ICV. If that fails, repeat initial calibration.	Analyst	HS-IC001 Rev 9.3; Section 10.12
	Retention Time (RT) window width	Calculated for each analyte at method set-up and after major maintenance	RE width is ±3 times standard deviation for each analyte RT over the 24-hour period	N/A	Analyst	HS-IC001 Rev 9.3; Section 10.11.2 and 15.3

Instrument	Calibration Procedure/Range	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
		(e.g., column change)				
	Continuing Calibration Verification (CCV) with Retention time window verification and Continuing Calibration Blanks (CCB)	CCV and CCB daily before samples and then after every 10 injections and at the end of the analysis sequence. CCV levels must be alternated between the high- and low-level standards on days when no initial calibration is performed Calculated RT window width for each calibration verification	All reported analytes within ±10% of expected value Analytes in CCB < ½ PQL RT window width ± 10% of previous RT	Prepare and analyze a fresh calibration curve	Analyst	HS-IC001 Rev 9.3; Section 10.13 and 11.14
Dissolved Organic Carbon	Initial Calibration Curve (ICAL) Minimum 5 point Initial Calibration Blank (ICB)	After major maintenance or failed CCV	r≥0.995 Analytes in ICB < ½ PQL	Correct problem, then repeat initial calibration	Analyst	HS-WC021 Rev 6.6 Section 13
TOC Analyzer	Initial Calibration Verification (ICV)	Separate source from ICAL; After multi-point initial calibration	All analytes within ±10% of expected value.	Correct problem and/or prepare fresh ICV, then rerun ICV. If that	Analyst	HS-WC021 Rev 6.6 Section 18.2

Instrument	Calibration Procedure/Range	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
SW-846 9060A SOP HS-WC021				fails, repeat initial calibration.		
	Continuing Calibration Verification (CCV) and Continuing Calibration Blanks (CCB)	CCV and CCB daily before samples and then after every 10 injections and at the end of the analysis sequence.	All reported analytes within ±10% of expected value Analytes in CCB < ½ PQL	Correct problem then repeat CCV or prepare new curve and new CCV. Reanalyze any affected samples since last passing CCV.	Analyst	HS-WC021 Rev 6.6 Section 18.3
Ammonia and Sulfide UV-Vis Spectrophotometer	Initial Calibration Curve (ICAL) Minimum 5 point	After major maintenance or failed CCV Ammonia samples are undistilled.	r≥0.995 Analytes in ICB < ½ PQL	Correct problem, then repeat initial calibration	Analyst	HS-WC026 Section 11.2, 16.3 HS-WC035 Section 15.3
	Initial Calibration Verification (ICV)	Separate source from ICAL; After multi-point initial calibration Ammonia samples are undistilled.	All analytes within ±20% of expected value.	Correct problem and/or prepare fresh ICV, then rerun ICV. If that fails, repeat initial calibration.	Analyst	HS-WC026 Section 11.3, 16.4 HS-WC035 Section 15.5
Ammonia SM 4500 NH3+B&F SOP HS-WC026	Continuing Calibration Verification (CCV)	CCV daily before samples and then after every 10 injections and at the end of the analysis sequence. Ammonia	All reported analytes within ±20% of expected value	Correct problem then repeat CCV or prepare new curve and new CCV. Reanalyze any affected	Analyst	HS-WC026 Section 11.4, 16.5 HS-WC035 Section 15.4

Instrument	Calibration Procedure/Range	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
Sulfide SM 4500S2-D SOP HS-WC035		samples are undistilled		samples since last passing CCV.		
	Initial and Continuing Calibration Blanks (ICB & CCB) undistilled (applies only to Ammonia)	ICB after calibration, CCB daily before samples and then after every 10 injections and at the end of the analysis sequence.	Analytes < ½ PQL	Correct problem then repeat CCB and reanalyze any affected samples since last passing CCB.	Analyst	HS-WC026 Section 11.4, 16.6 Not Applicable to HS-WC035
Alkalinity Automated ManTech Analyzer SM 2320B SOP HS-WC001	Meter Calibration/standardization using 1413, 2820, and 10,000 conductivity standards and 4, 7, and 10 pH standards	Daily prior to sample analysis	Assign calibration points to instrument. pH points within ±0.05 of the expected value	Correct problem, then repeat initial calibration	Analyst	HS-WC001 Section 15.4
Alkalinity Automated ManTech Analyzer SM 2320B SOP HS-WC001	Initial Calibration Curve (ICAL) Minimum 5 point	After major maintenance or failed CCV	Subtracting the 5.0 mg/L Standard mV reading from the 50 mg/L Standard mV reading, the range should be between 54 to 60 mV	Correct problem, then repeat initial calibration		HS-WC033 Section 10.3
	Initial Calibration Verification (ICV)	Separate source from ICAL; After multi-point initial calibration	All analytes within ±20% of expected value.	Correct problem and/or prepare fresh ICV, then rerun ICV. If that	Analyst	HS-WC033 Section 10.4

Instrument	Calibration Procedure/Range	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
				fails, repeat initial calibration.		
	Continuing Calibration Verification (CCV)	CCV daily before samples and then after every 10 injections and at the end of the analysis sequence.	All reported analytes within ±20% of expected value	Correct problem then repeat CCV or prepare new curve and new CCV. Reanalyze any affected samples since last passing CCV.	Analyst	HS-WC033 Section 10.5
	Initial and Continuing Calibration Blanks (ICB & CCB)	ICB after calibration, CCB daily before samples and then after every 10 injections and at the end of the analysis sequence.	Analytes < ½ PQL	Correct problem then repeat CCB and reanalyze any affected samples since last passing CCB.	Analyst	HS-WC033 Section 16.4
Carbon dioxide GC-FID RSK-175 SOP VOA-DISGAS	Initial Calibration Curve (ICAL) Minimum 5 points	Prior to sample analysis	RSD <20% Retention time within 0.10 minutes of mean RT over the ICAL range	Correct problem and repeat initial calibration	Analyst	VOA-DISGAS, Rev 18.0; Section 9.4.1, 11.4.1, 12.3
	Initial Calibration Verification (ICV)	Separate source from ICAL; After multi-point initial calibration	All analytes within ±15% of expected value.	Correct problem and repeat initial calibration	Analyst	VOA-DISGAS, Rev 18.0; Section

Instrument	Calibration Procedure/Range	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
						9.4.2, 11.5, 12.4
	Continuing Calibration verification (CCV)/ Continuing Calibration Blank (CCB)	Beginning of analytical sequence, after 10 samples and at the end of the analysis sequence	CCV- All analytes within ± 15% of expected value; CCB: no analytes greater than the LOQ	Correct problem, then repeat initial calibration verification and reanalyze all samples since last successful calibration verification	Analyst	VOA-DISGAS, Rev 18.0; Section 9.4.1, 11.7, 12.5

CCV = Continuing Calibration Verification
GC = Gas Chromatography
IS = Internal Standard
LCS = Laboratory Control Sample
LCSD = Laboratory Control Sample duplicate
MS = matrix spike
MSD = matrix spike duplicate
RL = reporting limit
RSD = Relative Standard Deviation
VOC = volatile organic compound

26 QAPP Worksheet #25: Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table

ALS Environmental
10450 Stancliff Road, Suite 210, Houston, TX 77099
R.J. Modashia, rj.modashia@alsglobal.com, 281-530-5656

Analytical Parameter	Instrument/ Equipment	Maintenance Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
BTEX by 8260C; Naphthalene by 8270D	Gas Chromatograph/ Mass Spectrometer	Clean the source and replace the filaments. Replace the seal, liner, and septum. Change the column.	Check the gas supply. Check the seal, liner, and septum.	Source cleaning is performed when the instrument response deteriorates. Other instrument maintenance is done as needed to keep the instrument performing at peak performance.	The minimum RF for SPCCs must meet limits stated in method. All analytes must be ≤ 20 percent difference.	Recalibrate and/or perform the necessary equipment maintenance. Check the calibration standards. Reanalyze the affected data.	Analyst/ Supervisor	HS-MSV001, HS-MSSV003
TPH-DRO by 8015C; Methane by RSK-175	Gas Chromatograph/Flame Ionization Detector	Check pressure and gas supply daily. Bake out column, change septa, liner, seal as needed, cut	Liner, seal, septum, column	Prior to initial calibration or as necessary	Percent difference ≤ 20%	Recalibrate and/or perform the necessary equipment maintenance. Check the calibration	Analyst/ Supervisor	HS-GCFID003, HS-GCFID010

Analytical Parameter	Instrument/ Equipment	Maintenance Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
		column as needed.				standards. Reanalyze the affected data		
Metals (Total and Diss.) and Cations by 6020A	Inductively Coupled Plasma Mass Spectrometer	Clean the torch assembly and the spray chamber when they become discolored or when degradation in data quality is observed. Clean the nebulizer, and check the argon supply. Replace the peristaltic pump tubing as needed	Inspect the torch, nebulizer chamber, pump, and tubing	Maintenance is performed prior to initial calibration or as necessary.	Percent difference ≤ 10%	Recalibrate and/or perform the necessary equipment maintenance. Check the calibration standards. Reanalyze the affected data.	Analyst/ Supervisor	HS-MET003
Sulfide, Ammonia, (for Total Nitrogen calc.) by SM 4500S2-D and SM4500 NH3-B-F	Spectro-photometer	Clean reagent tubes. Change lamp, as needed.	Check wavelength	At the beginning of every run.	ICV/CCV 90-110% of true value	Recalibrate and/or perform necessary equipment maintenance. Check calibration standards.	Analyst/ Supervisor	HS-WC035, HS-WC026, HS-WC033

Analytical Parameter	Instrument/ Equipment	Maintenance Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
						Reanalyze affected data.		
Anions	Ion Chromatograph	Replace column, seals	Check gas supply, check for leaks, check pistons	Daily or as needed	ICV/CCV 90-110% of true value	Recalibrate and/or perform necessary equipment maintenance. Check calibration standards. Reanalyze affected data	Analyst/ Supervisor	HS-IC001
Dissolved Organic Carbon (DOC)	Total Organic Carbon Analyzer	Clean syringe, replace scrubber as needed, change filters as needed	Check gas supply, check lamp, tubing, reagent volumes	Prior to sample analysis, or when instrument does not meet method criteria	CCV ≤10% difference waters CCV ≤30% difference soils	Recalibrate and/or perform necessary equipment maintenance. Check calibration standards. Reanalyze affected data	Analyst/ Supervisor	HS-WC021
Alkalinity by SM 2320B	Man Tech	Change buffer solutions or pH probe	Change buffer solutions or pH probe	Before analysis begins, check every 3 hours	4 and 7 + 0.05 pH units, pH 10 ± 0.10 pH units,	Recalibrate and/or perform necessary equipment maintenance.	Analyst/ Supervisor	HS-WC001

Analytical Parameter	Instrument/ Equipment	Maintenance Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
					± 0.20 pH units for check	Check calibration standards. Reanalyze affected data		
Total Kjeldahl Nitrogen (TKN) for Total Nitrogen Calc.by SM 4500 NH3+D	Ion Selective Electrode	Change buffer solutions or probe	Change buffer solutions or probe	Before analysis begins and after installation of a new probe	Standard mV reading, the range should be between 54 to 60 mV	Recalibrate and/or perform necessary equipment maintenance. Check calibration standards. Reanalyze affected data	Analyst/ Supervisor	HS-WC033
Carbon dioxide by RSK-175 (ALS Simi Valley)	Gas Chromatograph/ Flame Ionization Detector	Check pressure and gas supply daily. Bake out column, change injection port liner, septa, or ferrule, as needed. Cut column, as needed. Clean detectors when needed or with noticeable	Liner, seal, septum, ferrule, column	Prior to initial calibration or as necessary	ICV/ CCV Percent difference < 15%	Recalibrate and/or perform the necessary equipment maintenance. Check the calibration standards. Reanalyze the affected data	Analyst/ Supervisor	VOA-DISGAS

Analytical Parameter	Instrument/ Equipment	Maintenance Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
		change in background interference and peak definition.						
Weighing samples and certified standards	Balances	Cleaning, levelling, professional service	Calibration verification against certified weights	Annual service contract and daily calibration verifications prior to use	Acceptable service report, daily readings within 0.1% of certified value	Clean balance, assess working environment, and reattempt verification. If acceptable reading cannot be obtained, do not use balance, and call professional service provider.	Analyst/ Supervisor	HS-EQ001
Volumetric measurement of samples and certified standards	Mechanical Volumetric Pipettes	Cleaning and inspect for deterioration	Calibration verification against certified balance weights	Clean as required. Inspect prior to use. Quarterly verification required against certified weights	Percent Recovery 98-102%; Bias ± 2%; Precision ± 1% based on 5 replicates	Perform cleaning and maintenance as needed. Replace o-rings as needed. Repeat verification.	Analyst/ Supervisor	HS-EQ003

GC = Gas Chromatography
MS = matrix spike
NA = not applicable
SOP = Standard Operating Procedure
VOC = volatile organic compound

27 QAPP Worksheet #26: Sample Handling System

SAMPLE COLLECTION, PACKAGING, AND SHIPMENT

- Sample Collection (Personnel/Organization): GeoMonitoring Services
- Sample Packaging (Personnel/Organization): GeoMonitoring Services
- Coordination of Shipment (Personnel/Organization): GeoMonitoring Services
- Type of Shipment/Carrier: UPS/FedEx overnight delivery or laboratory courier

SAMPLE RECEIPT AND ANALYSIS

- Sample Receipt (Personnel/Organization): ALS Environmental personnel
- Sample Custody and Storage (Personnel/Organization): ALS Environmental personnel
- Sample Preparation (Personnel/Organization): ALS Environmental personnel
- Sample Determinative Analysis (Personnel/Organization): ALS Environmental personnel

SAMPLE ARCHIVING

- Field Sample Storage (No. of days from sample collection): Samples will be shipped the day they are collected for overnight delivery. If field conditions require storage of samples on-site, they will be kept on ice or in a refrigerator at or below 6°C.
- Sample Extract/Digestate Storage (No. of days from extraction/digestion): See Worksheet #19
- Biological Sample Storage (No. of days from sample collection): No biological samples are scheduled to be collected.

SAMPLE DISPOSAL

- Personnel/Organization: ALS Environmental personnel
- Number of Days from hold time expiration: >7

28 QAPP Worksheet #27: Sample Custody Requirements

Field Sample Custody Procedures (sample collection, packaging, shipment, and delivery to laboratory):

Each sample collected will be assigned a unique identification number and placed in an appropriate sample container. Each sample container will have a sample label affixed to the outside with the date, time of sample collection and project name. In addition, this label will contain the sample identification number, analysis required, and chemical preservatives added, if any. All documentation will be completed in waterproof ink.

The analytical laboratory will provide pre-cleaned and prepared sample containers for this project. The laboratory will also prepare and supply trip blanks. Trip blanks will be placed into metal or plastic coolers and will be received by the field sampling.

Samples collected in the field for laboratory analysis will be placed directly into the laboratory-supplied sample containers. Individual sample containers will be sealed by hand-tightening container lids. To maintain and document sample possession, chain of custody procedures will be followed.

Coolers containing the samples and associated QA/QC samples will be received at the laboratory within 24 hours of their shipment from the field. The temperature in the coolers containing samples and associated QA/QC samples will be maintained at a temperature of 4 degrees Centigrade while on-site and during shipment.

The establishment of a standard sample designation/labeling protocol is essential to ensure adequate quality assurance/quality control and to allow tracking of each sample and the associated analytical data. Proper labeling allows for the tracking of samples beginning from the time of sample collection, through analysis, and following project completion should future data correlation be deemed necessary. The proper labeling of samples is also critical in ensuring that samples are analyzed within the required sample holding times. All samples will be identified using a unique sample identification scheme suitable to the project and the sampling protocol detailed scopes of work.

The sample identification number will be recorded on the chain-of-custody forms accompanying each sample shipment submitted for analysis and will be recorded in the field logbooks. The custody program will be followed during sample handling activities in both field and laboratory operations. The primary purpose of chain of custody procedures is to document the possession of the samples from collection through shipping, storage and analysis to data reporting and disposal. Each person who takes possession of the samples, except the shipping courier, is responsible for sample integrity and safe keeping.

The following Chain of Custody procedures are provided below:

- Chain of custody will be initiated by the laboratory supplying the pre-cleaned and prepared sample containers. Chain of custody forms will accompany the sample containers.
- At the time of sample collection, the chain of custody form will be completed for the sample collected. The sample identification number, date and time of sample collection, analysis requested and other pertinent information (e.g., preservatives) will be recorded on the form. All entries will be made in waterproof, indelible blue or black ink.

- Field technicians will be responsible for the care and custody of the samples collected until the samples are transferred to another party, dispatched to the laboratory, or disposed. The Field Supervisor will be responsible for enforcing chain of custody procedures during field work.
- When the form is full or when all samples have been collected that will fit in a single cooler, the FM or designee will check the form for possible errors and sign the chain of custody form. Any necessary corrections will be made to the record with a single strike mark, dated, and initialed. Each cooler will be accompanied by a separate chain of custody form, sealed in a Ziploc bag (or equivalent), and placed on top of the samples or taped to the inside of the cooler lid.
- Samples will be packaged for shipment and dispatched to the analytical laboratory with the appropriate chain of custody form. A copy of the chain of custody form will be retained by the FM or designee for the project file and the original will be sent with the samples. Bills of lading or shipping bills will also be retained as part of the documentation for the chain of custody records.
- When transferring custody of the samples, the individuals relinquishing and receiving custody of the samples will verify sample numbers and condition and will document the sample acquisition and transfer by signing and dating the chain of custody form. This process documents sample custody transfer from the sampler, usually through an express courier, to the analyst in the analytical laboratory.

Laboratory Sample Custody Procedures (receipt of samples, archiving, disposal):

Sample Receiving

ALS Environmental can accept samples Monday through Friday from 7:30 a.m. until 7:00 p.m., and Saturday from 8:00 a.m. until 12:00 p.m. Commercial and Cargo carriers, UPS, Federal Express shipments, and client deliveries received are completely unpacked, logged into the computer system, properly stored, and in some cases, analysis is started if short holding times or rush TAT testing is scheduled in advance.

Sample Storage

Samples are stored in locations that are assigned based on intended analysis and/or cooler space at the proper temperature. When employees need access to samples for testing, they requisition them through the LIMS. The LIMS tracks the personnel requesting the samples, the date and time the sample was taken out of storage, and the date and time returned. Samples are retained for 30 days after the invoice date, unless otherwise directed. All samples are disposed of following proper local, state, and federal regulations. Sample receipt, unpacking, storage and disposal practices and procedures are outlined in company SOPs that are available upon request.

Sample Disposal

The laboratory protects the public and the environment by adhering to strict waste disposal practices. ALS Environmental waste disposal practices comply with all applicable federal, state, and local regulations. When the retention time for a stored sample has expired, a discard list is generated from the computerized sample management system (CSMS). Samples are removed from their assigned storage area by a sample custodian. All sample containers, whether they are empty or have remaining

sample, are completely destroyed in their original containers by incineration. Manifests and Certificates of Destruction are kept on-site for a minimum of five years.

Data Archiving

All raw data, lab notebooks, and instrument printouts are stored in a locked archive area on-site for 6 months and then transferred to an off-site storage area for a minimum of 10 years. Data submitted to the archivist for storage is catalogued by test area, batch description, date stored, and date for destruction. Each analytical group regularly receives computerized listings of the data filed to facilitate retrieval should data be needed after storage. Technical groups keep magnetic tapes within the group for several months prior to archiving. A fireproof room houses the archives. An alarm system using both smoke and heat detectors monitors the data storage area. Halon fire extinguishers protect the records in the area.

Sample Identification Procedures:

All samples will be identified using a unique sample identification scheme suitable to the project and the sampling protocol detailed in the NSZD Work Plan.

Chain-of-custody Procedures:

Laboratory chain of custody will be maintained throughout the analytical processes as described in the laboratory's Quality Assurance Manual. The chain of custody form becomes the permanent record of sample handling and shipment.

29 QAPP Worksheet #28: QA Sample Table

ALS Environmental
10450 Stancliff Road, Suite 210, Houston, TX 77099
R.J. Modashia, rj.modashia@alsglobal.com, 281-530-5656

Matrix	Water
Analytical Group	BTEX
Sampling SOP	HS-MSV001
Analytical Method/ SOP Reference	SW-846 8260C

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
Method Blank (MB)	Accuracy/Bias/ Contamination	One per batch of 20 analytical samples	Analyte concentrations <1/2 LOQ	Analyte concentrations <1/2 LOQ	Correct problem. If required, re-prep and reanalyze Method Blank and all QC samples and field samples processed with the contaminated blank. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control Sample (LCS)	Accuracy/Bias	One per batch of 20 analytical samples	Benzene: 74-120% Toluene: 77-118% Ethylbenzene: 77-117% Xylenes, Total: 75-122%	Benzene: 74-120% Toluene: 77-118% Ethylbenzene: 77-117% Xylenes, Total: 75-122%	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available.

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
					If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Matrix Spike (MS)	Accuracy/Bias	One per batch of 20 analytical samples	Benzene: 70-127% Toluene: 70-123% Ethylbenzene: 70-124% Xylenes, Total: 70-130%	Benzene: 70-127% Toluene: 70-123% Ethylbenzene: 70-124% Xylenes, Total: 70-130%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.
Matrix Spike Duplicate (MSD)	Precision	One per batch of 20 analytical samples	RPD ≤ 20%	RPD ≤ 20%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.
Surrogates	Accuracy/ Bias	Each QC and Field Sample	Lab Samples (MB, LCS): 1,2-Dichloroethane-d4 70-123% 4-Bromofluorobenzene 82-115% Dibromofluoromethane 73-126% Toluene-d8 81-120% Field Samples (including MS/MSD): 1,2-Dichloroethane-d4 70-126%	Lab Samples (MB, LCS): 1,2-Dichloroethane-d4 70-123% 4-Bromofluorobenzene 82-115% Dibromofluoromethane 73-126% Toluene-d8 81-120% Field Samples (including MS/MSD): 1,2-Dichloroethane-d4 70-126%	Correct problem, then re-prep and reanalyze all failed samples for all surrogates in the associated preparatory batch if sufficient sample material is available and within holding time. If obvious chromatographic interference is present, reanalysis may not be necessary, but the failures must be discussed in the Case Narrative.

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
			4-Bromofluorobenzene 81-113% Dibromofluoromethane 77-123% Toluene-d8 82-127%	4-Bromofluorobenzene 81-113% Dibromofluoromethane 77-123% Toluene-d8 82-127%	

DQI = data quality indicator
LCS = laboratory control sample
LOQ = limit of quantification
MB = method blank
MS = matrix spike
MSD = matrix spike duplicate
QC = quality control
RPD = relative percent difference
SOP = standard operating procedure

Matrix	Water
Analytical Group	Naphthalene
Sampling SOP	HS-MSSV003
Analytical Method/ SOP Reference	SW-846 8270D

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
Method Blank (MB)	Accuracy/Bias/ Contamination	One per batch of 20 analytical samples	Analyte concentrations <1/2 LOQ	Analyte concentrations <1/2 LOQ	Correct problem. If required, re-prep and reanalyze Method Blank and all QC samples and field samples processed with the contaminated blank. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control Sample (LCS)	Accuracy/Bias	One per batch of 20 analytical samples	45-120%	45-120%	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
Matrix Spike (MS)	Accuracy/Bias	One per batch of 20 analytical samples	45-120%	45-120%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.
Matrix Spike Duplicate (MSD)	Precision	One per batch of 20 analytical samples	RPD ≤ 20%	RPD ≤ 20%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.
Surrogates	Accuracy/ Bias	Each QC and Field Sample	2-Fluorobiphenyl: 40-125% 4-Terphenyl-d14: 40-135% Nitrobenzene-d5: 41-120%	2-Fluorobiphenyl: 40-125% 4-Terphenyl-d14: 40-135% Nitrobenzene-d5: 41-120%	Correct problem, then re-prep and reanalyze all failed samples for all surrogates in the associated preparatory batch if sufficient sample material is available and within holding time. If obvious chromatographic interference is present, reanalysis may not be necessary, but the failures must be discussed in the Case Narrative.

DQI = data quality indicator
LCS = laboratory control sample
LOQ = limit of quantification
MB = method blank
MS = matrix spike
MSD = matrix spike duplicate

QC = quality control
RPD = relative percent difference
SOP = standard operating procedure
DQI = data quality indicator
LCS = laboratory control sample
LOQ = limit of quantification
MB = method blank
MS = matrix spike
MSD = matrix spike duplicate
QC = quality control
RPD = relative percent difference
SOP = standard operating procedure

Matrix	Water
Analytical Group	TPH-DRO
Sampling SOP	HS-GCFID003
Analytical Method/ SOP Reference	SW-846 8015C

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
Method Blank (MB)	Accuracy/Bias/ Contamination	One per batch of 20 analytical samples	Analyte concentrations <1/2 LOQ	Analyte concentrations <1/2 LOQ	Correct problem. If required, re-prep and reanalyze Method Blank and all QC samples and field samples processed with the contaminated blank. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control Sample (LCS)	Accuracy/Bias	One per batch of 20 analytical samples	70-130%	70-130%	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
Matrix Spike (MS)	Accuracy/Bias	One per batch of 20 analytical samples	70-130%	70-130%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.
Matrix Spike Duplicate (MSD)	Precision	One per batch of 20 analytical samples	RPD ≤ 20%	RPD ≤ 20%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.
Surrogates	Accuracy/ Bias	Each QC and Field Sample	60-135%	60-135%	Correct problem, then re-prep and reanalyze all failed samples for all surrogates in the associated preparatory batch if sufficient sample material is available and within holding time. If obvious chromatographic interference is present, reanalysis may not be necessary, but the failures must be discussed in the Case Narrative.

DQI = data quality indicator
LCS = laboratory control sample
LOQ = limit of quantification
MB = method blank
MS = matrix spike
MSD = matrix spike duplicate
QC = quality control
RPD = relative percent difference
SOP = standard operating procedure

Matrix	Water
Analytical Group	Methane
Sampling SOP	HS-GCFID010
Analytical Method/ SOP Reference	RSK-175

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
Method Blank (MB)	Accuracy/Bias/ Contamination	One per batch of 20 analytical samples	Analyte concentrations <1/2 LOQ	Analyte concentrations <1/2 LOQ	Correct problem. If required, re-prep and reanalyze Method Blank and all QC samples and field samples processed with the contaminated blank. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control	Accuracy/Bias	One per batch of 20 analytical samples	75-125%	75-125%	Correct problem, then re-prep and

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
Sample (LCS)					reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Matrix Spike (MS)	Accuracy/Bias	One per batch of 20 analytical samples	75-125%	75-125%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
Matrix Spike Duplicate (MSD)	Precision	One per batch of 20 analytical samples	RPD ≤ 30%	RPD ≤ 30%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.

DQI = data quality indicator
LCS = laboratory control sample
LOQ = limit of quantification
MB = method blank
MS = matrix spike
MSD = matrix spike duplicate
QC = quality control
RPD = relative percent difference
SOP = standard operating procedure

Matrix	Water
Analytical Group	Metals and Cations
Sampling SOP	HS-MET003
Analytical Method/ SOP Reference	SW-846 6020A

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
Method Blank (MB)	Accuracy/Bias/ Contamination	One per batch of 20 analytical samples	Analyte concentrations <1/2 LOQ	Analyte concentrations <1/2 LOQ	Correct problem. If required, re-prep and reanalyze Method Blank and all QC samples and field samples processed with the contaminated blank. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control Sample (LCS)	Accuracy/Bias	One per batch of 20 analytical samples	All Analytes 80-120% Iron Manganese Calcium Magnesium	All Analytes 80-120% Iron Manganese Calcium Magnesium	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
			Potassium Sodium	Potassium Sodium	material is available. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Matrix Spike (MS)	Accuracy/Bias	One per batch of 20 analytical samples	All Analytes 80-120% Iron Manganese Calcium Magnesium Potassium Sodium	All Analytes 80-120% Iron Manganese Calcium Magnesium Potassium Sodium	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.
Matrix Spike Duplicate (MSD)	Precision	One per batch of 20 analytical samples	RPD ≤ 20%	RPD ≤ 20%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
Post Digestion Spike (PDS)	Accuracy/Bias	As needed for MS/MSD criteria failures	80-120% of true value	80-120% of true value	Unacceptable results indicate a possible matrix effect. Perform dilution test.
Serial Dilution Test Check (SD)	Accuracy/Bias	As needed for PDS criteria failures	Dilution must agree within ±10% of the original determination for analytes present >10 times the MQL.	Dilution must agree within ±10% of the original determination for analytes present >10 times the MQL.	Results indicate possible matrix effect. Narrate.

DQI = data quality indicator
LCS = laboratory control sample
LOQ = limit of quantification
MB = method blank
MS = matrix spike
MSD = matrix spike duplicate
PDS = post digestion spike
QC = quality control
RPD = relative percent difference
SD = serial dilution test check
SOP = standard operating procedure

Matrix	Water
Analytical Group	Anions
Sampling SOP	HS-IC001
Analytical Method/ SOP Reference	EPA 300.0

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
Method Blank (MB)	Accuracy/Bias/ Contamination	One per batch of 20 analytical samples	Analyte concentrations <1/2 LOQ	Analyte concentrations <1/2 LOQ	Correct problem. If required, re-prep and reanalyze Method Blank and all QC samples and field samples processed with the contaminated blank. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control Sample (LCS)	Accuracy/Bias	One per batch of 20 analytical samples	All Analytes 90-110% Chloride Sulfate Nitrate Nitrite	All Analytes 90-110% Chloride Sulfate Nitrate Nitrite	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
Matrix Spike (MS)	Accuracy/Bias	One per batch of 20 analytical samples	All Analytes 80-120% Chloride Sulfate Nitrate Nitrite	All Analytes 80-120% Chloride Sulfate Nitrate Nitrite	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.
Matrix Spike Duplicate (MSD)	Precision	One per batch of 20 analytical samples	RPD ≤ 20%	RPD ≤ 20%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.

DQI = data quality indicator
LCS = laboratory control sample
LOQ = limit of quantification
MB = method blank
MS = matrix spike
MSD = matrix spike duplicate
QC = quality control
RPD = relative percent difference
SOP = standard operating procedure

Matrix	Water
Analytical Group	Dissolved Organic Carbon
Sampling SOP	HS-WC021
Analytical Method/ SOP Reference	SW-846 9060

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
Method Blank (MB)	Accuracy/Bias/ Contamination	One per batch of 20 analytical samples	Analyte concentrations <1/2 LOQ	Analyte concentrations <1/2 LOQ	Correct problem. If required, re-prep and reanalyze Method Blank and all QC samples and field samples processed with the contaminated blank. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control Sample (LCS)	Accuracy/Bias	One per batch of 20 analytical samples	85-115%	85-115%	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
Matrix Spike (MS)	Accuracy/Bias	One per batch of 20 analytical samples	80-120%	80-120%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.
Matrix Spike Duplicate (MSD)	Precision	One per batch of 20 analytical samples	RPD ≤ 20%	RPD ≤ 20%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.

DQI = data quality indicator
LCS = laboratory control sample
LOQ = limit of quantification
MB = method blank
MS = matrix spike
MSD = matrix spike duplicate
QC = quality control
RPD = relative percent difference
SOP = standard operating procedure

Matrix	Water
Analytical Group	Ammonia
Sampling SOP	HS-WC026
Analytical Method/ SOP Reference	SM 4500 NH3+B&F

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
Method Blank (MB)	Accuracy/Bias/ Contamination	One per batch of 20 analytical samples	Analyte concentrations <1/2 LOQ	Analyte concentrations <1/2 LOQ	Correct problem. If required, re-prep and reanalyze Method Blank and all QC samples and field samples processed with the contaminated blank. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control Sample (LCS)	Accuracy/Bias	One per batch of 20 analytical samples	85-115%	85-115%	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
Matrix Spike (MS)	Accuracy/Bias	One per batch of 20 analytical samples	80-120%	80-120%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.
Matrix Spike Duplicate (MSD)	Precision	One per batch of 20 analytical samples	RPD ≤ 20%	RPD ≤ 20%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.

DQI = data quality indicator
LCS = laboratory control sample
LOQ = limit of quantification
MB = method blank
MS = matrix spike
MSD = matrix spike duplicate
QC = quality control
RPD = relative percent difference
SOP = standard operating procedure

Matrix	Water
Analytical Group	Sulfide
Sampling SOP	HS-WC035
Analytical Method/ SOP Reference	SM 4500S2-D

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
Method Blank (MB)	Accuracy/Bias/ Contamination	One per batch of 10 analytical samples	Analyte concentrations <LOQ	Analyte concentrations <LOQ	Correct problem. If required, re-prep and reanalyze Method Blank and all QC samples and field samples processed with the contaminated blank. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control Sample (LCS)	Accuracy/Bias	One per batch of 10 analytical samples	85-115%	85-115%	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
Matrix Spike (MS)	Accuracy/Bias	One per batch of 10 analytical samples	77-124%	77-124%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.
Matrix Spike Duplicate (MSD)	Precision	One per batch of 10 analytical samples	RPD ≤ 20%	RPD ≤ 20%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.

DQI = data quality indicator
LCS = laboratory control sample
LOQ = limit of quantification
MB = method blank
MS = matrix spike
MSD = matrix spike duplicate
QC = quality control
RPD = relative percent difference
SOP = standard operating procedure

Matrix	Water
Analytical Group	Alkalinity
Sampling SOP	HS-WC001
Analytical Method/ SOP Reference	SM 2320B

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
Method Blank (MB)	Accuracy/Bias/ Contamination	One per batch of 20 analytical samples	Analyte concentrations < LOQ	Analyte concentrations < LOQ	Correct problem. If required, re-prep and reanalyze Method Blank and all QC samples and field samples processed with the contaminated blank. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control Sample (LCS)	Accuracy/Bias	One per batch of 20 analytical samples	85-115%	85-115%	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
					sufficient sample material is available. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Sample Duplicate (DUP)	Precision	One per batch of 20 analytical samples	RPD ≤ 20%	RPD ≤ 20%	MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.

DQI = data quality indicator
DUP = sample duplicate
LCS = laboratory control sample
LOQ = limit of quantification
MB = method blank
QC = quality control
RPD = relative percent difference
SOP = standard operating procedure

Matrix	Water
Analytical Group	Total Kjeldahl Nitrogen (TKN) for Total N Calculation
Sampling SOP	HS-WC033
Analytical Method/ SOP Reference	SM 4500 NH3+D

TKN = total Kjeldahl nitrogen

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
Method Blank (MB)	Accuracy/Bias/ Contamination	One per batch of 20 analytical samples	Analyte concentrations < LOQ	Analyte concentrations < LOQ	Correct problem. If required, re-prep and reanalyze Method Blank and all QC samples and field samples processed with the contaminated blank. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control Sample (LCS)	Accuracy/Bias	One per batch of 20 analytical samples	75-125%	75-125%	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
					preparatory batch for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Sample Duplicate (DUP)	Precision	One per batch of 20 analytical samples	RPD ≤ 20%	RPD ≤ 20%	MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.

DQI = data quality indicator
DUP = sample duplicate
LCS = laboratory control sample
LOQ = limit of quantification
MB = method blank
QC = quality control
RPD = relative percent difference
SOP = standard operating procedure

Matrix	Soil Gas
Analytical Group	Carbon Dioxide
Sampling SOP	VOA-DISGAS ALS Simi Valley
Analytical Method/ SOP Reference	RSK-175

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
Method Blank (MB)	Accuracy/Bias/ Contamination	One per batch of 20 analytical samples	Analyte concentrations <LOQ	Analyte concentrations <LOQ	Correct problem. If required, re-prep and reanalyze Method Blank and all QC samples and field samples processed with the contaminated blank. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.
Laboratory Control Sample (LCS)	Accuracy/Bias	One per batch of 20 analytical samples	59-113%	59-113%	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative.

QC Sample	Data Quality Indicator (DQI)	Frequency/Number	Method/SOP QC Acceptance Limits	Acceptance Criteria/ Measurement Performance Criteria	Corrective Action
Laboratory Control Sample Duplicate (LCSD)	Precision	One per batch of 20 analytical samples	RPD ≤ 12%	RPD ≤ 12%	If RPD indicates obvious analysis difficulties, sample volume available and reanalyze batch. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.
Matrix Spike (MS)	Accuracy/Bias	One per batch of 20 analytical samples	50-150%	50-150%	If RPD indicates obvious extraction/analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.
Matrix Spike Duplicate (MSD)	Precision	One per batch of 20 analytical samples	RPD ≤ 30%	RPD ≤ 30%	If RPD indicates obvious analysis difficulties, sample volume available and reanalyze MS/MSD. Qualify the specific analyte(s) if acceptance criteria are not met and explain in the Case Narrative.

CCV = Continuing Calibration Verification
DQI = data quality indicators
LCS = laboratory control sample
LCSD = laboratory control sample duplicate
MS = matrix spike
MSD = matrix spike duplicate
ND = non detectable
QC = quality control
RPD = relative percent difference
SOP = Standard Operating Procedure
TBD = to be determined
VOA = Volatile Organic Analysis

* MDL verification and studies are performed and updated annually (every December) by the laboratory per 40CFR 136 appendix B. MDLs for VOCs will be updated accordingly.

30 QAPP Worksheet #29: Project Document and Records Table

Sample Collection Documents and Records	On-site Analysis Documents and Records	Off-site Analysis Documents and Records	Data Assessment Documents and Records	Other
Field Notes Digital Photographs Chain-of-Custody Records Field Instrument Records Daily Health and Safety Briefing Sheets Subcontractor Sign-In Sheets	Instrument calibration records	Analytical data deliverables	Data usability review	HASP

HASP = Health and Safety Plan

31 QAPP Worksheet #30: Analytical Services Table

Matrix	Analytical Group	Sample Locations/ID Numbers	Concentration Level	Data Package Turnaround Time	Laboratory/ Organization (Name and Address, Contact Person and Telephone Number)	Backup Laboratory/ Organization (Name and Address, Contact Person and Telephone Number)
Aqueous	VOCs (BTEX), Naphthalene, TPH-DRO Alkalinity, Cations (Total Fe & Mn), Anions (Cl and SO_4), Nitrate and Nitrite, Dissolved Fe and Mn, Sulfide, Ammonia, TKN, Methane, and DOC	See Worksheet #17	TBD	Standard (10 Business Days)	ALS Environmental 10450 Stancliff Road, Suite 210, Houston, TX 77099 R.J. Modashia, rj.modashia@alsglobal.com, 281-530-5656	Not Assigned
Soil Gas	Carbon Dioxide	See Worksheet #17	TBD	Standard (10 Business Days)	ALS Environmental 2655 Park Center Drive Suite A Simi Valley, CA 93065 R.J. Modashia, rj.modashia@alsglobal.com, 281-530-5656	Not Assigned

BTEX = benzene, toluene, ethylbenzene, and xylene
SOP = Standard Operating Procedure
TBD = to be determined
VOC = volatile organic compound

32 QAPP Worksheet #31: Planned Project Assessment Table

Assessment Type	Frequency	Internal or External	Organization Performing Assessment	Person(s) Responsible for Performing Assessment (Title and Organizational Affiliation)	Person(s) Responsible for Responding to Assessment Findings (Title and Organizational Affiliation)	Person(s) Responsible for Identifying and Implementing Corrective Actions (CA) (Title and Organizational Affiliation)	Person(s) Responsible for Monitoring Effectiveness of CA (Title and Organizational Affiliation)
Field Audit	Intermittent	Internal	GeoMonitoring Services	Brad Freeman, FM	Nigel Goulding, TD	Nigel Goulding, TD	Brad Freeman, FM
Safety Audit	Intermittent	Internal	GeoMonitoring Services	Rick Dolan, CSP	Nigel Goulding, TD	Nigel Goulding, TD	Shannon Barr, H&S Manager

CA = Corrective Action
FM = Field Manager
H&S = Health and Safety
PM = Project Manager

33 QAPP Worksheet #32: Assessment Findings and Corrective Action Responses

Assessment Type	Nature of Deficiencies Documentation	Individual(s) Notified of Findings (Name, Title, Organization)	Timeframe of Notification	Nature of Corrective Action Response Documentation	Individual(s) Receiving Corrective Action Response (Name, Title, Org.)	Timeframe for Response
Missing field QC	Notification to Proper Personnel via email	Nigel Goulding, TD (EHS Support), or Brad Freeman PM (GeoMon)	24-72 hours	Notification to Proper Personnel via email	Brad Freeman, FM Nigel Goulding, TD (EHS Support)	48 hours after notification

FM = Field Manager
PM = Project Manager
QC = quality control

34 APP Worksheet #33: QA Management Report Table

Type of Report	Frequency (daily, weekly monthly, quarterly, annually, etc.)	Projected Delivery Date(s)	Person(s) Responsible for Report Preparation (Title and Organizational Affiliation)	Report Recipient(s) (Title and Organizational Affiliation)
Data Validation	As necessary	TBD	Amy Coats, QA Manager, EHS Support	Nigel Goulding, TD (EHS Support) Brad Freeman, PM (Geomon)

PM = Project Manager
QA Manager = Quality Assurance Manager
TBD = to be determined

35 QAPP Worksheet #34: Verification (Step I) Process Table

Verification Input	Description	Internal / External	Responsible for Verification (name, organization)
Audit/assessment reports	A copy of all audit reports will be kept in the project file. If corrective actions are required, those records will also be kept in the project file.	I	
Field notes, logbook, sampling records	Field notes will be reviewed internally and placed in the project file. A copy of the field notes will be appended to the final report.	I	
Sample receipt	For samples shipped via commercial carrier, EHS staff will verify receipt of samples by the laboratory the day following shipment.	I	
Chain of custody records	When chain of custody forms are completed, they will be reviewed internally and verified against the packed sample coolers they represent. Upon sample receipt at the laboratory, chain of custody forms will be reviewed by laboratory staff and compared with cooler contents. Chains of custody will be signed by any party that has custody of the samples, except for commercial carriers.	I, E	
Sample logins	Upon receipt of sample acknowledgement forms, sample login information will be reviewed and verified for completeness in accordance with the chain of custody form, as well as for accuracy.	I	Bonnie Stadelmann or designee, EHS Support
Laboratory data prior to release	Laboratory data will be reviewed for completeness based on the analyses requested on the chains of custody (and analyses requested in any subsequent correspondence) and all laboratory data packages will be verified for technical accuracy by the laboratory performing the work.	E	
Laboratory data completeness and accuracy	Data will be reviewed as outlined in Worksheet #37.	I	Amy Coats or designee, EHS Support or validator at external validation firm.
Data upload verification	Electronic data from the laboratory will be transferred to the database. Ten percent will be checked against the lab report pdf to verify accuracy.	I	EQiUS staff, EHS Support

EDMS = Enterprise Database Management System

36 QAPP Worksheet #35: Validation (Steps IIa and IIb) Process Table

Step IIa / IIb	Validation Input	Description	Responsible for Validation (name, organization)
Step IIa	Sampling procedures	Ensure that appropriate sampling procedures are followed for all analyte group/ matrix combinations, and that any deviations are documented.	
Step IIa	Field documentation	Field logbooks and forms will be reviewed weekly for accuracy and to verify that field measurements met performance criteria, or that any deviations were documented.	
Step IIa	Chain of custody forms	Chain of custody forms will be reviewed each time laboratory sample acknowledgement forms are received. Project information, requested analyses, and number of field QC samples collected will be reviewed to verify that the requirements of this QAPP are met.	Bonnie Stadelmann, EHS Support
Step IIa	Analytical methods	Verify that the required analytical methods were used and any deviations documented.	Laboratory staff, Bonnie Stadelman, EHS Support
Step IIa	Laboratory performance	The laboratory will provide that QC samples met relevant acceptance criteria and that any deviations were documented.	
Step IIa	Laboratory data prior to release	Laboratory data will be reviewed to ensure that the data are accurate and meet the requirements in this QAPP. Before they are released, data will be validated as follows:	
		100 percent of the data comply with the method- and project-specific requirements; any deviations or failure to meet criteria are documented for the project file.	
		100 percent of manual entries are free of transcription errors and manual calculations are accurate; computer calculations are spot-checked to verify program validity; data reported are compliant with method- and project- specific QC requirements; raw data and supporting materials are complete; spectral assignments are confirmed; descriptions of deviations from method or project requirements are documented; significant figures and rounding have been appropriately used; reported values include dilution factors, results are reasonable, and data in the EDD matches that in the hard copy.	
		Data reported comply with method- and project-specific QC requirements; the reported information is complete; the information in the report narrative is complete and accurate; and results are reasonable. Analytical methods are performed in compliance with approved SOPs.	

Step IIa / IIb	Validation Input	Description	Responsible for Validation (name, organization)
	Laboratory data packages	All laboratory data packages will be validated by the laboratory performing the work for technical accuracy before they are submitted.	
Step IIb	Documentation of QAPP QC sample results	Verify that all QAPP-required QC samples were collected and analyzed, or document discrepancies.	Bonnie Stadelmann or member of the project team, EHS Support
Step IIb	Project quantitation limits	Determine whether quantitation limit goals were achieved	Amy Coats or Bonnie Stadelamnn, EHS Support
Step IIb	Data usability reports	Evaluate QC data associated with samples against the project-specific performance criteria specified in this QAPP. Present data review findings in summary reports.	Amy Coats or designee, EHS Support or validator at external validation firm.

EDD = electronic data delivery
QAAP – Quality Assurance Project Plan
QC = Quality Assurance

37 QAPP Worksheet #36: Validation (Steps IIa and IIb) Summary Table

Step IIa / IIb	Matrix	Analytical Group	Concentration Level	Validation Criteria	Data Validator (title and organizational affiliation)
IIa and IIb	Groundwater and Soil Gas	All	All	Provided in worksheet #12: Laboratory statistical limits, method criteria, USEPA Contract Laboratory Program National Functional Guidelines.	Amy Coats, Project Chemist, EHS Support.

VOC = volatile organic compound
USEPA = United State Environmental Protection Agency

38 QAPP Worksheet #37: Usability Assessment

Data Validation and Usability

After completion of the Step IIa tasks in Worksheet #35, the rest of the data review process, upon which the data usability assessment is based, can be performed. The objective of data review is to establish whether reported results are of acceptable quality and to identify any reported results that are invalid. Based on the data review findings, it can be determined whether analytical data is deemed usable.

Data for any potential constituents of concern will be included in this review; data from analyses such as grain size, pH, alkalinity, total suspended solids, etc. will be excluded. A data usability assessment will be performed for all target analyte data associated with the St. Croix Site. Ten percent of data will also undergo tier II validation. Data will be reviewed/ validated using this QAPP, method criteria, and USEPA Contract Laboratory Program National Functional Guidelines.

Usability reviews – for all target analyte data

Usability reviews will be conducted, and data usability summaries prepared for all target analyte data. Reviews will be performed by Amy Coats or designee, EHS Support or by a validator at an external firm. The purpose of this process is to identify and reject any results that are not usable. Those results will be rejected in the database so that only usable data are included in the data pool. Rejected data will not be used. Due to significant QC problems, those results are invalid and provide no information as to whether the analyte is present or not. Analytes with "R" values will not appear on data tables because they cannot be referenced for any reason.

This evaluation includes review of:

- Chain of custody – verify that it is completed and signed, and that custody was maintained.
- Holding time and preservation
- Laboratory method blanks
- Field blanks (including trip, field, and equipment blanks)
- LCS – only significantly low recoveries (less than 10% for organics) will be discussed.
- MS samples - only significantly low recoveries (less than 10% for organics) will be discussed.
- Surrogates - only significantly low recoveries (less than 10%) will be discussed.
- If the laboratory report narrative indicates that significant QC variances were observed for any elements not included in the above list, those variances will be included in the review; they will be investigated, associated discussions will be included in the data review reports, and data will be rejected if appropriate.

No results will be qualified during this process. Results that are deemed not usable will be rejected. All other results will be used as-is.

The reason that only significantly low results for surrogates, LCS, or MS are explored is that only they impact usability. Results that are greater than the upper control limit, as well as results that are less than the lower control limit but greater than 10% or 30% (for organics) do not lead to rejection of data.

Detections in blanks will be listed, but will not be quantitatively compared with associated field sample results. Tier II validation – for 10% of target analyte data

Data validation is a process by which laboratory packages are reviewed. Reported results are evaluated by comparing them with associated QC. Then a determination is made as to whether the laboratory was operating within applicable limits and which (if any) environmental sample results were related to QC results that were outside control limits. Results associated with non-compliant QC may be qualified. Validation reports will include documentation of variances discovered during the course of the data review & consequent qualification of results.

Tier II validation will be conducted and validation reports prepared for ten percent of the target analyte data. Validation will be performed by Amy Coats or designee, EHS Support. The unusable data will be identified during the Tier II validation (for 10%) and the usability review (for the other 90%). This validation process includes evaluation of the following:

- Chain of custody – verify that it is completed and signed, and that custody was maintained.
- Holding time + preservation
- Laboratory method blanks
- LCS/LCSD
- MS/MSD samples
- Surrogates
- Field duplicates
- Lab duplicates
- Laboratory reporting limits meet QAPP specified criteria

If the laboratory report narrative indicates that QC variances were observed for any elements not included in the above list, those variances will be included in the review; they will be investigated, associated discussions will be included in the data review reports, and data will be qualified if appropriate.

The Tier II data validation reports will include discussions of all the above-listed topics. It will also present any qualifiers that are appended to analytical results as a consequence of the validation process. However, these validation qualifiers will not be applied to the data in the database or in the project tables/ reports. Data qualifiers do not necessarily invalidate data. Qualified data can provide useful information. As described above, data that are not considered usable will be rejected; all other data will be considered usable as-is.

The DQIs used to evaluate conformance with the project (DQOs are generally defined in terms of six parameters: accuracy, precision, sensitivity, completeness, representativeness, and comparability. These are defined below.

- *Accuracy*: Accuracy is evaluated by comparison of a measured result to the true value. It can be monitored through initial and continuing calibration of instruments, reference standards, matrix spikes, laboratory control spikes, and surrogates.
- *Precision:* Precision is a measure of the reproducibility of sample results; it is maximized by consistent adherence to sampling and analytical procedures. Precision can be assessed by comparing duplicate matrix spike recoveries, duplicate laboratory control spike recoveries, laboratory replicates, and/or field duplicate sample results.

- *Sensitivity:* Sensitivity refers to the capability of a method and/or instrument to reliably quantitate a given analyte at a given concentration. It is important that this concentration (at which the instrument and/or method is capable of reliable quantitation) not be greater than the applicable standard.
- *Completeness*: Completeness is defined as the percentage of valid data in a data set. Completeness of a data set will be calculated by comparing the number of valid sample results generated to the total number of results generated. The measurement performance criteria limit specified in this QAPP is 90%.
- *Representativeness:* Representativeness is the degree to which data accurately represent site conditions. It is dependent on variability in sampling and analysis, as well as in the environmental media at the site. This QAPP presents the rationale for sample locations and quantities and includes field sampling and laboratory analytical methods. Adherence to the sampling plan and to specified field and laboratory analytical methods is intended to provide representative data. This parameter cannot be directly evaluated during data validation.
- *Comparability:* Comparability is the degree of confidence with which one data set can be compared to another. Comparability will be maintained by consistently using of the same sampling methods, analytical methods, and QA/QC procedures as well as by using appropriately trained personnel. This parameter cannot be directly evaluated during data validation.

The laboratory must be able to demonstrate proficiency/capability in performing the method and LCS recoveries with few exceptions should fall within specified QC criteria. If LCS recoveries are not within criteria ALS will follow corrective action steps (e.g., reanalysis) as identified in the SOP. LCS recoveries will be monitored for repeated failure as this will indicate the need for further evaluation by the laboratory.

Database

After validation, the database will be updated so that it will include only usable data.

Field Data

Field data (generated from measurements made in the field) is not reviewed by the data validator; it is reviewed by a member of the project team. This data may include GPS locations, survey information, and/or sampling records.

Data Usability

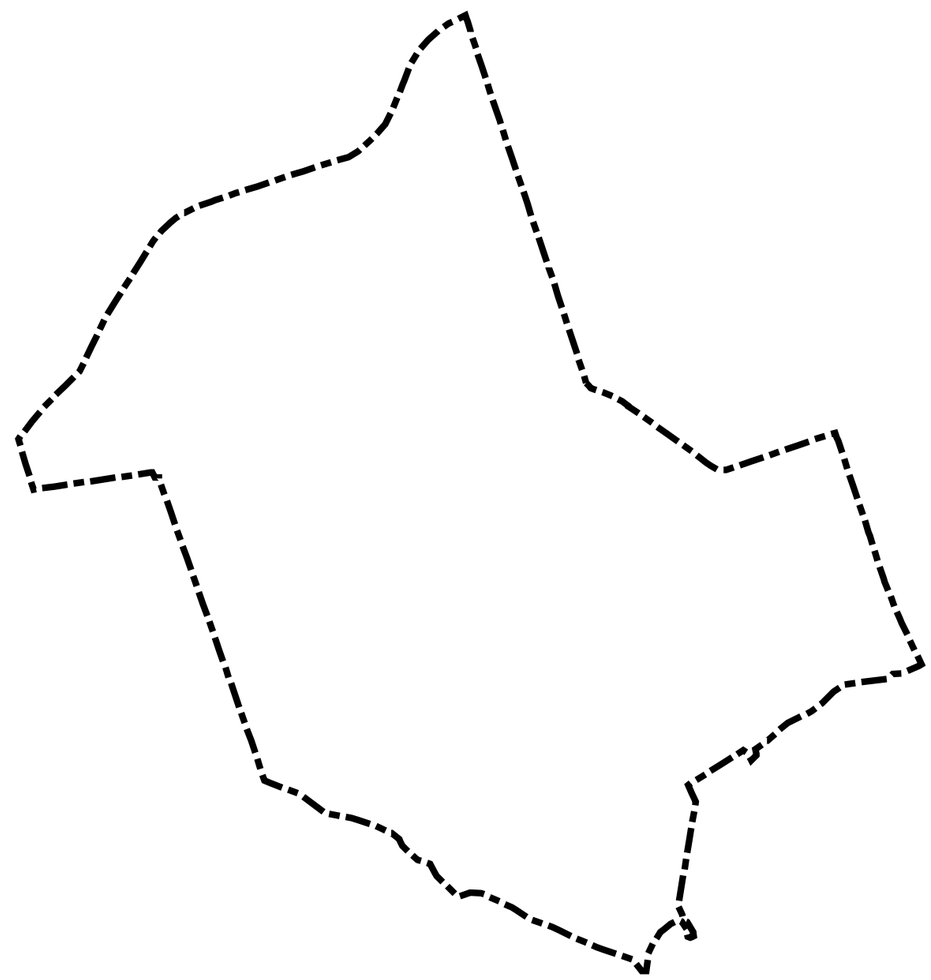
Data that has been rejected will not be used. All other data will be considered useable. This is sufficient performance criteria for the current scope of work for this project. If a future scope of work for this project requires, validated data demonstrating that analyte concentrations are equal to- or less than-applicable criteria, a different validation plan will be set forth at that time.

If observed performance does not meet performance objectives for critical data, any or all of the following steps may be taken as corrective actions: request additional information, request re-extraction and/or re-analysis of sample (when appropriate), recalculate or reinterpret laboratory results. These actions often resolve identified issues or gaps. The data validator will communicate with laboratory personnel as needed in order to resolve issues regarding laboratory performance or deliverables.

If these actions do not improve the data quality to an acceptable level, one or more of the following additional actions may be taken: extrapolation of missing data from existing data points, use of historical data, and/or evaluation of the critical/noncritical nature of the sample.

If the data gap cannot be resolved by the above-listed actions, the data bias and potential for false negatives and positives will be evaluated. If the resultant uncertainty level is unacceptable, additional sample collection and analysis will be conducted.

Figures



Legend

Site Boundary

1,600 800 0 1,600

Feet

Service Layer Credits: Copyright:© 2013 National Geographic Society, i-cubed

Site Location

ST. CROIX ALUMINA SITE
ST. CROIX, US VIRGIN ISLANDS

[redacted]

FIGURE 1

Reviewed By:

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Legend

- Existing Monitoring Well - To be Sampled
- Existing Monitoring Well - No Sampling
- Former Monitoring Well
- Well Fields
- Site Boundary
- Shipping Canal

1,000 500 0 1,000

Feet

Monitoring Well Sampling Location

ST. CROIX ALUMINA SITE
ST. CROIX, US VIRGIN ISLANDS

[redacted]

FIGURE 2

Reviewed By:

Service Layer Credits: Esri, HERE, Garmin, (c) OpenStreetMap contributors
Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community

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Appendix A Example COC

Chain of Custody Form

Page _____ of _____

COC ID: 123456

☐ Cincinnati, OH +1 513 733 5336
☐ Holland, MI +1 616 399 6070
☐ Salt Lake City, UT +1 801 266 7700
☐ Everett, WA +1 425 356 2600
☐ Houston, TX +1 281 530 5656
☐ Spring City, PA +1 610 948 4903
☐ Fort Collins, CO +1 970 490 1511
☐ Middletown, PA +1 717 944 5541
☐ York, PA +1 717 505 5280

ALS Project Manager:		Work Order #:	

Customer Information		Project Information		Parameter/Method Request for Analysis	
Purchase Order		Project Name		A	
Work Order		Project Number		B	
Company Name		Bill To Company		C	
Send Report To		Invoice Attn.		D	
Address		Address		E	
				F	
City/State/Zip		City/State/Zip		G	
Phone		Phone		H	
Fax		Fax		I	
e-Mail Address		e-Mail Address		J	

No.	Sample Description	Date	Time	Matrix	Pres.	# Bottles	A	B	C	D	E	F	G	H	I	J	Hold
1																	
2																	
3																	
4																	
5																	
6																	
7																	
8																	
9																	
10																	

Sampler(s): Please Print & Sign	Shipment Method:	Required Turnaround Time: ☐ STD 10 Wk Days ☐ 5 Wk Days ☐ 2 Wk Days ☐ 24 Hour ☐ Other _____	Results Due Date:

Relinquished by:	Date:	Time:	Received by:	Notes:
Relinquished by:	Date:	Time:	Received by (Laboratory):	Cooler Temp.
Logged by (Laboratory):	Date:	Time:	Checked by (Laboratory):	

QC Package: (Check Box Below)

- ☐ Level II: Standard QC
- ☐ Level III: Std QC + Raw Data
- ☐ Level IV: SW846 CLP-Like
- ☐ Other: _____

Preservative Key: 1-HCL 2-HNO3 3-H2SO4 4-NaOH 5-Na2S2O3 6-NaHSO4 7-Other 8-4 degrees C 9-5035

Note: Any changes must be made in writing once samples and COC Form have been submitted to ALS Environmental.

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Appendix B Laboratory SOPs

DATA REVIEW AND REPORTING

DOCUMENT I.D. ADM-DATA_REV

Approved By: Kate Kaneko Date: 5/23/18
Interim Laboratory Director – Kate Kaneko

Approved By: Chaney Humphrey Date: 5/23/18
Quality Assurance Manager – Chaney Humphrey

Approved By: Robin Gill Date: 5/23/18
Reporting Department Team Leader – Robin Gill

Doc Control ID:	Uncontrolled	Archived Date:	

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1) Scope and Applicability

1.1 The results of each test shall be reported clearly, legibly, unambiguously and objectively, and shall include all the information necessary for the interpretation of the test results. Specific instructions in the referenced method(s), laboratory's standard operating procedures, and Quality Assurance Manual shall be followed.

1.2 This document is intended to describe the requirements and guidelines by which raw data and final reports produced by the laboratory undergo review and reporting. The procedures described herein attempt to establish a uniform method for checking calculations and data transfers (to ensure that data is free of transcription and calculation errors), compliance with QC parameters, and to determine that reports are both complete and correct before they are sent to the client.

1.3 The data review process provides information on analytical limitations of reported data based on specific quality control (QC) criteria. Data review is a critical process in reporting the data. It should not only be correct and accurate, but the results should make sense and comply with both laboratory and any applicable client specified and agency requirements.

1.4 This document applies to raw data, reports, and associated documentation generated and reported by the laboratory. High quality assurance standards ensure that all data produced and reported by the laboratory is reviewed and is properly documented. All personnel who review data and/or reports must do so in accordance with this document, the *SOP for Laboratory Ethics and Data Integrity*, and applicable method SOPs.

2) Summary of Procedure

2.1 It is unrealistic to provide the exact processes the analyst and secondary reviewer use to review raw data because of the diversity of the analytical methods; therefore only general processes are described. Specific requirements are found in method standard procedures and are listed on data review checklists.

2.2 The goal of the laboratory is to produce reliable and defensible data and supporting documentation that is both accurate and consistent and one of the prerequisites for achieving this is proper data review. Our ability to produce such data and documents is critical to our on-going success as a laboratory.

2.3 Specific data review and validation processes or logistics may vary for data generated using different methodologies; however, the procedure described herein and in the method specific SOP shall be followed (including the method specific data review checklists). In general, the data review and validation practices will meet the requirements of the TNI Standards, ISO/IEC 17025:2005, and the DoD Quality Systems Manual.

3) Definitions

3.1 Raw Data This data is sample data that has been acquired or documented at the analytical bench level.

3.2 Report A laboratory report is a document that has completed full editorial and technical review and may be submitted to the client. It includes the project manager's signature along with all technical information necessary for data interpretation. The report describes the process employed, the resultant findings and any conditions or occurrences that may affect data quality.

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3.3 Primary Review A mandatory review, performed by the analyst who performed the analysis, consists of ensuring the correctness of the raw data and that the quality control criteria have been met. This review follows each analysis data review checklist as specified by the applicable method and/or project specified requirements.

3.4 Secondary or Peer Review A mandatory review performed by a trained and approved secondary analyst, to determine the correctness of the reported data as determined from the raw data. This review secondarily checks the data against the data review checklist as specified in the applicable method standard operating procedure and/or client and project specified requirements.

3.5 Tertiary Review A mandatory review, performed by a data validation coordinator, to ensure the report is on the correct forms, typing or transcription errors have not occurred and client or project specific requirements have been met (i.e. special report formats, additional analytes, special QC limits have been met). Review that reporting requirements such as the appropriate footnotes and flags are indicated is also performed. In addition, the tertiary review may incorporate an electronic data deliverable (EDD) review if this is supplied to the client. Either a data validation coordinator or a person trained in generating this deliverable may perform this review.

3.6 Abbreviations

3.6.1 COC - chain of custody
3.6.2 ICAL - initial calibration
3.6.3 LCS/LCSD - laboratory control sample / laboratory control sample duplicate; may also be denoted as DLCS
3.6.4 MB - method blank
3.6.5 MS/MSD - matrix spike / matrix spike duplicate; may also be denoted as DMS
3.6.6 QC - quality control
3.6.7 DoD – Department of Defense

3.7 Quality Assurance Project Plan (QAPP) A document describing in comprehensive detail the necessary quality assurance, quality control, and other technical activities that must be implemented to ensure that the results of the work performed will satisfy the stated performance criteria.

3.8 Data Validation Data validation is used to determine if the available project data satisfy the project's data quality objectives. It is the process of comparing the data against criteria established for the data, and is performed after the primary and secondary reviews. Validation determines if the data are acceptable by an evaluation that includes but is not limited to error checks, completeness, and performance.

3.9 Data Package (Report) Completeness This review confirms that the laboratory has provided the deliverables required by the contract, method, and/or project plan. During data validation, receipt and completeness of deliverables is checked and documented against the project requirements.

3.10 Performance Laboratory performance can be evaluated from the following elements, which are common to most methods.

- Holding times (did the laboratory analyze the samples within the required time frame?)
- Calibration (were instruments calibrated at the correct levels and frequencies?)
- Blanks (did the blanks contain target analyses that indicate samples may be contaminated from laboratory procedures?)

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- Bias (do laboratory spiking tests show high or low recoveries that may bias associated sample results?)
- Precision (are results reproducible when duplicated?)
- Other quality control (QC) results (did method-specific items meet the QC goals?)

3.11 Error Checks Checking for quantitative and qualitative error is performed using supporting instrument and source data (raw data). Data transcriptions of both sample and QC data are reviewed; analyte identifications are evaluated; and quantitation of analyte concentrations are evaluated against method reporting and detection limits.

3.12 Data Qualification and Qualifiers (Flags) A qualifier is a character or string of characters that is included in the data field and defines the data. These data qualifier flags provide data users with information about the quality of the data. Results are either acceptable or reported with data qualifiers or flags. Refer to the Quality Assurance Manual for a list of possible qualifiers. However, specific client requirements may supersede these qualifiers; refer to the project requirements, if available. DoD Requirement: In the absence of project-specific requirements, the minimum standard data qualifiers to be used by laboratories can be found in Section 5.10.3.1.1 of the DoD QSM.

3.13 Limit of Detection (LOD) Limit of Detection is an estimated value reflecting the minimum amount of a substance that an analytical process can reliably detect. An LOD is analyte- and matrix-specific and may be laboratory-dependent. DoD Clarification: The smallest amount or concentration of a substance that must be present in a sample in order to be detected at a high level of confidence (99%). At the LOD, the false negative rate (Type II error) is 1%.

For non-DoD applications LOD = MDL. For DoD applications, the LOD is the detection limit verification spike concentration and is at or above the method detection limit (MDL) and is less than or equal to the LOQ/MRL. The LOD is approximately 2-4 times the MDL. Refer to specific method SOPs for verification requirements and other essential information.

3.14 Limits of Quantitation (LOQ) The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence. DoD Clarification: The lowest concentration that produces a quantitative result within specified limits of precision and bias. For DoD projects, the LOQ shall be set at or above the concentration of the lowest initial calibration standard. For our purposes (laboratory) the LOQ is at or above the low standard of the initial calibration, is verified, and is the same as the method reporting limit (MRL) as it has the same requirements.

4) Responsibilities

4.1 The multi-tiered internal data review process shall include all aspects of data generation, data reduction, QC assessment, and final report production. Each employee performing data review and reporting or supporting documentation review is responsible for the specific items and guidelines listed in this document. However, this SOP is primarily directed to the tertiary review process, but because data review occurs on many levels during the analytical process all have been mentioned. Due to the diversity of the analytical processes in which data review is performed, it is impractical to describe the review criteria for the primary and secondary reviews pertaining to the individual tests. Please see appropriate method SOPs for specific analytical data review information. Specific responsibilities are defined in the procedure section of this document.

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4.2 Project Manager (PM)

The Project Manager is responsible for generating and setting up the project (as an SDG in LIMS) and providing complete and accurate instructions regarding any special requirements or analytical protocol based on client specified requests. In addition, the PM must also provide a review and approval of the final report ensuring that the data is complete and the cover letter and case narrative includes all of the appropriate information. This review is documented by the signature approval of the final report as well as the approval of the folder in LIMS. Additional information regarding the responsibilities of the PM may be found in the *SOP for Project Management*.

The Project Manager will review all complete reports prior to signing the report and submitting to the client. The review of the reported data will focus on the following items.

a. Consistency with client, contract, and/or project specifications.
b. Acceptability of any data qualifier or footnotes.
c. Accuracy and completeness of explanations or discussion in the report case narrative.
d. As needed depending on the scope of testing, an additional level of technical review of all data generated.
e. A general overview of the completed service request file with respect to overall reasonableness, and if available, with historical project information.

4.3 Primary Review

The analyst is responsible for performing and documenting the first review, which shall be performed on 100 percent of the data after it has been acquired, documented and reduced at the analytical bench level. All reviews begin with the initiation of a data review or ICAL review checklist included in each method SOP.

4.4 Secondary or Peer Review

A secondary reviewer shall be a different analyst that has approved documented training to review or perform the analytical method in question. The analyst must be provided with all of the necessary information to perform the review. If an error is detected, the primary analyst shall be notified and the error corrected and approved by both analysts. The secondary or peer review is documented by utilizing the data review or ICAL review checklist initiated by the primary reviewer. The secondary or peer reviewer must in some cases, depending on the method, review the report as generated by the analyst.

4.5 Tertiary Review

The Data Validation Coordinator (DVC) conducts this review according to this SOP and any special client requirements. Responsibilities of the DVC include verifying client analyses, and sample information, along with correct reporting format (units, reporting limits, canister pressures, footnotes, quality control forms). In addition, the DVC verifies reporting limits and unit conversions and checks for transcription errors entered into computer forms (i.e., Excel spreadsheets and report forms).

4.6 Quality Assurance Manager

The Quality Assurance Manager will perform random quarterly audits of reviewed data and data packages. All types of laboratory analyses will be examined through these reviews and the findings along with any corrective actions shall be retained on file.

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5) Procedure

5.1 The reviewers must identify biases inherent in the data in question, including assessment of laboratory performance, overall precision and accuracy, representativeness, and completeness, which can be performed using the principles and requirements found in this document. Using these, the data reviewer can be focused to meet the needs and requirements of the laboratory and data user. All reviews must be documented according to this document as well as the method specific SOPs. It is important to relate that each project may have unique quality assurance/quality control (QA/QC) requirements; therefore, all supporting documentation must be available for review/comparison.

Note: The specific documentation for reviews is specified in method SOPs.

5.2 Review Requirements

The following are general requirements for the review of laboratory data and must be adhered to.

- All reviews and/or changes must be documented, signed or initialed, and dated.
- Manual integrations must follow the documentation guidelines as stated in the SOP titled *Manual Integration Policy*. Refer to Table 1 for abbreviations that may be used to document manual integrations and rational for not reporting a "hit" or compound result.
- Regardless of the stated concentration (<MRL or <MDL) on the quantitation report, all target analytes must be reviewed and the concentrations and integrations verified. Therefore, all integrations and peak selections must be reviewed for correctness, regardless of analyte concentration and software reliability with regards to a particular analyte (i.e., non-detects must also be reviewed as the instrument software may have chosen the wrong peak or integrated incorrectly).
- All QC (contamination, precision, accuracy and bias) including batch QC must be reviewed and out of control issues including batch QC noted on the Data Review Checklist, Analysis Summary form or as specified in the *SOP for Laboratory Storage, Analysis, and Tracking.* This requirement is independent of the tier level requested.
- Determination of whether the results meet the laboratory-specific quality control criteria.
- Checks to ensure that all calibration and quality control requirements were met.
- Review compounds which may interfere with the results for target analytes and make the appropriate notations and qualifiers.
- All data must be processed and reviewed in accordance with the *SOP for Laboratory Ethics and Data Integrity.*
- Review field duplicates, trip blanks, inlets and outlets and make appropriate notations on the Analysis Summary form as stated in the *SOP for Laboratory Storage, Analysis, and Tracking*.
- Additional guidelines include the following.

  Verify Reported Results against Method and/or Project Requirements
  - Method/analyte list
  - Reporting and detection limits/units
  - QC data provided and linked to samples
  - Correct surrogate and spike analytes added
  - Calibration data for all analytes provided and linked to samples

  Evaluate Reported Results against Method and/or Project Requirements
  - Identify QC outliers (holding times, precision, accuracy)

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  - Identify calibration outliers
  - Identify field and laboratory contamination
  - Identify results below the reporting or detection limit
  - Assign data review qualifiers
- Checks to determine consistency with project-specific measurement quality objectives (MQOs).
- Checks to ensure that the appropriate sample preparatory and analytical SOPs and methods were followed, and that chain-of-custody and holding time requirements were met.
- Checks for complete and accurate explanations of anomalous results, corrective action, and the use of data qualifiers in the case narrative.
- The final administrative review shall verify that previous reviews were documented properly and that the data package is complete.

DoD Requirement: Data review must consist of a 100% review by the analyst, 100% secondary review, and a final administrative review.

5.3 Data Qualification Guidelines

Data qualification is an integral component of data review and validation and is a necessary tool to alert end users to quality problems or issues that may impact the usability of the data (e.g., QC acceptance limits that were not met). All data qualifiers or flags must be clearly defined. Project-specific requirements may determine the types of qualifiers that are required. However, in the absence of more appropriate conventions for data qualification, the flags defined in the QA Manual should be utilized.

Qualifiers are to be used to designate an issue with the *reported* data and not as an indication of method and/or laboratory limitations; therefore, repetitive (systematic) out of control situations must be identified and corrected. Out of control situations can either be random or systematic errors. Systematic errors are biases in measurements which lead to measured values being consistently too high or too low.

The end user ultimately determines the acceptability of the data and is based on a number of factors including the data quality objectives of the project. It is important to understand that the application of data qualifiers does not ensure that the data will be acceptable to the end user.

5.4 Primary Review

This review must focus on the validity of the analysis and raw data generated, the technical accuracy and correctness of the analysis (the analytical procedure is in control), use of valid and approved procedures and methods, and interpretation of sample results. This review is to ensure the correctness of the raw data, the completeness of the quality control measures and that all criteria including special client requirements have been met.

The analyst is responsible for processing all data according to the analytical method and corresponding method SOP. Additionally, due to the nature of Enviroquant software, processing data through screen dumping is not permitted. Once the analyst has processed the data and generated the quantitation report and any other necessary documentation a checklist for that method is completed and submitted for secondary review. The analyst must follow Sections 5.2 and 5.3 above when reducing and reviewing data. Refer to Section 5.7.4 for information on the addition of information to the case narrative.

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5.5 Secondary Review

The secondary review will be performed by someone other than the technical primary reviewer. The secondary review will make the same assessments as the primary reviewer, and check the interpretations, data manipulations, and decisions made by the primary reviewer. Additionally, the secondary reviewer will review the outputs from the initial review to the raw data. This includes such things as data processing results/outputs, calculations, runlogs, benchsheets, QC analyses, etc. The secondary review certifies the completeness and validity of the data to be reported.

The peer reviewer must use the appropriate method data review checklist and all associated documentation including client specific requirements to ensure compliance. In addition, they must determine that any manual calculations and integrations are documented and correct. A secondary review shall also check that generated data is correct and accurately reflects the analysis. It must consist of reviewing proper frequency of quality control samples as specified in the method specific SOP checklist as well as acceptance criteria. In addition to Section 4.2 and 4.3, the following must be reviewed.

- The reviewer will ensure that the primary analyst is processing data using appropriate techniques, methodologies and SOPs.
- In addition, make sure all samples were analyzed under the current calibration curve and correct data processing method.
- All manual calculations, transcriptions, and computer-generated transcriptions must be checked to 100 percent, where necessary. If a spreadsheet is properly validated and includes a version number and/or validation date then the computer-generated numbers do not require checking.
- Also, the secondary reviewer is responsible for ensuring that none of the data has been produced through screen dumping.
- If errors are found then the primary analyst should be notified, or at a minimum another qualified analyst should be consulted; two reviews must be conducted for the approval of any change to a primary analyst's data.
- Review all qualifiers including interference flags to determine acceptability.

5.6 Tertiary Review

All client-ready final reports will undergo review in this format, and is presented to the client; either by analysis fraction or in its entirety. This review will include verification of the accurate and correct reporting of sample and QC results; including accurate translation of results from data to report forms, report format, use of qualifiers and flags, and method citations. This review will also include verification of the correct project information, such as client name, project name, sample IDs, etc. The report review should ensure that the report is error-free and contains no inconsistencies. Refer to the Quality Assurance Manual – Table 21-1 for a list of standard data deliverables associated with each tier level.

The reviewer must use the Data Validation Review Checklist (Attachment 1) to ensure method compliance. They must ensure all documentation arriving with the sample is accurate compared with the client submitted chain of custody as well as all laboratory generated and client supplied documentation. This review is documented by the completed checklist.

Data shall be reviewed and verified based on the following, where applicable: Chain of Custody, SR Form, Client supplied documentation, raw laboratory data, and laboratory spreadsheets. The information detailed in the checklist in Attachment 1 shall be the minimum that must be reviewed and validated, where applicable.

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The reviewer performs calculations to ensure transcription errors did not occur during final report production. These are some of the frequently used calculations, for additional equations please reference the appropriate method SOP.

- Calculate the method reporting limits.

  Calculation: $\frac{\text{method reporting limit x total dilution}}{\text{volume analyzed}}$

- Calculate $\mu g/m^3$ or mg/m^3 from concentration units in raw data.

  Calculation: $\frac{\text{concentration units x total dilution}}{\text{volume analyzed}}$

5.7 Data Submission

A complete report including case narrative, project manager's signature, along with the data report pages are submitted to the client in accordance with requested report tier level or client specified report requirements.

The date of analysis and time of analysis is to be reported if the holding time is 72 hours or less or when time critical steps are included in the analysis (e.g., extractions and incubations). DoD Requirement: Both date and time of preparation and analysis are considered essential information, regardless of the length of the holding time, and shall be included as part of the laboratory report. If the time of the sample collection is not provided, the laboratory must assume the most conservative time of day (i.e., earliest).

The client is contacted in writing (email is sufficient) or by phone (with applicable notes added to the job file) regarding any event that casts doubt on the validity or completeness of results. All information of this type is included in the final report and the following describes each section of the final report and the information that should be consistently provided to the client for proper interpretation of the results.

5.7.1 Laboratory Report Format and Contents The information included in the report issued is listed below, which complies with all applicable accrediting body requirements. The laboratory certifies that the test results meet the requirements of the appropriate accrediting body or accrediting body standard or will provide reasons and/or justification if they do not.

1) A title, (i.e., "Test Report" or "Laboratory Report")
2) Name and address of laboratory, and location where the test was carried out if different from the address of the laboratory and phone number with name of contact person for questions
3) Certification identification
4) Unique identification of the report (such as serial number), and on each page an identification in order to ensure that the page is recognized as part of the test report and a clear identification of the end of the report. This requirement may be presented in several ways:
   - The total number of pages may be listed on the first page of the report as long as the subsequent pages are identified by the unique report identification and consecutive numbers, or
   - Each page is identified with the unique report identification, the pages are identified as a number of the total report pages (example: 3 of 10, or 1 of 20). Other methods of identifying the pages in the report may be acceptable as long as it is clear to the reader that discrete pages are

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associated with a specific report, and that the report contains a specified number of pages.

5) Name and address of client and project name if applicable
6) Description and unambiguous identification of the tested sample including the client identification code.
7) Identification of test results derived from any sample that did not meet sample acceptance requirements such as improper container, holding time, or temperature.
8) Date of receipt of sample, date and time of sample collection, and time of sample preparation and/or analysis if the required holding time for either activity is less than or equal to 72 hours (unless a DoD project, where the date and time are required, regardless of the holding time requirement).
9) The following are the laboratory criteria for evaluating compliance with required hold times.
   - If no sampling time is provided, hold times are considered valid until the end of the day. However, for projects that require compliance with the DOD Quality Systems Manual, the most conservative time (earliest) will be utilized.
   - Time zones are not taken into consideration unless requested by the client.
   - Dates and times of collection must be taken into account when provided. If not provided, a notation will be made on the Sample Acceptance Check Form.
   - The start of sample preparation (e.g., addition of solvent), where applicable, is considered the end of the hold time.
10) Identification of the test method used, or unambiguous description of any nonstandard method used.
11) If the laboratory collected the sample, reference to sampling procedure.
12) Any deviations from (such as failed quality control), additions to or exclusions from the test method (such as environmental conditions), and any non-standard conditions that may have affected the quality of results, and including the use and definitions of data qualifiers.
13) Test results that do not meet the requirement, or for which the laboratory is not certified, must be documented with the reason why the result does not meet the requirements and justification as to why the result was reported.
14) For reports for samples obtained within the State of Minnesota (for EPA TO-15) when the laboratory analyses samples by a procedure other than as written (EPA TO-15 Modified), the laboratory record must include: (1) the sample identification traceable to client; (2) the modification to the procedure; (3) the reason for the modification; and (4) the client's authorization or acknowledgement of the modification.
15) The measurements, examinations, any failures identified and derived test results with, when appropriate, the units of measurements; whether data are calculated on a dry weight or an "as received" basis; the reporting or detection limit for each sample with appropriate units of measurement.
16) When required, a statement of the estimated uncertainty of the test result.
17) A signature and title, or an equivalent electronic identification of the person(s) accepting responsibility for the content of the certificate or report (however produced), and date of issue.
18) Statements to the effect that the results relate only to the items tested or to the sample as received by the laboratory and the report shall not be reproduced except in full, without the written approval of the laboratory.

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a. The results included in this report relate only to the sample(s) submitted and identified herein, and in the documented condition received by the laboratory.
b. All results are intended to be considered in their entirety, and the laboratory is not responsible for utilization of less than the complete report.

19) Subcontracted results - clear identification, name and address and certification number of all test data provided by outside sources, such as subcontracted laboratories, clients, etc.
    a. For reports for samples obtained within the State of Minnesota (for EPA TO-15), the phrase "This report contains data that were produced by a subcontracted laboratory certified for the fields of testing performed".
20) Clear identification of numerical results with values outside of quantitation levels.

5.7.2 Initial Results Submission To meet client needs, a report may be transmitted to the client via email (PDF or only excel worksheets), electronic data deliverable (EDD), and/or ALS Limited Secure File Sharing system (Accellion) pursuant the client's instructions. The case narrative and supporting documentation will not be included if the client requests an email of the excel worksheets; however, as with all client submissions the data must have been through all reviews (in accordance with this document). A disclaimer is sent with each transmission and is dependent on the completeness of the results/report being supplied.

5.7.3 Electronic Data Deliverable (EDD) is created by a trained individual and then checked. This review should include, at a minimum, a 10% review of the data and is to be noted in the space provided on the Data Validation Checklist. This checklist indicates the file pathway for the document, the creator and reviewer's initials (if different from the creator) and the sample(s) and QC reviewed for correctness. The reviewer may be the creator as long as training has been completed.

5.7.4 Case Narrative and Cover Letter Preparation and Approval

The report shall include a statement to the effect that the results relate only to the samples. In addition, at the laboratory's discretion, a statement included that the report shall not be reproduced except in full, without the written approval of the laboratory.

Once the log-in folder has been approved in LIMS by the Project Manager, the cover letter and case narrative are to be initiated and saved in G:\STARLIMS\Coverletter. The person generating the framework (method autotext included) of these documents should initiate the Case Narrative Checklist (Attachment 2) and must verify the sample data based on the following documentation, when available – Chain of Custody, Media Request/Sample Supplies Summary, Service Request, Sample Acceptance Check Form and any additional paperwork sent with the samples. Each method autotext is to be added with the initial setup of these documents.

Analysts are to add any necessary text to the case narrative based on any anomalies observed with the samples and/or analyses as described in the *SOP for Laboratory Storage, Analysis, and Tracking*. Alternatively, someone other than the analyst (such as the Project Manager) may add the necessary text, as long as the final case narrative and cover letter conform to the requirements of

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this document and Quality Assurance Manual. The Project Manager is responsible for the final review of the cover letter and case narrative and ensuring that all of the necessary information regarding the samples and analyses is included.

The cover letter, case narrative and final report pages are given to the Project Manager for final approval and signature. The Project Manager assumes responsibility for the laboratory by signing the final report. The final signed report is paginated and submitted to the client via United States Postal Service, commercial delivery service (FedEx, UPS, etc.), PDF email to the client, and/or ALS Limited Secure File Sharing system (Accellion) submission.

5.7.5 Data Packages

Data packages will be assembled according to a standard format unless a client specified criteria has been requested and agreed upon by the client and the Project Manager. For upper tier deliverables where the client has requested a hardcopy report, a Data Validation Coordinator or other trained employee will verify that all deliverables are included in the report package. If the report is submitted electronically the verification of deliverables may be performed by the PM or other qualified employee.

Standard format includes but is not limited to final report of analyses, raw data, QC forms, initial calibrations, continuing calibrations, tunes (GC/MS only) and run logs. (Note: Standard format will vary based on type of GC or GC/MS analyses performed; i.e., not all GC analyses have QC forms.) If available, previous data packages for those projects are referenced to ensure the correct client specified format when compiling the data package. Specific QC levels must follow the current levels detailed in the most recent Quality Assurance Manual.

5.8 Reporting Uncertainty

The laboratory is only responsible for estimating the portion of measurement uncertainty that is under its control. Test reports shall include a statement of the estimated uncertainty of measurement only when requested by client instruction.

DoD Project: If a DoD project requires measurement uncertainty to be reported, the laboratory shall report the estimated uncertainty based on project-specific procedures or, if not available, any other scientifically valid and documented procedures. The estimated measurement uncertainty can be expressed as a range (±) around the reported analytical results at a specified confidence level. A laboratory may report the in-house, statistically-derived LCS control limits based on historical LCS recovery data as an estimate of the minimum laboratory contribution to measurement uncertainty at a 99% confidence level.

5.9 Report Revision

After issuance of a formal report to the client, the original laboratory report shall remain unchanged. However, a revised report may be issued and regardless of the circumstances of the revision, the procedures described below shall be consistently followed.

5.9.1 Electronic Submittals: The revised report pages shall be indicated by “Revised Page” located at the bottom of the page.

5.9.2 A revision letter (approved and signed by the Project Manager) shall accompany the revised report and shall include:

- Date of revision

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- Report file number being revised
- Identification of revision including all affected samples
- Statement detailing that the enclosed is a revised report as indicated by the "Revised Page" footer
- Project Manager contact and phone number

5.10 Report Addendum

An addendum may be issued if there is an omission of data information from the original report such as quality control data or analytical results.

5.10.1 Electronic Submittals: The report in its entirety shall be resubmitted to the client and the added report pages shall be indicated by "Added Page" located at the bottom of the page. The report will be repaginated following the addition of the added pages.

5.10.2 An addendum letter (approved and signed by the Project Manager) shall accompany the addendum report or pages and include:

- Report file number
- Identification of addendum including all affected samples
- Statement detailing that the enclosed is an addendum report and how added pages are identified
- Project Manager contact and phone number

5.11 Data Transference

The transfer of data from one place to another or from one medium to another is a potential source of error. Reducing data transfers to a minimum is strongly recommended. However, when transfers are inevitable, proper guidance must be given on the techniques and reviews necessary in order to minimize error. Computer programs or templates that calculate results can be used as long as they are validated and properly protected to prevent alterations to the program or template.

5.12 Spreadsheet Requirements and Validation

All templates in use must be validated to ensure they provide data that is both complete and accurate. These templates include but are not limited to the following:

- Method spreadsheets for calculating results
- Spreadsheets that calculate recoveries, percent differences and relative percent difference for batch QC and QC
- Reporting templates used to perform calculations and/or rounding

Validations shall be documented, reviewed and approved by the appropriate employees and QA Manager. The following documentation guidelines are the minimum requirements when providing a validation for approval and subsequent use.

Spreadsheet Requirements

- Each spreadsheet must include a unique file name, version or the date of generation or revision.
- Each subsequent revision of a spreadsheet must be given a new version number and/or date.
- Date of analysis or date work is performed
- Job number
- Method (or other task performed)

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- Analyst(s)
- Sample identifications
- QC which may include all continuing calibration verification standards within the sequence necessary to show that each sample and batch QC sample result is acceptable.
- Batch QC including method blank, laboratory control sample, laboratory control sample duplicate (if applicable), and laboratory duplicate (for batch precision evaluation).

Validation Documentation Requirements

- Identification of method or task
- Date of validation
- Version or Revision of spreadsheet
- Initial employee performing validation
- Pathway on the network (including unique filename), where it is saved
- All formulas and/or any macros must be printed
- Example manual calculations for each formula used in the spreadsheet (used to compare with the spreadsheet results)
- Example spreadsheet calculations for each formula used in the spreadsheet (used to compare with the manual results)
- The template shall not be used until the approval process is complete

Additions or changes to any spreadsheet formulas made after validation must be re-validated and the spreadsheet template properly secured before implementation.

Lock-Out and/or Access Control

Once a template has been approved and prior to use, it shall be appropriately protected to prevent any unauthorized editing of formulas.

5.13 Review of Training Records

The record keeping system must allow historical reconstruction of all laboratory activities that produce analytical data. As applicable, demonstration of capability naming conventions must be consistent between chain-of-custody records, extraction or desorption records, laboratory benchsheets, and quantitation reports. Traceability must be maintained.

Training records must be performed in the same manner as routine sample analyses. For example, if routine sample analysis requires a front and back section of a tube to be analyzed, training records must also include front and back sections. Laboratory records must include this documentation on desorption records and benchsheets. For example the following naming convention could be used: IDC-1 (Back), IDC-2 (Back), IDC-3 (Back), IDC-4 (Back), IDC-1 (Front), IDC-2 (Front), IDC-3 (Front), and IDC-4 (Front).

Training records will be reviewed using the checklist in Attachment 3. This review may be performed by the Data Validation Department or QA Manager. If completed by the Data Validation Department the training record along with the completed checklist will be turned into the QA office. The QA Manager may also perform this review prior to approving and documenting the training record as complete.

6) Quality Assurance

6.1 Primary and secondary data reviews will be performed by qualified personnel who have documented training on either the analysis itself or training specific to the data review

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and method SOPs. Personnel preparing reports (data validation coordinators) who may do some level of clerical review or proofreading do not need technical knowledge of the test, but must be knowledgeable of reporting systems and requirements. In addition, they must be knowledgeable in the calculations, conversions, etc. for obtaining the final results.

6.2 Hold Times

In the event that a method and/or method SOP *recommended/suggested* hold time was exceeded, a statement must at a minimum be denoted in the case narrative as to the occurrence.

6.3 Control Limits

Control limits and assessment procedures may be project-specific. Project-specific requirements may supersede routine protocols. Use any applicable Quality Assurance Project Plan (QAPP) for assessment procedures and limits.

6.4 Nonconformity

All nonconformities shall be generated and documented in accordance with the appropriate method SOP as well as the *SOP for Nonconformance and Corrective Action*.

6.5 Systematic Errors

If an analysis has systematic errors, a nonconformity and corrective action report (NCAR) must be completed and all experiments, procedural changes and subsequent validations documented and appropriately approved and maintained by the Quality Assurance department.

6.6 Data Qualifiers

Refer to the most recent version of the Quality Assurance Manual for the list of applicable qualifiers; however, client and project specific qualifiers (i.e., Arizona, DoD qualifiers) may be used. In addition, these qualifiers may be modified depending on the specific need.

7) Documentation and Records

7.1 Documentation and Records

This document is used in conjunction with the *SOP for Laboratory Storage, Analysis, and Tracking* and the *SOP for Project Management*; therefore, those records may apply as well. Records produced by the execution of the procedures specified herein are documented on the appropriate checklist(s) specific to the type of review or documented on the hardcopy data by signature (or initials and date) of the final report.

- Primary and secondary data review checklists
- Tertiary review checklist (Data Validation Review Checklist)
- Case narrative checklist
- Approved cover letter
- Approved initial report page (produced during tertiary review)

7.2 All of the reviews shall be documented by a checklist (primary, secondary), initials (tertiary, with checklist) or report signature (Project Manager).

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8) Summary of Changes

Table 9.1 Summary of Revision Changes			
Revision Number	Effective Date	Document Editor	Description of Changes
15.0	6/02/2018	C. Humphrey	New SOP template. Applied updated SOP formatting style to first two pages and header/footer. Section reference updated throughout SOP as necessary.
			5.7.2 – removed facsimile
			5.9 – revised to remove hardcopy report details
			5.9.1 – removed Hardcopy Submittals section and renumbered
			5.9.2 – revised to remove hardcopy report details
			5.10.1 – removed Hardcopy Submittals section and renumbered
			5.10.2 – revised to remove hardcopy report details
			5.13 – removed 3rd paragraph containing obsolete methods
			7.1 – First Sentence revised to include SOP names verses references to section 9; 2nd bullet – added clarification
			9 – removed references to laboratory SOPs and renumbered
			9.1 – updated reference
			9.2 – updated reference
			Attachment 1 – updated
			Attachment 3 – removed last item from list – obsolete methods

9) References and Related Documents

9.1 2009 TNI Standard and 2016 TNI Standard

9.2 DoD/DoE Quality Systems Manual Version 5.1, 2017; and Version 5.1.1, 2018.

9.3 *General Requirements for the Competence of Testing and Calibration Laboratories*, ISO/IEC 17025, second edition, 2005-05-15.

9.4 Minnesota Administrative Rules, Department of Health, Chapter 4740, Laboratories; Accreditation Requirements.

10) Attachments

10.1 Tables

Table 1 Reporting and Manual Integration Abbreviations

10.2 Attachments

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Attachment 1 Data Validation Review Checklist

Attachment 2 Case Narrative and Data Package Checklist

Attachment 3 Demonstration of Capability Review Checklist

Table 1

Reporting	Manual Integrations
E; Estimated	MP; Missed Peak
FP; False positive	BLC; Baseline Correction
NR; Non-target compound, not reported	IPC; Interfering Peak Correction
<RL; Concentration less than reporting limit	SP; Split Peak Correction
<DL; Concentration less than detection limit	RTS; Retention Time Shift
NC; Compound not confirmed	WRT; Wrong Retention Time
CE; Co-eluting compounds (target &/or non-target)	WP; Wrong Peak
<3X; Peak height less than 3 times the baseline noise	PIM; Pattern Integration Missed
QFP; Quadratic false positive	IC_____; Integration correction
ABS; After Background Subtraction	
BBS; Before Background Subtraction	
M; Matrix Interference	

Note: This table is also included in the *SOP for Laboratory Storage, Analysis, and Tracking* (Table 1). The abbreviation categories may be used interchangeably to fit the situation.

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Attachment 1

Data Validation Review Checklist

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Data Validation Review Checklist

Project ID: P180_____

Reviewer: _____ **Tier:** _____

Review Date:	____/____/2018	TO-3M	TO-11A	TO-15	TO-17	325B	P9290	OSHA
Due Date:	____/____/2018	25C	3C	APH	BTU-CHONS	RSK175	Amines	
		Acids	Siloxanes	Sulfur	S8	NCASI	Other_____	

Sample Data: *(Data has been verified based on the following documentation when available -- COC, scheduling form, login, paperwork shipped with samples, raw laboratory data, laboratory spreadsheets). Check if complete or NA if not applicable:*

_____Client Information (name, contact, project name, project ID, sample ID)
_____Chemist & Instrument
_____Date Sampled
_____Date Received & Date Analyzed (check for method/media/client hold time requirements)
_____Check for Correct Method Including Modifications
_____Volume Analyzed (including dilution volumes) per analyte
_____Correct Sampling Volume (matches COC or other associated documentation)
_____Spreadsheet injection volumes and canister pressures
_____Canister Pressures: Second Pressures ___ Backfill ___
_____Trip blank canister pressure correct
_____Tedlar Bags (analysis time: 24hr - sulfurs; 72 hr - all others)
_____Correct units (results, reporting and detection limits)
_____Correct method reporting and detection (where applicable) limits based on volumes analyzed
_____Unit conversions are correct
_____Cross-comparison quantitation report and spreadsheet results with final report forms
_____Footnotes & Flags
_____Non-Accredited analytes X flagged
- TO-15 (ACF Compounds – no certification)
- RSK175 (Flag Propene & Propane – no certification)

_____DoD Projects:
- Manual integration noted in case narrative
- DoD LCS Limits
- TO-15 LCS/DLCS

_____AZ Projects: Non-Accredited methods and analytes T flagged
_____QC data (appropriate to method and any client requirements)
_____Analysis Summary Form (correct notations and case narrative information)
_____Client specific requests/requirements are fulfilled and included
_____Final report pages moved to R:\Reports\0_Excel Final Reports upon completed validation

EDD Review:
File Pathway: R:\EDDGE\ClientFiles_____ Initials: _____ Date: _____
File Pathway: R:\Copy_____ Initials: _____ Date: _____
Reviewed: ☐ All Data ☐ Samples/QC _____ ☐ ____% of Data
Reviewer Initials: _____ Date: _____

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Attachment 2

Case Narrative and Data Package Checklist

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Case Narrative and Data Package Checklist

Initiated By:_____ Date:_____ Project ID:_____

General:

_____ Condition of samples as received and client's consent to proceed with analysis noted, if necessary?

_____ Data verified based on the following documentation when available – Chain of Custody, SR Form, Sample Acceptance Check Form, and paperwork sent with samples.

_____ All Methods have Summaries

_____ TO-15 canisters pressurized with helium or Nitrogen? Use AutoText: TO15HE or TO15N2

State Specific Information:

Arizona

_____ AZR (Result not obtained by method approved for compliance)

_____ AZTO (Certified for EPA TO-15 and 3C, other air methods not compliant)

Massachusetts APH - CAM Compliant

AutoText: ☐ CAMAPH ☐ CAMTO151 ☐ CAMTO152

_____ MassDEP Analytical Protocol Certification Form included

_____ Flow Controller Calibration RPD Form included

_____ QC Certification Summary included

_____ Media Request Included

DOD Requirements:

_____ Insert AutoText DODMI: 3C 3CM RSKFID RSKTCD TO3 1946
SIM TO15BAG TO15CAN TO15HE TO15N2

S8 Analysis:

_____ S8ALL (Non-Suspect and Suspect and Inconclusive)

_____ S8NSS (Non-Suspect or Suspect)

Other:

_____ All required notes from Yellow sheet added (special sample prep information, QC failure, etc.)?

Data Package Compilation:

Raw Instrument QC Data			
	Samples		ICAL
	Method Blank		CCV
	LCS/DLCS		BFB
	Duplicate		Run Log

Data Package Compilation and Case Narrative Review Completed by:_____ Date:_____

(Note: PM signature on final report is equivalent to the data package compilation and case narrative review and therefore it is not required that this section of the checklist be completed.)

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Attachment 3

Demonstration of Capability Review Checklist

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Demonstration of Capability Review Checklist

Analyst: _____ Method: _____ Demonstration Date: _____

_____ Instrument Identification

_____ Prep Date (if applicable)

_____ Date Analyzed

_____ Data on summary sheet verified against quant reports and/or benchsheet

_____ % Recoveries meet current control limits

_____ Traceability verified between CoC (TO-11A In-House Sampling), extraction records, laboratory benchsheets, and quantitation reports, etc. (as applicable)

_____ Sample volumes correct (if applicable)

_____ Fronts and Backs of tubes included (if applicable)

Comments:

Reviewed By: _____ Date: _____

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Procurement and Control of Laboratory Services and Supplies

DOCUMENT ID: ADM-PROC, REV 0

Approved By: Kate Kaneko Date: 2/26/19
Laboratory Director – Kate Kaneko

Approved By: Chaney Arend Date: 2/21/19
Quality Assurance Manager – Chaney Arend

Approved By: Date: 2/21/19
Technical Manager (Volatiles GC/MS) – Chris Parnell

Doc Control ID:	UNCONTROLLED	Archived Date:	

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1) Scope and Applicability

1.1 The purpose of this Standard Operating Procedure (SOP) is to describe procedures for requesting laboratory products and materials from vendors, purchasing those products, and approving the vendors.

1.2 Procedures used to evaluate suppliers and critical consumables are also described.

1.3 Procedures described in this SOP apply to all laboratory purchases of supplies and materials made by ALS through the purchasing department. This includes reagents, standards, consumables, and metrology calibration services.

1.4 Maintenance and use of vendor list is also discussed.

1.5 This SOP does not address the additional requisition considerations required for capital expenditure purchases (CAPEX; please consult with the Laboratory Director regarding CAPEX purchases).

1.6 This SOP does not address the evaluation and qualification of subcontract laboratories, which is described in the *SOP for Qualification of Subcontract Laboratories and Internal Subcontracting Protocol.*

2) Summary of Procedure

2.1 All supplies and materials ordered must meet all applicable technical requirements as defined by the appropriate Department Manager. An ALS Purchase Order Requisition is used to document the purchase request. Packing slips are used to document receipt. All received materials are inspected for damage; some materials require verification before use. Material certifications, as applicable, are turned into the QA department. All materials are stored in an appropriate area, under suitable environmental conditions. Some supplies (e.g., standards, reagents, solvents), are subject to additional cataloging and labeling requirements. Evaluation of services provided is the responsibility of the Manager that procured the service rendered.

3) Definitions

3.1 Vendor: Supplier of laboratory supplies, materials, consumables, and services. This includes subcontract laboratories.

3.2 Purchaser: the Purchasing Supervisor or designated purchasing staff.

4) Responsibilities

4.1 Laboratory management (Laboratory Director and Supervisors)

It is the responsibility of the laboratory management to perform required vendor evaluations, use vendors and select materials that are suitable for the intended purpose, and to properly complete the purchase order requisition. It is also the laboratory management responsibility to manage the verification of materials, as applicable; to retain material certifications, as applicable; and to ensure that storage and ancillary cataloguing and labeling requirements are met.

4.2 Laboratory Quality Assurance Manager (QAM)

The QAM is responsible for performing or facilitating required vendor evaluations and for monitoring ongoing compliance with this SOP.

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4.3 Procurement Manager (PM)

The corporate PM will be responsible for directing and coordinating activities of personnel engaged in buying materials and supplies. The PM will be responsible for maintaining an approved vendor list.

5) Procedure

5.1 Vendor selection

5.1.1 Vendors and suppliers must be established businesses or entities which are capable of providing the materials, goods, or services meeting the requirements of ALS and its customers.

5.1.2 Vendors of supplies and services which affect the quality of test results, including critical consumables, must be evaluated following the procedure described below. Records on the evaluation are maintained by the laboratory. After successful evaluation, these vendors may be selected for these types of supplies and services.

5.1.3 Vendors of supplies, materials, consumables, and services not expected to affect the quality of test results do not need an evaluation, unless required by contract between ALS and its customer.

5.1.4 In the event that problems arise with quality, availability, or possible financial concerns, vendors on the approved list will be removed.

5.2 Identification of items requiring vendor evaluation

5.2.1 The following list defines laboratory supplies and services which potentially affect the quality of test results and require vendor evaluation.

- Analytical calibration and QC standards, including neat chemicals
- QC reference materials
- Acids and solvents
- Reagents used in test procedures
- Laboratory gases
- Consumables potentially impacting test performance or accuracy of test results. Examples include:
  - Sampling cartridges and tubes
  - Filters (used in sample analysis)
  - Pipets, syringes, and volumetric ware
  - Autosampler vials
- Critical consumables – Refer to the *SOP for Consumable Materials*
- Equipment consumables (syringes, tubing, chromatography columns, injection parts, etc.)
- Proficiency testing provider products
- Support equipment (balances, thermometers, weights)
- Sample containers
- Laboratory deionized water systems, components, and service
- Calibration and calibration verification services
- Analytical equipment (instruments and manually used lab equipment used to produce sample results)

5.2.2 Suppliers of other items may be evaluated using the appropriate supervisor's professional judgement.

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5.3 Vendor evaluation - If a required product or service is not available from an approved vendor and a new vendor is being evaluated, the following steps are taken:

NOTE: this section applies only to supplies and services identified in Section 5.2.

5.3.1 Business Evaluation and approval

5.3.1.1 The corporate purchasing department obtains a W-9 from the business. This establishes that the vendor is a viable business entity and is required before the vendor is set up in the requisition and payment systems.

5.3.1.2 A Purchasing approved vendor list will be maintained by the Procurement Manager or designee.

5.3.2 Laboratory evaluation and approval

5.3.2.1 The person needing a supply, material, or service from a vendor not already evaluated will notify the QAM. This is usually the supervisor of the lab work area.

5.3.2.2 The QAM, or designee, will complete a Laboratory Vendor Evaluation Form (example form in Attachment A).

- All fields should be completed or marked otherwise
- Accompanying documents should be identified
- Requirements for Certificates of Analysis (or similar product documentation) must be identified
- Vendors of laboratory gases must be capable of providing traceability to certificates of analysis for gases.
- Vendors of de-ionized water systems and maintenance will also be evaluated by the vendor's ability to provide systems which generate water meeting the specifications for the laboratory.
- Vendors of calibration services of metrology equipment (balances, weights, thermometers, etc) must be pre-approved by the laboratory QAM. Approval is performed by obtaining the required certifications or accreditations required by the laboratory quality program. The vendor (and documentation) must meet the requirements of NELAP, DoD QSM, Navy LAP and ISO 17025.

5.3.2.3 Evaluation is based on relevant evaluation items, such as those listed on the example Laboratory Vendor Evaluation Form in Attachment A. For established vendors who have the business approval and whose product has been in use, approval may be based on evaluation of historical product or service acceptability and performance by the appropriate laboratory supervisor and QAM.

5.3.2.4 Once the form is completed and accompanying information is obtained, and it is acceptable, it is approved by the QAM and kept on file. The department supervisor requesting the evaluation will be notified that the form has been approved.

5.3.2.5 A Laboratory approved vendor list will be maintained by the QAM. This is a list of vendors for which the laboratory evaluation is complete.

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5.4 Purchasing from approved vendors

5.4.1 ALS Environmental – Simi Valley uses the ALS Requisition System. The person filling out the purchase requisition will ensure that the product or service meets the requirements or specifications in the SOP or method. An adequate description of the quality or specification should be provided on the purchase requisition or attachment (e.g. grade, class, specification, purity, etc.). This may be incorporated by reference with the vendor's product or catalogue number. Refer to the *SOP for Quality of Reagents and Standards*, for additional information on determining reagents and standards quality.

5.4.2 Purchase requisitions may be processed for vendors where the business evaluation is complete the laboratory evaluation is underway and expected to be completed. The lack of a final completed laboratory evaluation, including critical consumable testing, should not prevent purchasing as long as the evaluation and/or testing is completed prior to product use.

5.4.3 If a new critical consumable product or service is required from an approved vendor, the products or services must be evaluated prior to use as described in Section 5.5.

5.5 Critical consumables, supplies, and services

5.5.1 Critical products and services must be evaluated prior to use. Refer to the *SOP for Consumable Materials* for a list of critical products requiring pre-testing. Vendors of calibration services of metrology equipment must be pre-approved by the laboratory QAM. Vendors must be listed as an approved vendor in order to purchase items or calibration services.

5.5.2 Refer to method SOPs for applicable pre-testing requirements.

5.5.3 Lot pretesting

- Refer to the *SOP for Quality of Reagents and Standards* and the *SOP for Consumable Materials*, for details on critical consumable testing procedures.
- A sample of the product will be requested and will be analyzed to determine it meets the laboratory requirement, as applicable to the specific use.
- If it is determined it meets the lab's criteria the vendor and lot number will be forwarded to corporate purchasing. Subsequent orders must specify or sequester the defined lot number.

5.6 Receiving Incoming Materials

5.6.1 A general inspection of the materials is performed and the appropriate supervisor or manager is notified that the materials have arrived. The supervisor will release for use based on receipt inspection results.

5.6.1.1 The products are inspected for damage by the ordering department.

5.6.1.2 The packing list and/or products are verified as being what was requested in the associated requisition.

5.6.1.3 The packing list is compared to the physical product, label, or identification to verify the correct product was received.

5.6.2 For items not affecting the quality of test results the receipt of undamaged

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materials is the extent of the acceptability evaluation that needs to be conducted. Hence, in these cases, relocation of these items to the appropriate lab department or general supply area constitutes release for use.

5.6.3 Receipt of products or materials not meeting inspection requirements will be held and either returned or further evaluated for use by the appropriate supervisor prior to release for use. Documentation of in-house evaluations shall be retained by the department.

5.6.4 Incoming materials may be kept in the Receiving area until the department who ordered them, relocates the items. The items may also be delivered directly to the supervisor who initiated the order. This may be done to avoid misplacement, loss, or potential contamination, as well as to keep the items segregated should further evaluative testing need to be conducted before the items are put into use.

NOTE: All materials, but with particular note of reference materials, shall be handled and stored safely, and in a manner that preserves the material's integrity. Where additional evaluation practices exist, staff is not permitted to use the materials until the evaluation has been completed successfully.

5.7 Storage of Purchased Materials and Consumables

5.7.1 Reagent containers must be labeled with the date received and the Certificate of Analysis must be kept by the laboratory, as appropriate.

5.7.2 Materials received should be stored as recommended by the manufacturer to avoid degradation.

5.7.3 Temperature dependent materials are stored in designated temperature monitored refrigerators or freezers.

5.7.4 Standards and mixtures must be segregated from sample material to prevent the possibility of cross-contamination.

5.7.5 Solvents are segregated based on flammability and stored in the appropriate cabinets in the prep laboratory. Reference standard/material integrity is protected by separation from incompatible materials and/or minimizing exposure to degrading environments or materials (using manufacturer's recommendations).

5.7.6 Flammable solvents must be stored away from potential sources of ignition and heat.

5.7.7 Acids and bases must be stored separately as required by the laboratory safety policy.

6) Quality Assurance

6.1 Contaminants traced back to a consumable material will result in the removal of the material from the laboratory use.

6.2 The laboratory will ensure that applicable laboratory employees are trained on the requirements of this SOP. The training shall be documented using an SOP Attestation Form.

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7) Documentation and Records

7.1 As part of the requirements of this SOP for checking new lots of chemicals, the testing records for the chemical pre-tested must be retained.

7.2 The Certificate of Analysis must be filed by the laboratory as appropriate.

7.3 Purchase requisitions will be used to document that the proper products were obtained to ensure the quality of subsequent testing results.

7.4 Receiving documents will be used to document that the purchased products are those requested and received, and meet the requirements of the requesting department.

7.5 Packing slips must be turned into the front office.

8) Summary of Changes

Table 8.1 Summary of Revision Changes

Revision Number	Effective Date	Document Editor	Description of Changes
0.0	03/02/2019	C. Arend	New local level SOP

9) References and Related Documents

9.1 TNI Standard Volume 1, 2009 and 2016

9.2 ISO/IEC 17025:2005 and ISO/IEC 17025:2017

9.3 Department of Defense (DoD) Quality Systems Manual (QSM) for Environmental Laboratories, Version 5.1, January 2017; Version 5.1.1, February 2018; Version 5.2, December 2018.

9.4 Naval Sea Systems Command Laboratory Accreditation Program (NAVSEA-LAP)

10) Attachments

10.1 Attachments

Attachment A – Vendor Laboratory Evaluation Form Example

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ATTACHMENT A - VENDOR LABORATORY EVALUATION FORM EXAMPLE

Laboratory Vendor Evaluation Form

ALS Environmental

Requested by: Date:

Vendor Information	
Vendor Name:	
Product or Service Provided:	
Contact:	
E-mail:	
Address:	
Telephone:	
Fax:	
Website:	

Evaluation

Evaluation Item	Result	Comment
1. Does the vendor have a formal Quality Assurance Program in place?		
• If so, what is the basis of the Quality System (i.e. ISO)?		
• Formal certification or accreditation of the Quality System (i.e. ISO)?		
2. Do products or services meet applicable standards?		
3. Vendor makes available products of suitable grades, quality, or purity meeting test requirements?		
4. For services, is the service readily available?		
5. Specific product certifications available (e.g. C of A) where applicable?		
6. Laboratory evaluation of historical product or service and acceptable performance?		
• Department Supervisor		
• QA Manager		
7. Alternative evaluation (explain)		

Approval	
QA Manager:	
Date:	
Comments:	

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ALS HOUSTON QUALITY ASSURANCE MANUAL

DOCUMENT ID: ALSHS-QAM, REV 11.6

Approved By: _____ Date: 9/18/2020
Hoai Van, Laboratory/Technical Director

Prepared By: _____ Date: 09/18/2020
Erica Marinez, Quality Assurance Manager

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QA MANUAL CROSS REFERENCE TABLE

ALS QAM and/or SOP	ISO 17025:2017 Section	TNI ELV1M2-2016 Module/Section
1	1	1.1
1.1	1	1.2
Appendix A	3.1	3.1
2	4.1	4.1
3.1-3.3	4.2	4.2
4	4.3	4.3
5	4.4	4.4
6	4.5	4.5
7	4.6	4.6
8	4.7	4.7
9	4.8	4.8
15	4.9	4.9
16	4.10	4.10
16	4.11	4.11
16	4.12	4.12
17	4.13	4.13
18.1	4.14	4.14
19	4.15	4.15
2, Appendix C	4.16	4.16
3	5.1	5.1
20	5.2	5.2
10	5.3	5.3
12	5.4	5.4
12	5.5	5.5
13	5.6	5.6
11	5.7	5.7
11, 12	5.8	5.8
12, 14,	5.9	5.9
21	5.10	5.10

1) Introduction and Scope

The purpose of this Quality Assurance Manual is to outline the quality system for the Houston division of ALS Group USA, Corp (ALS USA, Corp). The Quality Assurance Manual defines the policies, procedures, and documentations that assure analytical services continually meet a defined standard of quality that is designed to provide clients with data of known and documented quality and, where applicable, demonstrate regulatory compliance. ALS SOPs are referenced in this document to direct the reader to more complete information.

The Quality Manual sets the standard under which all laboratory operations are performed, including the laboratory's organization, objectives, and operating philosophy. This Standard is consistent with ISO/IEC 17025:2017 requirements that are relevant to the scope of environmental testing services and various accreditation and certification programs listed in Appendix J.

1.1 Scope of Testing

ALS Group USA, Corp provides analytical services for many matrices, including aqueous, soil, solid waste, and air using analytical protocols defined by EPA Approved Methods. ALS Group USA, Corp strives to provide analytical test results that are of the type and quality needed and expected by our customers.

ALS maintains certifications pertaining to various commercial and government entities. Each certification requires that the laboratory continue to perform at levels specified by the programs issuing certification. Program requirements can be rigorous; they include performance evaluations as well as annual audits of the laboratory to verify compliance.

1.2 Glossary and Acronyms Used

1.2.1 Glossary

The Terms and Definitions Section of the TNI Standard: Modules 1-7 in the 2016 TNI Environmental Laboratory Sector Standard – Volume 1 – Management and Technical Requirements for Laboratories Performing Environmental Analysis (EL-V1, M1 through M7, ISO/IEC 17025-2017).

1.2.2 Acronyms – See Appendix A

1.3 Management of the Quality Assurance Manual

1.3.1 The Quality Assurance Manager is responsible for maintaining the currency of the Quality Assurance Manual.

1.3.2 The Quality Manual is reviewed annually by the Quality Assurance Manager and laboratory personnel to ensure it still reflects current practices and meets the requirements of any applicable regulations or client specification.

1.3.3 The Quality Assurance Manual is considered confidential within the Houston division of ALS Group USA, Corp and may not be altered in anyway except by approval of the Laboratory Director, Technical Director and Quality Assurance Manager. If it is distributed to external users, it is for the purpose of reviewing the management system and may not be used for any other purpose without written permission.

2) Organization

2.1 The laboratory is responsible for carrying out testing activities that meet the requirements of the TNI Standard, the DOD/DOE Quality Systems Manual (QSM) for Environmental Laboratories and Standard, and that meet the needs of the client, the regulatory authorities or organizations providing recognition. Through application of the policies and procedures outlined in this Section and throughout the Quality Assurance Manual:

2.1.1 Management and technical personnel have the authority and resources to carry out their duties and have procedures to identify and correct departures from the laboratory's management system.

2.1.2 Personnel understand the relevance and importance of their duties as related to the maintenance of the laboratory's management system.

2.1.3 Ethics and data integrity procedures (see SOP CE-GEN001 Ethics) ensure personnel do not engage in activities that diminish confidence in the laboratory's capabilities.

2.2 Laboratory Organizational Structure

ALS Group USA, Corp is a wholly owned subsidiary of ALS Limited. The laboratory is a commercial operation located at 10450 Stancliff Road, Suite 210, Houston, Texas, 77099. The Laboratory director Hoai Van can always be reached at (281) 530-5656.

An organization chart is provided in Appendix B that shows the operational structure and reporting relationships in the laboratory.

Additional information regarding responsibilities, authority and interrelationship of personnel who manage, perform or verify testing is included in Section 3 – "Management" and Section 20 – "Personnel". These Sections also include information on supervision, training, technical management, job descriptions, quality personnel, and appointment of deputies for key managerial personnel.

2.3 Impartiality, Conflict of Interest and Undue Pressure

The organizational structure indicated above minimizes the potential for conflicting or undue interests that might influence the technical judgment of analytical personnel. In addition, procedures are in place to prevent outside pressures or involvement in activities that may affect competence, impartiality, judgment, operational integrity, or the quality of the work performed at the laboratory is described in SOP CE-GEN001 Laboratory Ethics and Data Integrity.

2.4 The laboratory management team is responsible for and committed to safeguarding against impartiality of laboratory activities, and therefore should not allow commercial, financial or other pressures to compromise impartiality.

All employees are required to enter into the following agreements:

- **Code of Conduct Agreement**
  Provides a framework for decisions and actions in relation to conduct in employment. The agreement covers a wide range of topics including personal and professional behavior, conflicts of interest, gifts, confidentiality, legal compliance, security of information, among others. The code of conduct agreement is administered by the USA Human

Resources department. This agreement is provided to the employee during the hiring and induction process and the agreement is reviewed and signed.

- **Confidentiality Agreement**
  Describes policies for identifying and protecting information owned by ALS and its customers, and for keeping this information in confidence. The confidentiality agreement is administered by the USA Human Resources department. This agreement is provided to the employee during the hiring and induction process and the agreement is reviewed and signed.

- **Ethics and Data Integrity Agreement**

  Provided to the employee as part of the hiring and induction process, and reviewed during periodic ethics refresher training. This is coordinated between the Human Resources and Quality Assurance (QA) departments. This agreement is provided to the employee during the hiring and induction process and the agreement is reviewed and signed. All employees are required to take annual ethics and data integrity refresher training

3) Management

3.1 Management Responsibility

3.1.1 The Laboratory Management includes the titles of Laboratory Director, Technical Director, Quality Assurance Manager, Information Technology Manager, Project Managers, Safety Officer and Department Supervisors/Managers. Roles and duties are defined in Section 3.2 below.

3.1.2 Management has overall responsibility for the technical operations and the authority needed to generate the required quality of laboratory operations.

3.1.3 Management ensures communication within the organization to maintain an effective management system and to communicate the importance of meeting customer, statutory, and regulatory requirements.

3.1.4 Management assures that the system documentation is known and available so that appropriate personnel can implement their part.

3.1.5 When changes to the management system occur or are planned, managers ensure that the integrity of the system is maintained.

3.1.6 Managers implement, maintain, and improve the management system, and identify noncompliance with the management system of procedures.

3.1.7 Managers initiate actions to prevent or minimize noncompliance.

3.1.8 Management must ensure technical competence of personnel operating equipment, performing tests, evaluating results, or signing reports, and limits authority to perform laboratory functions to those appropriately trained and/or supervised, HS-QS013 Employee Training.

3.1.9 Management is responsible for defining the minimal level of education, qualifications, experience, and skills necessary for all positions in the laboratory and assuring that technical staff have demonstrated capabilities in their tasks.

3.1.10 Management must ensure training is kept up to date by periodic review of training records and through employee performance review.

3.1.11 Management bears specific responsibility for maintenance of the management system. This includes:

3.1.11.1 Defining roles and responsibilities of personnel

3.1.11.2 Approving documents

3.1.11.3 Providing required training

3.1.11.4 Providing a procedure for confidential reporting of data integrity issues, and periodically reviewing data, laboratory procedures, and documentation.

3.1.11.5 The assignment of responsibilities, authorities, and interrelationships of the personnel who manage, supervise, perform, or verify work affecting the quality of environmental tests is documented in Section 20.

3.1.11.6 Management ensures that audit findings and corrective actions are completed within required time frames.

3.1.11.7 ALS management also views risk management as a key component of its governance responsibilities and an essential process in achieving and mandating a viable organization. ALS is committed to enterprise wide risk management to ensure its corporate governance responsibilities are met and its strategic goals are realized. See SOP HS-QS023 Risks and Opportunities.

3.2 Roles and Duties

3.2.1 Laboratory Director: Responsible for all laboratory activities as the highest level manager. The Laboratory Director provides administrative, operational, and technical leadership through planning, allocation and management of personnel and resources. Provides resources for implementation of the QA program and reviews and approves the Quality Assurance Manual. Requires a BS or BA degree in Science, Engineering or Management, and five years of supervisory experience in environmental laboratory operations. This individual is an approved signatory for all facility policies and procedures.

3.2.2 Technical Director: Assures reliable data through the following activities: method development, monitoring quality control performance, monitoring the validity of generated data and corroborating the analysis performed. The Technical Director certifies that personnel with appropriate educational and/or technical background perform all tests for which the laboratory is accredited; reviews new methods for their applicability to a project, implements new methodology at the facility, and directs, trains and supervises individuals participating in this effort; in the case of the Technical Director absence, Departmental Supervisors shall maintain these duties. Requires a BS or BA degree in Science, Engineering or Management (with at least 24 college semester credits in chemistry), and five years technical supervisory experience in environmental laboratory operations. This individual is an approved signatory for all facility policies and procedures, as well as training documentation. Changes must be communicated to accreditation bodies within 30 days of change to this position. In the event of the Technical Director is

absent for more than 45 days such as on leave, accreditation bodies must be notified of the Technical Director absence.

3.2.3 Quality Assurance Manager: Has the authority and responsibility for implementing, maintaining and improving the quality system; ensures that all personnel understand the quality system, and their contributions to it; facilitates communication throughout the facility regarding the effectiveness of the quality system; has direct access to the Corporate QA Manager and is independent of operations where the Quality Manager has oversight; is the focal point for the quality system and has oversight of quality control data; evaluates data objectively and performs assessments without managerial influence; arranges for, or conducts, internal audits annually; evaluates the effectiveness of training; and, notifies laboratory management of deficiencies (or opportunities for continuous improvement) and monitors corrective actions; keeps the Quality Assurance Manual current; signs the demonstrations of capability; responsible for maintaining QA records such as archived logbooks, PT results, maintaining the laboratories certifications and approvals; facilitates a QA Management System Review (SOP HS-QS017 Management Review); may place a stop work order on any non-compliant work area. The QA Managers maintains a general knowledge of the analytical test methods performed in the facility. In the case of his absence, the QA Specialist or the Technical Director shall maintain these duties. Requires a BS or BA degree in Science preferably in Chemistry or any other physical science and five years of experience in environmental laboratory and two years of experience in quality system management. This individual is an approved signatory for all policy and procedural documents within the facility. Changes must be communicated to accreditation bodies within 30 days of change to this position.

3.2.4 Information Technology Manager: Reports directly to the Laboratory Director; responsible for maintaining the Laboratory Information Management System (LIMS) and other specific computer software and hardware pertinent to laboratory function; functions include maintaining the computer network, education of analytical staff in the use of scientific software, software implementation and control, Electronic Data Deliverables (EDDs), data back-up, data archiving, and maintaining electronic data integrity and maintaining procedures and methodologies for:Maintaining historical file of software, software version and change control, defining acceptance criteria, testing, records, and approval for changes in LIMS hardware and communication equipment. The IT Manager requires an associate's degree in Information Systems or Computer Science, and five years of experience in computers and network information system hardware and software. This individual is an approved signatory for policy and procedures related to Information Technology.

3.2.5 Project Managers (PM): Senior level scientists that interface with both laboratory supervision and the client. Project Managers report to the Laboratory Director. Project Managers are responsible for ensuring that the analyses performed by the laboratory meet all project, contract, and regulatory-specific requirements. The PM relays the project details, requested by the customer, to the laboratory staff. The PM reviews all sample log-in information; helps direct turnaround time commitments and reviews all final reports. BS or BA degree in Science, Engineering or Management is preferred but not required and five years of experience in environmental laboratory operations. This individual is an

approved signatory for client reports.

3.2.6 Safety Officer: Responsible for the administration of the laboratory's safety program: Designated as the Chemical Hygiene Officer and reports directly to the Laboratory Director; coordinator for the Safety Committee Officer, implements safety policies, supervises new employee safety training, reviews any accidents or incidents, prepares prevention plan; monitors hazardous waste disposal, and conducts routine safety inspections. Requires a high school diploma, completion of a 40-hr OSHA Safety training course (or designate personnel) and two years of experience in the environmental laboratory. This individual is an approved signatory for all policies and procedures related to Safety.

3.2.7 Sample Management Supervisor: Supervision of the sample management Group who are responsible for sample receipt and log-in activities; maintaining sample custody, supervising storage and later the disposal of samples; reports to the Client Services Manager; Requires a high school diploma, and two years of experience in the environmental laboratory. This individual is an approved signatory for all policies and procedures related to Sample Management.

3.2.8 Department Supervisors/Managers: Responsible for a technical supervision of technical operation in their area of laboratory responsibility (e.g. Volatiles Supervisor). They report to the Technical Director; are full-time members of the staff and assure reliable data through the following activities: monitoring quality control, corroborating the analysis performed, and provide supervision to staff in training, assuring demonstrations of capability are performed by the departmental staff upon completion of training and then annually; they assist the Technical Director in certifying that personnel with appropriate educational and/or technical background perform all tests for which the laboratory is accredited. Requires a BS or BA degree in Science, Engineering or Management, and five years technical supervisory experience in environmental laboratory operations. Technical Supervisors are approved signatories for policies and procedures for their respective areas. They are also approved signatories on raw data. Changes must be communicated to accreditation bodies within 30 days of change to this position.

3.3 Laboratory Key Personnel Deputies

The following table defines who assumes the responsibilities of key personnel in their absence if the absence is more than 15 day:

Key Personnel	Deputy
Laboratory & Technical Director	Organic Manager Inorganics Manager
QA Manager	Deputy QA Manager
Technical Director	Organic Manager Inorganics Manager

3.4 Quality Policy

ALS is committed to producing legally defensible analytical data of known and documented quality acceptable for its intended use and in compliance with applicable regulatory programs. This QAM is designed to satisfy the applicable requirements of the Various States, United States Environmental Protection Agency (USEPA), American Industrial Hygiene Association (AIHA) policies (Current), Current TNI Volume 1 and current ISO 17025.

ALS corporate management has committed its full support to provide the personnel, facilities, equipment, and procedures required by this QAM and other client and project related requirements.

ALS management reviews its operations on an ongoing basis and seeks input from staff and clients to make improvements

Management's commitment to quality and to the management system is stated in the Quality Policy below, which is upheld through the application of related policies and procedures described in this Quality Assurance Manual and associated quality system documents

Quality Policy Statement

The objective of the quality system, and the commitment of management, is to consistently provide our customers with data of known and documented quality that meets their requirements. Our policy is to use good professional practices, to maintain quality, to uphold the highest quality of service, and to comply with TNI and the DOD ELAP Standard. However, the primary responsibility for quality rests with each individual within the laboratory organization. ALS managers are committed to continually improve the effectiveness of the management system. Every laboratory employee must ensure that the generation and reporting of quality analytical data is a fundamental priority. All laboratory employees are required to familiarize themselves with the quality documentation and to implement the policies and procedures in their work.

3.5 Ethics and Data Integrity System

3.5.1 The Data Integrity System employed by ALS Group USA, Corp is an integrated approach designed to ensure the production of defensible and quality data. The overall system consists of a three-tier approach as documented in CE-GEN001, Laboratory Ethics and Data Integrity (Corporate). See Appendix C for the Ethics Agreement. In addition to covering data integrity investigations, this Section covers all topics related to ethics and data integrity policies, procedures and training.

3.5.2 It is the policy of ALS to perform work for clients in the most efficient manner possible, avoiding waste of resources. It is the role of both ALS management and employees to ensure that work for clients is performed most efficiently and effectively by properly utilizing ALS purchased materials, equipment, and the time and ability of personnel.

3.5.3 ALS policy on waste, fraud, and abuse is described in ALS SOP CE-GEN-001, "Laboratory Ethics and Data Integrity." It is the policy of ALS to generate accurate and reliable data in accordance with contractual and regulatory requirements. As stated in the ALS policies manual, any undue pressure applied

to employees in the performance of their duties must be reported as per procedures for reporting listed in ALS SOP CE-GEN-001. It is against ALS policy to improperly manipulate or falsify data or to engage in any other unethical conduct as defined in ALS Corporate SOP CE-GEN-001. ALS provides mandatory initial and annual refresher training for all employees on SOP CE-GEN-001, "Laboratory Ethics and Data Integrity."

3.5.4 The pertinent ALS Project Manager must approve deviations from contractual requirements. The Project Manager obtains approval for any such deviations, either in writing or by phone (documented in a phone log) from pertinent contract authorities. In addition, ALS requires that deviations from contractual requirements that might affect data quality be reported to clients. Any employee who knowingly manipulates and/or falsifies data or documents or engages in any unethical conduct is subject to immediate release from employment.

3.5.5 ALS employees who are aware of, or reasonably suspicious of, any case of data manipulation, falsification of data, waste of resources, or other unethical practice or misconduct shall notify any manager. Under the direction of the laboratory director, every allegation of unethical conduct will be fully investigated

3.5.6 ALS is committed to ensuring the integrity of its data and providing valid data of known and documented quality to its clients. The elements Ethics and Data Integrity program include:

3.5.6.1 Documented data integrity procedures signed and dated by top management.

3.5.6.2 An Ethics and Data Integrity Policy signed by all management annually (SOP CE-GEN001 Ethics). This policy is signed, dated and distributed by the Quality Assurance Manager.

3.5.6.3 Annual data integrity training.

3.5.6.4 Procedures for confidential reporting of alleged data integrity issues.

3.5.6.5 An audit program that monitors data integrity and procedures for handling data integrity investigations and client notifications.

3.5.7 Ethics and Data Integrity Procedures

The Ethics and Data Integrity Policy provides an overview of the program. Written procedures that are considered part of the Ethics and Data Integrity program include:

3.5.7.1 Ethics and Data Integrity Policy (SOP CE-GEN001)

3.5.7.2 Manual Integrations (SOP HS-QS016)

3.5.7.3 Corrective Action Procedures (SOP HS-QS003)

3.5.7.4 Data recall procedures (SOP HS-QS011)

Management reviews data integrity procedures yearly and updates these procedures as needed.

3.5.8 Investigations

All investigations resulting from data integrity issues are conducted confidentially. They are documented and notifications are made to clients who received any negatively affected data that did not meet the client's data quality requirements. Procedures for investigation are included in CE-GEN001.

3.5.8.1 All reports of suspected improper action or errors in reporting must be investigated to determine the validity of the reported data. All results that require correction must be revised and changes must be communicated to the client in writing.

3.5.8.2 The Laboratory Director, with assistance of the Quality Assurance Manager, must develop a plan to confidentially investigate the issue, resolve the problem, and contact any affected clients. The investigation may include personnel interviews, data audits, training evaluations, data package review, internal method audits and surveillance to determine inappropriate practices.

3.5.8.3 The QA Manager must investigate if the inappropriate practice has an impact on data integrity and reported values. The QA Manager must complete a comprehensive report to management with investigations findings and recommendations for training, corrective actions, and communication of incident to ALS staff. The QA Manager will facilitate client contact procedures and notify all acredaintion boby of any instance of in appropriate and prohibited practice (and data recall if required) from the findings witin 15 days of discovery. Coprrective action or proposed correctiove actions must be submitted to accrediting bodies within 30 days of discovery.

3.5.8.4 ALS management will take necessary steps to prevent the problem from recurring, including the retraining of staff on ethics and other related procedures. If an investigation indicates improper, unethical or illegal practices by any ALS employee, disciplinary action will be taken. Disciplinary action may include termination and legal action.

3.5.9 Public Disclosure

3.5.9.1 In the event that and internal investigation reveals that improper, unethical or illegal practices have occurred, all affected clients and accrediting body must be notified as soon as possible, and full disclosure shall be made to all affected regulatory agencies. This disclosure must occur within 10 working days (or shorter period if required by law) after ALS has discovered that a violation has occurred or may have occurred and must be in writing to any relevant state regulatory agency or accrediting body. Corrective action(s) implemented must be submitted to all affect clients and accrediting bodies.

Note DOD requires notification of all affected customers and accrediting body of potential data quality issues resulting from nonconforming work within 15 business days. Notification shall be performed according to a written procedure.

Records of corrections taken or proposed corrective actions to resolve the nonconformance shall be submitted to the customer(s) and accrediting body within 30 business days of discovery.

3.6 Quality Assurance Manual

The Laboratory Management ensures that the laboratory's policies and objectives for quality are documented by reference or by inclusion in the Quality Assurance Manual (QAM) and that itis communicated to, understood by, and implemented by all personnel concerned. All employees are required to sign a form, kept on file with their training records in the Quality Assurance department that states that they have read and understood the QAM, including the quality policy statement. This manuals reviewed annually and maintained current and up-to-date by the Quality Assurance Manager.

The Quality Assurance Manual contains the following required items:

3.6.1 Document Title;

3.6.2 Laboratory's full name and address;

3.6.3 Name, address (if different from above), and telephone number of individual(s) responsible for the laboratory;

3.6.4 Identification of all major organizational units which are to be covered by this quality manual and the effective date of the version;

3.6.5 Identification of the laboratory's approved signatories;

3.6.6 The signed and dated concurrence (with appropriate names and titles), of all responsible parties including the quality manager(s), technical manager(s), and the agent who is in charge of all laboratory activities, such as the laboratory director or laboratory manager;

3.6.7 The objectives of the quality system and contain or reference the laboratory's policies and procedures;

3.6.8 The laboratory's official quality policy statement, which shall include management system objectives and management's commitment to ethical laboratory practices and to upholding the requirements of this Standard; and

3.6.9 A table of contents, and applicable lists of references, glossaries and appendices.

This Quality Manual contains or references all required elements as defined by the Current TNI Standard.

3.7 Standard Operating Procedures (SOPs)

3.7.1 SOP Preparation and Management can be found in SOP HS-GEN001. They contain sufficient details such that someone with similar qualifications could perform the procedures. There are two types of SOPs used in the laboratory: 1) test method SOPs, which have specific requirements as outlined below (approving authorities are the QA Manager, Technical Director, and Laboratory Director), and 2) general use SOPs which document general procedures (approving authorities are the QA Manager, Technical Director, and Laboratory Director).

3.7.2 Each accredited method has an SOP. Sometimes an SOP is a copy of a method and any additions are clearly described. The laboratory's test method SOPs include the following topics, where applicable:

- Identification of the Method
- Applicable Matrix or Matrices
- Limits of Detection and Quantitation
- Scope and Application, including Analytes to be analyzed
- Summary of the Method
- Definitions
- Interference
- Safety
- Equipment and Supplies
- Standards and Reagents
- Sample Collection, Preservation, Shipment and Storage
- Quality Control
- Calibration and Standardization
- Procedure
- Data Analysis and Calculations
- Method Performance
- Pollution Prevention
- Data Assessment and Acceptance Criteria for QC Measures
- Corrective Action for Out-Of-Control or Unacceptable Data
- Waste Management
- References
- Tables, Diagrams, Flowcharts and Validation Data
- Summary of Changes

3.8 Order of Precedence

3.8.1 In the event of a conflict or discrepancy between policies, the order of precedence is as follows unless otherwise noted:

3.8.1.1 Quality Assurance Manual

3.8.1.2 SOPs and Policies - Laboratory SOPs will have precedence over Corporate SOPs.

3.8.1.3 Other (Work Instructions, memos, flowcharts, etc.

4) Document Control

4.1 This Section describes how the laboratory establishes and maintains a process for document management. Procedures for document management include controlling, distributing, reviewing, and accepting modifications. The purpose of document management is to preclude the use of invalid and/or obsolete documents.

4.2 Documents can be SOPs, policy statements, specifications, calibration tables, charts, textbooks, posters, notices, memoranda, software, drawings, plans, etc. These may be on various media, whether hard copy or electronic, and they may be digital, analog, photographic or written.

Note: There is a difference between records and documents. Documents include statements, identify requirements, or provide an explanation related to operations in the laboratory. Records are data (observational, qualitative or quantitative) that are generated manually or electronically during laboratory activities.

4.3 Types of Documents: The laboratory manages three types of documents: 1) controlled, 2) approved, and 3) obsolete.

4.3.1 Controlled Documents - A Controlled Document is one that is uniquely identified, issued, tracked, and kept current as part of the management system. Controlled documents may be internal documents (i.e. SOPs) or external documents (i.e. published methodologies, instrument manuals, etc).

4.3.2 Approved Document: an approved document has been reviewed, and either signed and dated, or acknowledged in writing or secure electronic means by the issuing authority.

4.3.3 Obsolete documents are those that have been superseded by more recent versions or are no longer needed. Original obsolete internal documents (i.e. SOPs) are maintained in archive storage within the QA drive.

4.4 Document Approval: All documents that affect the quality of laboratory data are managed appropriate to the scope and depth required. Controlled internal/ Laboratory documents will be reviewed and approved for use by the QA Manager and/or the Technical Director and the department supervisor, where applicable. Internal documents are reviewed annually to ensure their contents are suitable and in compliance with the current quality systems requirements, and accurately describe current operations. Approved copies of documents (internal and external) are available at all locations where operations are essential to the effective functions of the laboratory.

4.4.1 Controlled internal documents are uniquely identified with 1) a unique name or number identification 2) Effective date, 3) revision identification, 4) page number, 5) the total number of pages (or a mark to indicate the end of the document), and 6) the signatures of the issuing authority (i.e. management).

4.5 Document Master List: A master list of controlled internal documents is maintained that includes distribution, location, and revision dates. A master list of controlled external documents is also maintained that includes title, author, copyright date, and date of publication, and location. The controlled document list is maintained by the QA Department. The controlled document list is updated each time a new document is added to the quality system.

4.6 Standard Operating Procedures: SOPs are approved controlled documents and are used to ensure consistency of application of common procedures.) Where equipment manuals or published methods accurately reflect laboratory procedures in detail, a separate SOP may not be required.

4.6.1 SOP Location: The laboratory SOPs for all test methods can be accessed on the local laboratory network.

4.6.2 Any deviation from a test method SOP must be documented and approved by QA, including both a description of the change made and a technical justification. The deviation from a test method in a SOP must be reported to the client or be agreed upon as part of client project specification or requirement.

4.6.3 All SOPs are written, maintained and archived according to the guidelines of the

SOP HS-GEN001 Preparation and Management of SOPs.

4.7 Electronic Signature Policy

4.7.1 It is a policy of ALS Environmental to allow the use of electronic signatures. For data reporting an electronic signature may be applied to the report by an approved report signatory and is binding to the same extent as a handwritten wet signature.

4.7.2 To authenticate the electronic signature, the identity of the signatory is verified before their electronic signature can be created. Each electronic signature shall be unique to a single individual and shall not be used by any other individual. Following login, these credentials are used to identify and document the user.

5) Review of Requests, Tenders and Contracts

5.1 The review of all new work assures that oversight is provided so that requirements are clearly defined, the laboratory has adequate resources and capability, and the test method is applicable to the customer's needs. This process assures that all work will be given adequate attention without shortcuts that may compromise data quality. Contracts for new work may be formal bids, signed documents, or other communication, either verbal or electronic.

5.2 The Laboratory Project Management Group and the Laboratory Director determine if the laboratory has the necessary accreditation, resources, including schedule, equipment, deliverables, and personnel to meet a work request. Every client is assigned to a designated Project Manager, who informs the client of the results of the review if it indicates any potential conflict, deficiency, lack of accreditation, or inability of the lab to the complete the work satisfactorily.

5.3 Projects submitted under the Department of Defense Quality System Manual for Environmental Laboratories (DoD-QSM), current version, must follow project-specific requirements for data quality objectives. These requirements are typically outlined in a project-specific quality assurance project plan (QAPP). See also SOP HS-GEN009. Where project-specific requirements are not provided, the quality control requirements and acceptance limits outlined in Appendix B of the Current DoD-QSM must be met.

5.4 The client must be informed of any deviation from a contract including the test method or sample handling processes. All differences between the request and a final contract are resolved and recorded before any work begins. It is necessary that the contract be acceptable to both the laboratory and the client. This review process is repeated when there are amendments to the original contract by the client. The participating laboratory personnel are given copies of the amendments.

5.5 Records are maintained for every contract or work request, when appropriate by the Project Manager. This includes pertinent discussions with a client relating to the client's requirements or the results of the work during the period of execution of the contract.

6) Subcontracting of Tests

6.1 A subcontract contract laboratory is defined as a laboratory external to ALS Environmental –Houston facility, or at a different location than the address indicated on

the front cover of this manual, that performs analyses on behalf of ALS Environmental Houston. When subcontracting analytical services, the project management group must assure work requiring accreditation is placed with an appropriately accredited laboratory or one that meets applicable statutory and regulatory requirements for performing the tests. To assure this, a list of accredited subcontractors is maintained for those fields of testing clients routinely requested. Where these requirements are not met, the final report must clearly identify the subcontracted data as non-accredited. ALS Environmental-Houston assumes responsibility for the subcontractor's work, except in the case where a client or a regulating authority has specified which subcontractor is to be used.

6.2 SOP HS-GEN-007 Subcontract Sample Submittal requires that :

6.2.1 clients are notified in advance when test subcontracting is required

6.2.2 all samples are shipped under COC to maintain the integrity of the samples

6.2.3 the subcontract labs must have the required TNI accreditation to process the submitted samples when TNI accredited testing is requested or other certification if required by QA Plan

6.2.4 results from subcontracted analyses are identified in the final test report

7) Purchasing Services and Supplies

7.1 The laboratory ensures that purchased supplies and services that affect the quality of environmental tests are of the required or specified quality by using approved suppliers and products. The laboratory has procedures for purchasing, receiving, and storage of supplies that affect the quality of environmental tests are found in SOP HS-QS001 Chemical Purchase & Receipt; Chemical Preparation, Storage & Tracking. The laboratory test method SOPs, in general, specify the chemicals and grade required by each.

7.2 The Technical Director, QA Manager or a Departmental Supervisor is responsible for review and approval of service providers supplies and also approves technical content of purchasing documents prior to ordering.

7.3 Evaluation of suppliers is accomplished by ensuring the supplier ships the product or material ordered and that the material is of the appropriate quality by signing packing slips or other supply receipt documents. The purchasing documents contain the data that adequately describe the services and/or supplies ordered and must be maintained by the lab. The laboratory maintains a list of approved suppliers on the laboratory network in LIMS.

8) Service to the Client

8.1 The laboratory collaborates with clients and/or their representatives in clarifying their requests and in monitoring of the laboratory performance related to their work. Each request is reviewed to determine the nature of the request and the laboratory's ability to comply with the request within the confines of prevailing statutes and/or regulations without risk to the confidentiality of other clients.

8.1.1 The laboratory actively seeks client feedback, both positive and negative, to identify areas of improvement within the quality system, testing activities and service to the client.

8.1.2 The laboratory will clarify requests if the customer has specified incorrect, obsolete, or improper methods.

8.1.3 The laboratory will notify customers when methods require modifications to ensure achievement of project-specific objectives contained in planning documents (e.g., difficult matrix, poor performing analyte).

8.1.4 The laboratory will communicate with customers when project planning documents (e.g., QAPP or Sampling and Analysis Plan (SAP)) are missing or requirements (e.g., action levels, detection and quantification capabilities) in the documents require clarification.

8.1.5 The laboratory will notify customers when a problem has been encountered with sampling or analysis that may impact results (e.g., improper preservation of sample).

8.2 Client Confidentiality

8.2.1 The laboratory confidentiality policy is to not divulge or release any information to a third party without proper authorization from the client. Third party requests for data and information are referred to the client. Data and records identified as proprietary, privileged, or confidential are exempt from disclosure. All electronic data (storage or transmissions) are kept confidential, based on technology and laboratory limits, as required by client or regulation. The procedures for maintaining client confidentiality are found in SOP HS-GEN004 Client Confidentiality of Electronic Data Transfers.

8.2.2 Communication with the client, or their representative, is maintained to provide proper instruction and modification for testing. Technical staff is available to discuss any technical questions or concerns the client may have.

8.2.3 The client, or their representative, may be provided reasonable access to laboratory areas for witnessing testing.

8.2.4 Delays or major deviations to the testing are communicated to the client immediately by the assigned Project Manager.

8.2.5 The laboratory will provide the client with all requested information pertaining to the analysis of their samples. An additional charge may apply for additional data/information that was not requested prior to the time of sample analysis or previously agreed upon.

8.2.6 Any information obtained from or about a customer or regulator will be kept strictly confidential unless sharing has been agreed to by the source.

8.2.7 All personnel including external bodies, contractors or any individual acting on the laboratory's behalf are required to keep all information obtained or created during the performance of their activities confidential except as required by law.

8.3 Client Feedback

8.3.1 The laboratory seeks both negative and positive feedback following the completion of projects and periodically for ongoing projects. Feedback provides acknowledgement, corrective actions where necessary, and opportunities for continuous improvement. Feedback is obtained via web surveys, the results of which are maintained by marketing and provided to the

Lab Director. A link is embedded in the email signature of all employees that regularly engage in communications with clients. An integral part of the client experience is to target recent clients on their recent laboratory experience via the client survey. For surveys with score of 6 or lower, the QA Department will create a correction action report in the NCAR system.

9) Complaints

9.1 The purpose of this section is to assure that customer complaints are addressed and corrected. This includes requests to verify results or analytical data.

9.2 For complaints received directly from a client, the personnel who receives the complaint performs any initial documentation and assessment of the issue to determine if it is related to laboratory activities. Depending upon the nature of the complaint, the Project Manager for that client will be notified of the issue. The project manager will inform the client that the laboratory acknowledges receipt of the complaint and provide regular updates as they arise on the progress of the resolution. The documented complaint is sent automatically via email through the NCAR system to the management personnel/s responsible for investigating, validating, addressing, following through and correcting the issue. The client will be contacted with a resolution in a timely manner, usually in the form of a formal letter once the complaint has been properly addressed.

9.3 If it is determined that a complaint is without merit, it is documented, and the client is contacted.

9.4 All complaints are entered into the nonconformance and corrective action database where they are tracked. See SOP HS-QS003 Nonconformance Corrective Action Reporting (NCAR).

10) Facilities and Equipment

10.1 The laboratory facilities are designed and organized to facilitate testing of environmental samples. Environmental conditions are monitored to ensure that conditions do not invalidate results or adversely affect the required quality of any measurement.

10.2 ALS Group USA, Corp, Houston Facility, is conveniently located in southwest Houston at 10450 Stancliff Road. The current facility has 26,000 square feet, in which 17,000 square feet is associated with laboratory work space, sample receiving and storage areas. A floor plan is found in Appendix D.

10.3 Separate work areas, or departments, are designated by application within the facility. The work space is complimented by special air handling and ventilation capabilities, sophisticated central gas supply, sensitive, modern and automated instrumentation, current data management software and computer hardware. The work area for volatile organic analysis has a separate, dedicated HVAC system. In addition, there are separate secure facilities for sample storage, solvent storage, laboratory inventory and hazardous waste management and storage. Large walking sample refrigerators/freezers are monitored 24 hours by ALS's security company. All large walk coolers/freezers are backed up by a standby natural gas generator, in the event there is a loss of power in the building.

10.4 The laboratory security features provide sample integrity and storage. Staff access to the facility is limited to the front and rear doors and the shipping and receiving door. Visitor access to laboratory is limited to the front entrance or client services door. All visitors must be escorted while on site. Access to ALS complex is controlled by electronic security gates during nonworking hours and holidays.

10.5 Access to the server room are restricted to only the necessary IT personnel, in order to maintain a safe temperature controlled area. The doors of the server room are kept locked with a cyber lock to prevent unauthorized access.

11) Sample Management

11.1 Chain of Custody

The laboratory does not have procedures for legal chain of custody services. Upon request a preprinted Chain-of-Custody is provided, custody seals are sent by the lab for sample cooler if the sampling containers are ordered from the laboratory. If required, custody seals for individual containers are available upon request. Shipping records are maintained with the chain of custody.

11.2 Processes to facilitate and document sample handling and management

11.2.1 Provide clients with appropriate sample collection materials to meets EPA sample collection guidelines. Materials and information provided are:

- Sample collection containers
- Sample bottle labels
- Preservative information
- Chain of custody forms
- Sample shipping containers
- Directions for collection, as needed
- A trip blank if volatile organics are to be collected
- A cooler temperature blank
- Custody seals for the shipping coolers plus individual sample containers, if requested
- Sample receipt policy
- Additional packing material, as needed
- Cooler packing and shipping instructions
- These items are provided as necessary based on client instructions through Project Management. SOP HS-SM002 Bottle Orders, describes procedures to supply clients with the above sample collection materials.

11.2.2 SOP HS-SM001 Sample Log-in Procedures –includes the procedures to perform the following for samples received:

11.2.2.1 Document time of receipt on c Chain of Custody and maintains all shipping documents related to sample custody (air-bill, cooler seals, import/customs documents, etc.)

11.2.2.2 Inspect Chain of Custody information against the samples received

11.2.2.3 Check for correct containerization, preservation, cooler receipt temperature.

11.2.2.4 Check for sample integrity (checks for VOC headspace, broken or missing containers, etc.)

11.2.2.5 Status of hold time for test requested on samples submitted, alert lab of short hold time samples or sample received within minimal holding remaining.

11.2.2.6 Checks for completeness of sample collection information – date and time of collection, location (state or country), identification of sample collector, sample collection location, and project identification.

11.2.2.7 Check for information regarding which tests are to be assigned for samples submitted.

11.2.2.8 Record information concerning the login process into the Sample Receipt Checklist (SRC) in LIMs, where any inconsistencies or non-conforming issues can be brought to the attention of Project Management.

11.2.2.9 Identifies non-conforming areas where immediate client contact must be made to request client instruction for handling samples submitted.

11.2.2.9.1 Samples received outside of temperature requirements

11.2.2.9.2 VOC samples having headspace issues

11.2.2.9.3 Missing or broken samples

11.2.2.9.4 Sample quantity insufficient to perform the tests requested

11.2.2.9.5 Samples received past the established hold-time requirement

11.2.2.9.6 Samples collected in inappropriate container

11.2.2.9.7 Samples preserved incorrectly

11.2.2.9.8 Sample collection information incomplete or missing Chain of Custody.

11.2.2.10 After all the inspection steps are completed a work order is created in LIMs where each sample is assigned a unique identifier and assigned the client requested tests.

11.2.2.10.1 The sample LIMS entries include date of collection and receipt to facilitate sample hold time monitoring by assigned test

11.2.2.11 After Samples are logged into LIMS, all sample receipt information is transferred to the assigned Project Manager, for review.

11.2.2.12 The Final Step is a Project Management review of all sample receipts and login documents for the accuracy and completeness of the work order

11.2.2.12.1 The Project Manager makes any required client contact and submits a Work Order Acknowledge (WOA) to the client (via email or fax) to inform the client of all samples received and the associated tests assigned.

11.2.2.12.2

11.2.3 SOP HS-QS008 Container Sub-sampling-metals, inorganics, semi-volatile organics and SOP HS-QS010 Container Sub-sampling-volatile organics, SW5035 are utilized when performing sub sampling as either the routine approach to handle samples or due to a circumstance where multiple tests are required and a limited number of containers are submitted for testing.

11.2.4 Sample Storage – The laboratory building is operated under a controlled access security system, where entrance requires use of a magnetic key for employees or and when entry access is granted internally, using an electronic door lock release switch system. The building security ensures that only laboratory employees have access to sample storage areas. For the samples received, specific cooler or freezer storage locations are assigned per SOP HS-SM001 sample receipt and Log –in.- Samples for volatile organic testing are segregated and stored in coolers that are separate from general storage (semi-volatiles, metals, etc.). Refrigerator / Freezer sample storage areas are monitored daily for the required storage temperatures (e.g. above 0 to 6˚C for water samples) according to SOP HS-EQ002 Thermometer Calibration and Temperature Monitoring.

11.2.4.1 Sample Transfer to subcontracted lab or return to client:

11.2.4.2 All samples are shipped under COC to maintain the integrity of the samples.

11.2.4.3 Shipping container must be shipped and packed in accordance with DOT regulations, such DOT approve shipping container, Haz Commination Labeling, etc.

11.2.5 Sample Disposal – Samples are held in storage for 30 days after invoice date, unless directed otherwise. Disposal of samples follow procedures identified in SOP HS-SAF-001 Hazardous and Non-Hazardous Waste Disposal Procedures. The SOP directs the following:

11.2.5.1 All Foreign and Regulated soil must be sterilized to comply with USDA Soil import permit requirements.

11.2.5.2 Neutral, non-hazardous aqueous waste may be disposed into the sanitary sewer system.

11.2.5.3 Hazardous waste are segregated according to type, stored as per RCRA hazardous storage rule (40 CFR 260-262).

11.2.5.4 The laboratory is Large Quantity Generator and must comply with TCEQ/EPA/RCRA waste reporting policies.

11.2.5.5 All Hazardous waste shipments are handled by a RCRA permitted waste transporter.

11.2.5.6 All Hazardous Waste is only shipped to a RCRA permitted waste disposal facility.

11.3 Sampling Containers

11.3.1 The laboratory offers clean sampling containers for use by clients. Empty containers returned to the lab will be destroyed and client may by charged the cost of the containers.

11.3.2 ALS does not provide sampling services. The laboratory's responsibility in the sample collection process lies in supplying the sampler with the necessary coolers, reagent water, sample containers, preservatives, sample labels, custody seals, COC forms, and packing materials required to properly preserve, pack, and ship samples to the laboratory.

11.3.3 All preserved sample containers must be labeled in accordance Globally Harmonized System of Classification and Labeling of Chemicals (GHS).

11.4 Sampling Containers, Preservation Requirements, Holding Times

11.4.1 See Appendix F for Sampling Containers, Preservation Requirements and Holding Time. If preservation or holding time requirements are not met, the procedures in Section 15 – "Control of Nonconforming Environmental Testing Work" are followed.

12) Analytical Procedures

All methods must be validated before they are put into use. Sources of methods employed are based on published methods. The following elements of method validation are: Demonstration of Capability, On-going proficiency, Initial Test Method Evaluation, Estimation of Uncertainty and Laboratory-Developed or Non-Standard Method Validation and Control of Data.

12.1 Initial Demonstration of Capability (IDOC) is a procedure to establish the ability of the analyst to generate data of acceptable accuracy and precision. This procedure requires the preparation and analysis of a known concentration of each analyte spiked in four separate aliquots of laboratory pure matrix. These samples are carried through the entire preparation and analytical procedure. The resulting recovery and the standard deviation are determined and compared to specified limits. This IDOC must be made at any time there is a significant change in instrument type, personnel or test methods. For analytes that do not lend themselves to spiking, the demonstration of capability may be performed using quality control samples. In cases of analytes for which spiking is not an option and for which quality control samples are not readily available, the procedure published in 40 CFR Part 136, Appendix A, test methods, is one way to perform this demonstration. The data for the DOC procedure is evaluated by either the section supervisor or the QA Department. Documentation for analyst IDOCs are maintained on the laboratory network by the QA Department as stored in analyst training records. After successful completion of the IDOC or on-going DOCs, certification statements are prepared and reviewed for approval by the Technical Director and the QA Manager.

12.2 On-going Proficiency-Annual ongoing DOCs are performed when either an analyst repeats the DOC annually or generates acceptable results when analyzing performance evaluation samples. All analysts, primary and backup must maintain yearly DOCs. The data for the DOC procedure is evaluated by either the section supervisor or the QA Department. Per TNI criteria, if DOCs lapse past one calendar year, analyst must perform IDOC prior to analyzing client samples or PT samples.

12.3 Initial Test Method Evaluation – This evaluation involves the determination of the Limit of Detection (LOD), confirmation of the Limit of Quantitation (LOQ), an evaluation of precision and bias, and an evaluation of the selectivity of the method.

12.3.1 The Limit of Detection (LOD) defines a range below the LOQ where detections

must be reported with the data qualifier "J", indicating the value reported is an estimated value. The LOD is an estimate of the minimum amount of a substance that an analytical process can reliably detect. The LOD is analyte- and matrix-specific and may be laboratory-dependent. The LOD is used to verify an MDL study. Further discussion of LOD is found in SOP HS-QS006 Limit of Detection (LOD) - Limit of Quantitation (LOQ) . LODs are are analyzed on a quarterly basis.

12.3.2 The Limit of Quantitation (LOQ) for an analytical method is established to be no lower than the lowest non-zero calibration standard for the determinative method. The LOQ defines the lower limit for an analyte working range where data may be reported without qualification. On a final analytical report, the LOQ may be labeled as the method quantitation limit (MQL) or practical quantitation limit (PQL). LOQs are are analyzed on a quarterly basis.

12.3.3 Evaluation of Precision and Bias: Precision and Bias are determined for standard and non-standard methods, where:

12.3.3.1 Precision is the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves. Precision is usually expressed as standard deviation, variance, or range, in either absolute or relative terms.

12.3.3.2 Bias is the systematic error that contributes to the difference between the mean of a significant number of test results and the accepted reference value.

12.3.3.3 Precision and bias criteria are based upon evaluation of control chart limits or based upon approved program limits (e.g. TCEQ QAPP for Superfund control limits). When criteria are not documented, they are determined through the performance of a Demonstration of Capability.

12.3.3.4 Precision and bias using non-standard, modified standard or laboratory-developed methods are compared to the criteria established by the client (when requested), the method, or the laboratory.

12.3.4 Evaluation of the Selectivity of the Method – This evaluates selectivity of a test method or instrument to respond to a target substance or constituent in the presence of non-target substances. The laboratory evaluates selectivity through procedures defined in the test method SOPs such as use of dual columns, interference checks, and analysis of method required QC samples (e.g. blanks, LCS, etc).

12.4 Estimation of Uncertainty – An Estimation of uncertainty consists of the sum (combining the components) of the uncertainties of the numerous steps of the analytical process, including, but not limited to, sample plan variability, spatial and temporal sample variation, sample heterogeneity, calibration/calibration check variability, extraction variability, and weighing variability. To the degree where the laboratory has a control over these processes, the laboratory estimates uncertainty using the standard deviation calculated from routine quality control samples (e.g. the LCS) See SOP HS-QS019.

12.5 Control of Data: All calculations and all relevant data are subject to appropriate checks in a systematic manner are addressed in the following laboratory SOPs:

12.5.1 SOP HS-IT001 LIMS Raw Data and Data Integrity, for the validation of software applications associated with data acquisition, calculation and reporting;

12.5.2 SOP HS-QS009 Data Reduction, Review and Validation, for procedure to insure that reported data are free from transcription and calculation errors and for procedures to address manual calculations, "reasonableness" of results, verification of manual integration, etc.

12.5.3 SOP HS-QS016 Manual Integration Policy, for procedures for manual integrations;

12.5.4 SOP-HS-IT002 and HS-IT007 Computer Software Installation and Maintenance, and Software Testing assures that computers, user-developed computer software, automated equipment, or microprocessors used for the acquisition, processing, recording, reporting, storage, or retrieval of environmental test data are properly installed and tested to document all computers and related software in use are validated as being adequate for use and:

12.5.4.1 Protected for integrity and confidentiality of data entry or collection, data storage, data transmission and data processing.

12.5.4.2 Maintained to ensure proper functioning and are provided with the environmental and operating conditions necessary to maintain the integrity of environmental test data.

12.5.4.3 Held secure including the prevention of unauthorized access to, and the unauthorized amendment of, computer records.

12.6 General Equipment Requirements include the following:

12.6.1 The laboratory has all the necessary equipment required for the correct performance of the scope of environmental testing presented in this Quality Manual.

12.6.2 All equipment and software used for testing and sampling is capable of achieving the accuracy required and complies with the specifications of the environmental test method as specified in the laboratory SOP.

12.6.3 Equipment is operated only by authorized and trained personnel.

12.6.4 Up-to-date instructions on the use and maintenance of equipment are readily available for use by laboratory personnel, including any relevant manuals provided by the manufacturer of the equipment.

12.6.5 SOP HS-QS–005 Validation of New Instrumentation and New Methods requires that all equipment is calibrated or checked, MDLs performed and Precision and Accuracy confirmed before being placed into use. This ensures that it meets laboratory specifications and the relevant standard specifications of the application.

12.6.6 SOPs HS-IT003 IT System Security, HS-IT007:Software Testing, HS-IT008: Software Development Methodology, and HS-IT009: Software Change Control are a part of the quality system to ensures that test equipment, including hardware and software, are safeguarded from adjustments which would invalidate the test results. This is accomplished by limiting access to the equipment and using password protection where possible. These SOPs also provide instructions for requesting, authorizing, testing, approving, implementing and establishing the priority of software change and software

version control.

12.6.7 Equipment that has been subject to overloading, mishandling, given suspect results, or been shown to be defective or outside specifications are: taken out of service, isolated to prevent its use, and clearly labeled as out of service until it has been shown to function properly. If it is shown that previous tests are affected, then procedures for non-conforming work must be followed.

12.6.8 SOP HS-EQ004 Preventative Maintenance also requires each item of equipment and the software used to generate test results be uniquely identified and records of equipment maintenance and software installed be maintained. Maintenance Logbooks are assigned to each instrument for the purpose of documenting maintenance activities. This information includes the following:

- Identity of the equipment and its software.
- Manufacturer's name, type identification, serial number or other unique identifier.
- checks that equipment complies with specifications of applicable tests;
- Current location.
- manufacturer's instructions, if available, or a reference to their location
- dates, results and copies of reports and certificates of all calibrations, adjustments, acceptance criteria, and the due date of next calibration.
- Maintenance plan where appropriate, and maintenance carried out to date; documentation on all routine and non-routine maintenance activities and reference material verifications.
- Any damage, malfunction, modification or repair to the equipment;
- date received and date placed into service (if available); and
- Condition when received, if available (new, used, reconditioned).
- Instrument status – Date taken out of service and date return to service.

12.7 Support Equipment Calibration – Various types of support equipment have calibration verification requirements based upon application. Refer to Appendix K.

12.8 Instrument Calibration Procedures –,

12.8.1 Initial Calibrations – In general, all initial calibrations are according to method requirements described in the llaboratory mmethod SOP. The SOPs require the use of a second source calibration verification standard, acquired from a different vendor or different lot if the same vendor. The calibration type (internal, external) and the calibration model options are described in the SOPs. The following general rules must be followed for all multi-point initial calibrations:

12.8.1.1 Select points from the middle of the curve may not be dropped in order to achieve acceptance criteria.

12.8.1.2 If the low or high calibration point is dropped from the curve, the working curve is adjusted and sample results outside the curve are qualified or re-analyzed at dilution.

12.8.1.3 Sufficient raw data records are retained to allow reconstruction of each initial calibration.

12.8.2 Continuing Calibration Verification and frequency are performed according to method requirements. Refer to analytical SOPS for established acceptance

criteria. The following general rules must be followed for continuing calibration verifications:

12.8.2.1 Continuing Calibration Verification (CCV) & Continuing Calibration Blank (CCB) is performed at the beginning, after every ten samples, and end of each analytical batch. Methods employing internal standards require continuing calibration verifications to be analyzed at the beginning of the each analytical batch or as required by the determinative method, whichever is more restrictive. NOTE: Some programs require closing CCV even for internal standard calibration, please consult Supervisor or QA. Other programs may require Continuing Calibration Blank (CCB) to be paired with the CCV. Continuing instrument calibration verification is performed whenever it is expected that the analytical system may be out of calibration or might not meet verification acceptance criteria.

12.8.2.2 Continuing instrument calibration verification is performed when the time period for calibration or the most recent calibration verification has expired.

12.8.2.3 Continuing instrument calibration verification is performed for all analytical systems that have a calibration verification requirement.

12.8.2.4 Calibration is verified for each compound, element, or other discrete chemical species.

12.8.2.5 The calculations and associated statistics for continuing instrument calibration are included or referenced in the test method SOP.

12.8.2.6 Sufficient raw data records are retained to allow reconstruction of the continuing instrument calibration verification. Continuing instrument calibration verification records connect the continuing verification date to the initial instrument calibration.

12.8.3 Unacceptable Continuing Instrument Calibration Verifications: If routine corrective action for continuing instrument calibration verification fails to produce subsequent consecutive (immediate) calibration verification within acceptance criteria, then a new calibration is performed or acceptable performance is demonstrated after corrective action with two consecutive calibration verifications.

12.8.3.1 For any samples analyzed on a system with an unacceptable calibration, some results may be useable if qualified and under the following conditions:

12.8.3.1.1 If the acceptance criteria are exceeded high (high bias) and the associated samples are below detection, then those sample results that are non-detects may be reported as non-detects.

12.8.3.1.2 If the acceptance criteria are exceeded low (low bias) and there are samples that exceed the maximum regulatory limit, then those exceeding the regulatory limit may be reported.

12.8.4 Corrective Actions for Calibration – see individual analytical SOPs.

12.9 Major Equipment List: For a list of test equipment in use, refer to Appendix E.

13) Measurement Traceability and Calibration

13.1 Measurement Quality Assurance comes in part from traceability of standards to standard reference materials. To achieve traceability, the following are performed:

13.1.1 All equipment used for generation of test results, including equipment for subsidiary measurements, must be calibrated prior being put into service and on a continuing basis.

13.1.2 Calibration standards must be traceable to certified reference materials of known quality, where available, for the preparation of the calibration standard(s);

13.1.3 For standards in use for calibration, second source standards are also acquired, to verify the calibration standards in use.

13.1.4 SOP HS-QS001 Chemical Purchase & Receipt; Chemical Preparation, Storage & Tracking describes the laboratory procedures for documenting chemical reference standards purchased for use in the laboratory and procedures for tracking chemical standards and solutions prepared in house. ..

The following records be kept for purchased standards:

- Assignment of a unique tracking ID,
- Standard name,
- Manufacturer name or vendor name,
- Certificate of analysis or purity (if available),
- Lot ID,
- Receipt date,
- Expiration date,
- Standard storage requirements are specified in the method SOPs.

13.1.5 The following records are kept for solutions prepared in house:

- An assignment of a unique tracking ID,
- The tracking IDs of stock standards or reagents used in the preparation,
- Amounts and concentration of standards used,
- The final volume and concentration,
- Date prepared
- An assigned expiration data (as per stability of the analyte based on the method,/ manufacturers expiration date, etc) and
- Identification of the analyst associated with the preparation,
- Standard storage requirements are specified in the method SOPs.

13.1.6 When traceability of measurements to SI units is not possible or not relevant, evidence for correlation of results through inter laboratory comparisons, proficiency testing, or independent analysis may be provided.

13.1.7 Equipment used for generation of test results are calibrated according to the minimum frequency identified in the laboratory SOP, as specified by the method, the manufacturer, by regulation, or as needed.

13.1.8 Additionally, clients may further verify a required level of uncertainty is achieved by: a review of internal quality control data, provided as requested by a client;

and through a use of a third party data validation service, to review the data (as requested by a client).

13.1.9 Reference Material requirements for the Metrology equipment (analytical balances, thermometers, etc.) are identified is SOP HS-EQ001 Use and Maintenance of Balances - SOP HS-EQ002 Thermometer Calibration and Temperature Monitoring and SOP HS-EQ003 Lab Volumetric Ware Calibration .

13.1.9.1 SOP HS-EQ001 requires the annual analytical balance service and calibration verification using an outside service. Class 1 weights are used for daily calibration verifications of analytical balance bracketing the range of use. Class 1 weights must be certified every year.

13.1.9.2 SOP HS-EQ002 requires that ASTM Reference thermometers calibrations be verified yearly by a NVLAP calibration laboratory. Thermometers in use for various temperature monitoring activities (e.g. storage refrigerators, drying ovens, etc.) are verified for accuracy annually using the ASTM reference thermometers at temperature bracketing the monitored range.

13.1.9.3 SOP HS-EQ003 requires at least five measurements, and the precision, bias and individual % Recovery calculated and recorded. All volumetric labware shall be initially and thereafter annually inspected for possible defects.

14) Assuring the Quality of Results

14.1 The quality of test results are defined by the use, collection, and monitoring of essential quality control elements of the test procedures. Procedures employed to accomplish this may include the following:

14.1.1 Defining acceptance criteria based upon method defined criteria, which may be static (e.g. ±20%) or statistically derived (e.g. ± 3 standard deviations from a mean). Acceptance criteria for the testing procedures are typically defined by the QC sample type (ICV, CCV, LCS, MS, etc.) and are in general based on either defined method criteria or a statistical method.

- Acceptance criteria and frequency for calibration and calibration verifications by method are found in the associated method SOP or in LIMS.
- Acceptance criteria and frequency for Laboratory Control Samples (LCS) by method are found in the associated method SOP or in LIMS.

14.1.2 Control Charting and Trending

14.1.2.1 The generation of control charts must be performed annually in accord with SOP HS-QS004 Control Charting. Surrogate, Matrix Spike and LCS recoveries are charted updated in LIMS annually. Control charts are available to each individual laboratory unit to monitor the data generated in its facility using control reporting

14.1.2.2 Charts that have been programmed to identify various trends in the analytical results.

14.1.2.3 Trend Analysis: collection of LCS results by the Laboratory LIMS system enables trend monitoring of a method. SOP HS-QS004 Control

Charting provides a procedure to monitor trends to ensure the method remains is control. When a method LCS trend is found to be out of control, a corrective action must be initiated.

14.1.3 Participation in semi-annual Proficiency Test studies (per matrix) provides data to assess the validity of the testing procedures employed.

14.1.4 Replicate tests using the same or different methods.

14.1.5 Retesting of retained samples to confirm analysis

14.1.6 Correlation of results for different characteristics of a sample.

14.1.7 The required use of second source calibration verification standards ensure the quality of reference materials used to prepare calibrations and other quality control samples employed in the testing processes.

14.1.8 All Test and Preparation SOPs define the quality control samples that are required in the test processes, based on the most restrictive requirements of an analytical methods, regulatory requirements, or internally generated QC criteria. When the most restrictive criteria are not apparent, the mandated method or regulatory criteria is employed. These QC samples include:

14.1.8.1 Initial Calibration Standards defined and acceptable calibration models and criteria

14.1.8.2 Initial Calibration Verification and Continuing Calibration criteria and frequency

14.1.8.3 Calibration or instrument blanks acceptance criteria and frequency

14.1.8.4 Method Blanks acceptance criteria and frequency Laboratory Control Samples acceptance criteria and frequency

14.1.8.5 Duplicate acceptance criteria (whether as sample, LCSD or MSD)

14.1.8.6 Interference checks as defined by a method

14.1.8.7 Internal / external calibration criteria as per method

14.1.8.8 Quality of reagents or solvents use to prepare standards and samples

14.1.8.9 Evaluation of method capability through limit of detection evaluation and analyst demonstration of capability

14.1.9 Employment of Positive and Negative control for Testing Procedures – The following are procedures employed as negative or positive:

14.1.9.1 Blanks (negative)

14.1.9.2 Laboratory control sample (positive)

14.1.10 Method Selectivity is assured through:

14.1.10.1 Absolute and relative retention times in chromatographic analyses;

14.1.10.2 Two-column confirmation when using non-specific detectors (e.g. dual ECD);

14.1.10.3 Use of acceptance criteria for mass-spectral tuning (found in test method SOPs);

14.1.10.4 Use of the correct method, according to its scope assessed during method validation.

14.2 Laboratory Quality Control Batch Sample types and typical corrective actions – (see Batch Definitions in Appendix A). These essential Quality Control components are processed in exactly the same manner as field samples.

14.2.1 Method Blanks (MB) –

14.2.1.1 MB is prepared from analyte free water (or other acceptable analyte free matrix)

14.2.1.2 Contaminated blanks are identified according to the acceptance limits in the test method SOPs, typical criteria <1/2 LOQ or < LOQ if a common lab contaminant (e.g. methylene chloride for VOC analysis).

14.2.1.3 When a blank is determined to be contaminated, the cause must be investigated and measures taken to minimize or eliminate the problem.

14.2.1.4 Batch Data that are unaffected by the blank contamination (non-detects or other analytes) are reported unqualified.

14.2.1.5 Batch Sample data that are suspect due to the presence of a contaminated blank are reanalyzed, qualified, or not reportable.

14.2.2 Laboratory Control Samples (LCS)

14.2.2.1 LCS are prepared from analyte free water (or other acceptable analyte free matrix), and spiked with verified and known amounts of analytes for the purpose of establishing precision or bias measurements.

14.2.2.2 LCS are analyzed at a frequency mandated by method, regulation, or client request, whichever is more stringent (1 per batch of 20 or less depending on the method is the practice in the laboratory SOPs as per method).

14.2.2.3 LCS data is calculated in percent recovery that allows comparison to established acceptance criteria.

14.2.2.4 When the LCS does not meet criteria, the cause must be investigated and measures to correct the problem must be taken.

14.2.2.5 For any batch samples analyzed with the unacceptable LCS, some results may be useable if qualified and under the following conditions:

- If the acceptance criteria are exceeded high (high bias) and the associated samples are below detection, then those sample results that are non-detects may be reported as non-detects.
- If the acceptance criteria are exceeded low (low bias) and there are samples that exceed the maximum regulatory limit, then those exceeding the regulatory limit may be reported.

14.2.2.6 For those batch samples having unusable data, reprocessing and reanalysis is required (after the cause of the LCS failure has been corrected),

14.2.2.7 Should re-analysis be an impossibility, any data reported must be

qualified and discussed in the data report narrative to the client

14.2.3 Matrix Spikes and Matrix Spike Duplicates - prepared from a portion of client sample, and spiked with verified and known amounts of analytes for the purpose of evaluating the effect of sample matrix on the test measurements.

14.2.3.1 The MS are analyzed at a frequency mandated by method, regulation, or client request, whichever is more stringent (1 per batch of 20 or less is the practice in the laboratory SOP as per most method).

14.2.3.2 MS are calculated in percent recovery that allows comparison to established acceptance criteria (the LCS criteria is utilized for most methods).

14.2.3.3 When the MS does not meet criteria, it is evaluated in comparison with the LCS to assess whether there is a matrix effect present. A reproducible duplicate MS (the MSD) would assist the confirmation that a matrix effect is likely present.

14.2.3.4 For any batch samples analyzed with the unacceptable MS, like the LCS some results may be useable under the following conditions:

- If the acceptance criteria are exceeded high (high bias) and the associated samples are below detection, then those sample results that are non-detects may be reported as non-detects.
- If the acceptance criteria are exceeded low (low bias) and there are samples that exceed the maximum regulatory limit, then those exceeding the regulatory limit may be reported.

14.2.3.5 All batch samples associated with a MS outside of criteria are identified for the client or program data usability decisions. The cause of an MS exceedance may be due to many reasons, most often due to an interference present that is not easily removed by a practice stated in the method. In these cases, the data is reported with the qualified MS results and noted on a laboratory data review checklist exception report.

14.2.4 Duplicates - prepared from a portion of client sample, for the purpose of evaluating method precision.

14.2.4.1 The duplicate is analyzed at a frequency mandated by method, regulation, or client request, whichever is more stringent (1 per batch of 20 or less is the practice in the laboratory SOP as per most methods). The duplicate may take the form as a duplicate, a matrix spike duplicates (MSD), or a laboratory control sample duplicate, depending on the availability of additional sample and the type of test method.

14.2.5 Surrogate Spikes - Surrogates are substances with chemical properties and behaviors similar to the analytes of interest used to assess method performance in individual samples.

14.2.5.1 Surrogates are added to all samples (in test methods where surrogate use is appropriate) prior to sample preparation or extraction.

14.2.5.2 Surrogate recovery results are compared to the acceptance criteria as

established in the test method SOP or from program guidance (CLP or DOD) or from laboratory established limits.

14.2.5.3 For surrogate results outside established criteria, data is evaluated to determine the impact. Corrective actions include reprocessing and reanalysis to determine whether a matrix effect is present, qualifying the data and/or narrating the occurrence on the data review checklist exception report.

14.3 Proficiency Test Samples - The laboratory participates in proficiency test (PT) studies twice a year. These studies include all applicable fields of proficiency testing and are obtained from an approved proficiency test provider.

14.3.1.1 The laboratory does not share PT samples with other laboratories, does not communicate with other laboratories regarding current PT sample results, and does not attempt to obtain the assigned value of any PT sample from the PT provider.

14.3.1.2 Proficiency Testing (PT) samples are treated as typical samples in the normal production process where possible, including the same preparation, calibration, quality control and acceptance criteria, sequence of analytical steps, number of replicates, and sample log-in. PT samples are not analyzed multiple times unless routine environmental samples are analyzed multiple times.

14.3.1.3 The laboratory initiates corrective action procedures for any unacceptable PT result. Additionally, the laboratory must successfully complete two of the most recent three proficiency tests for each field of proficiency testing. In the event that this requirement is not met, the laboratory institutes corrective action procedures, including participation in 2 supplemental PT studies to demonstrate corrective action. Supplemental PT studies are performed at least 15 days apart from each other.

- For a PT studies, a “Not Acceptable” result for any analyte on two of the most recent PT studies results in a “Fail” score for that analyte.

14.4 Data Review - The laboratory reviews all data generated in the laboratory, hardcopy and electronic, for compliance with method, and, whereapplicable, client requirements. Procedures for Data Reduction, Review and Validation are described in SOP HS-QS009.. In general, the procedure includes:

14.4.1.1 Initial analyst calibration, and applicable batch QC data (method blank, LCS, MS, Duplicate, etc,), including the raw data and calculated data entered into the lab LIMS. Batch QC limits by method are stored in LIMS to facilitate checks for meeting Batch QC acceptance limits by method. The LIMS also contains LOQ and LOD information along with upper calibration limits by method, to facilitate accurate evaluation of detections against the method applicability range for reporting, to ensure required dilutions were performed and reported correctly, when necessary. The initial process includes the use of LIMS QC Checking tools that the analyst and any later peer reviewer can use to evaluate whether reportable client data entered in LIMS is correctly referenced (or linked) to the correct supporting QC data. A Data Assessment checklist is prepared during the initial review of the data by the analyst.

14.4.1.2 A second peer review is performed by a qualified analyst or supervisor. The same LIMS QC checks are reviewed and include search for the required QC sample types to assure that all supporting QC data are present in LIMS for evaluation against the QC acceptance criteria stored in LIMS for each test performed. A nominal 10 % of the raw data is reviewed to verify the correct data has been calculated and entered correctly.

14.4.1.3 QC exceedances are identified in LIMS by the application of the appropriate data qualifying flags. The data qualifying flags may either initiate corrective actions for nonconforming data and/or require supporting comment information to be entered into LIMS batch report or entered into the batch data review checklist exception report

14.4.1.4 Comments for data flags are documented in LIMS and in the batch data review checklist exception report for inclusion in the project Case Narrative, as necessary.

14.4.1.5 A Final Project Manager review of the data is performed to review the data for completeness against any client specified requirements, evaluate the reasonableness of results and prepare a narrative to discuss any anomalies associated with assigned data flags.

14.4.1.6 QA Department reviews data as appropriate and during internal method audits.

15) Control of Non-Conforming Environmental Testing Work

Non-conforming work is work that does not meet acceptance criteria or requirements. Non-conformances can include unacceptable quality control results or departures from standard operating procedures or test methods. Requests for departures from laboratory procedures are approved by Quality Assurance Manager or the Technical Director and documented, see SOP HS-GEN005, Departures from Approved Procedures.

The policy for control of non-conforming work is to identify the non-conformance, determine if it will be permitted, and take appropriate action. All employees have the authority to stop work on samples when any aspect of the process does not conform to laboratory requirements.

The responsibilities and authorities for the management of non-conforming work are detailed in SOP HS-QS003 Nonconformance Corrective Action Reporting.
The laboratory evaluates the significance of the nonconforming work, and takes corrective action immediately, when necessary. The client is notified if their data has been impacted. Resumption of work after non-conformance is authorized by the Quality Assurance Manager or the Technical Director.

For nonconforming work performed by vendors for example calibrations, the nonconforming items are checked and deviations if any recorded by the personnel who requested the test. Tested items that do not conform to specifications will not be used in the performance of analysis for any lab data.

16) Corrective Action and Preventive Action.

16.1 Corrective action is the action taken to eliminate the causes of an existing non-conformity, defect, or other undesirable situation in order to prevent recurrence.

16.1.1 Deficiencies cited in external assessments, internal quality audits, data reviews, customer feedback/complaints, control of nonconforming work or managerial reviews are documented and require corrective action. Corrective actions taken are appropriate for the magnitude of the problem and the degree of risk.

16.1.2 Any of the Technical Staff (e.g. an analyst, supervisor or project manager) may initiate a corrective action when performing a routine data review. All deficiencies are investigated and a corrective action plan developed and implemented if determined necessary. The implementation may be monitored for effectiveness. Corrective action reporting for routine, non-recurring exceedances can be records in logbooks, email, or other informal documents. More serious corrective actions require a more formal corrective action report that is reported to the QA department for monitoring as per SOP HS-QS003 Nonconformance Corrective Action Reporting The QA Manager is responsible for monitoring and recording corrective actions in these cases. Specific corrective action protocols specified in test methods may over-ride general corrective action procedures specified in this manual.

16.1.3 Selection and Implementation of Corrective Actions: Once an exceedance or nonconformance is noted, the first action is an investigation to determine the root cause. The root cause is investigated to define the condition or event that, if corrected or eliminated, would prevent the recurrence of the noted deficiency. Based on the root cause investigation potential corrective actions, most likely to prevent recurrence of the nonconformance, are identified. Records are maintained of non conformances requiring corrective action to show that the root cause(s) was investigated, and includes the results of the investigation where uncertainty arises regarding the best approach for analysis of the cause of an exceedance that require corrective action, the appropriate personnel (e.g. The Technical Director or a Department Supervisor) will recommend corrective action to be initiated and completed within the agreed upon time frame.

16.1.4 Monitoring of Corrective Action: Corrective actions are monitored to ensure the successful implementation of changes in laboratory processes as a result of a corrective action plan. Monitoring is executed by the QA Manager, in cooperation with the Department Supervisor. Department supervisors are responsible for monitoring corrective actions associated with routine laboratory activities, including implementation of procedural changes as stated in the appropriate SOP. Serious corrective actions, those related to systematic problems, are monitored by the QA Manager. All monitoring of Corrective Actions is documented through the NCAR database. .

16.1.5 Additional Audits: Additional audits are required when non conformances or departures cast doubt on the laboratory's compliance with approved policies and procedures, or with standards on which these policies and procedures are based (i.e., TNI Standard, or DOD Standard). These audits are conducted as soon as possible according to SOP HS-QS012 Internal Auditing.

16.1.6 Technical Corrective Actions: A cause analysis in corrective action investigates

the root cause of the problem. Sample data associated with an exceeded quality control are evaluated for the need to be reanalyzed or qualified. Unacceptable quality control results are documented, and if the evaluation requires cause analysis, the cause and solution are recorded. The analyst is responsible for initiating or recommending corrective actions and ensuring that exceedances of quality control acceptance criteria are documented. Analysts routinely implement corrective actions for data with unacceptable QC measures. First level correction may include re-analysis without further assessment. If the test method SOPs addresses the specific actions to take, they are followed. Otherwise, corrective actions start with assessment of the cause of the problem. Area supervisors review corrective action results and suggest improvements, alternative approaches, and procedures where needed. If the data reported are affected adversely by the nonconformance, the client is notified in writing. The discovery of a non-conformance for results that have already been reported to the client must be immediately evaluated for significance of the non-conformance, its acceptability to the client, and determination of the appropriate corrective action. Where possible, samples are reported only if all quality control measures are acceptable. Where unacceptable, quality control measures must be reported, all sample associated with the failing control measures are reported with the appropriate data qualifiers.

16.1.7 Departures from Approved Procedures: SOP HS-GEN005, Departures from Approved Procedures allows exceptionally permitting departures from documented policies and procedures, the laboratory allows the release of non-conforming data only with approval by the Technical Director or his designee on a case-by-case basis (e.g. meeting a client specification). Planned departures from procedures or policies do not require audits or investigations. Permitted departures for non-conformances, such as QC exceedances, are fully documented and include the reason for the departure, the affected SOP(s), the impact of the departure on the data, and the data. Refer to.

16.2 Preventative action is a pro-active process to identify opportunities for improvement, rather than a reaction to the identification of problems or complaints. The process maximizes the quality of service provided by the laboratory.

16.2.1 Opportunities for improvement and potential sources of non conformances, either technical or concerning the quality system, are proactively identified through various actions including, but not limited to, review of QC data to identify quality trends (SOP HS-QS004 Control Charts), regularly scheduled staff quality meetings (SOP HS-GEN-006 Resource Review), and annual managerial reviews (SOP HS-QS017 Management Review), scheduled instrument maintenance (SOP HS-EQ004 Preventative Maintenance), running a new LIMS system in tandem with the old system to assure at least one working system (SOP HS-IT002 Computer Software Installation and Maintenance) and other actions taken to prevent problems.

16.2.2 Once potential preventive actions are identified, an action plan is developed, implemented, and monitored to reduce the likelihood of the nonconformance occurrence and to tack advantage of the opportunity for improvement.

16.2.3 All employees have the authority to recommend preventive action procedures, however management is responsible for implementing and monitoring the effectiveness of preventive actions.

17) Control of Records

Laboratory records are a subset of documents, usually data recordings that include annotations, such as daily refrigerator temperature recordings, raw data entered laboratory logbooks, spreadsheets, analyst notes on a chromatogram, and copies of test reports, etc. Records may be on any form of media, including electronic and hard copy. Records allow for the historical reconstruction of laboratory activities related to sample handling and analysis.

17.1 Records Maintained

Records of all procedures to which a sample is subjected while in the possession of the laboratory are kept. The laboratory retains all original observations, calculations and derived data (with sufficient information to produce an audit trail), calibration records, personnel records and a copy of the test report for a minimum of ten (10) years from generation of the last entry in the records. At a minimum, the following records are maintained by the laboratory to provide the information needed for historical reconstruction:

All raw data, whether hard copy or electronic, for calibrations, samples and quality control measures, including analysts' worksheets and data output records (chromatograms, strip charts, and other instrument response readout records);

17.1.1 A written description or reference to the specific method(s) used, which includes a description of the specific computational steps used to translate parametric observations into a reportable analytical value (a copy of all pertinent Standard Operating Procedures);

17.1.2 Laboratory sample ID code;

17.1.3 Date of analysis;

17.1.4 Time of analysis is required if the holding time is seventy-two (72) hours or less, or when time critical steps are included in the analysis (e.g., extractions and incubations);

17.1.5 Instrumentation identification and instrument operating conditions/parameters (or reference to such data);

17.1.6 All manual calculations (including manual integrations);

17.1.7 Analyst's or operator's initial/signature or electronic identification;

17.1.8 Sample preparation, including cleanup, separation protocols, ID codes, volumes, weights, instrument printouts, meter readings, calculations, reagents;

17.1.9 Test results (including a copy of the final report);

17.1.10 Standard and reagent origin, receipt, preparation, and use;

17.1.11 Calibration criteria, frequency and acceptance criteria;

17.1.12 Data and statistical calculations, review, confirmation, interpretation, assessment and reporting conventions;

17.1.13 Quality control protocols and assessment;

17.1.14 Electronic data security, software documentation and verification, software and hardware audits, backups, and records of any changes to automated data entries;

17.1.15 Method performance criteria including expected quality control requirements;

17.1.16 Proficiency test results;

17.1.17 Records of demonstration of capability for each analyst;

17.1.18 Record of names, initials, and signatures for all individuals who are responsible for signing or initialing any laboratory record;

17.1.19 Correspondence relating to laboratory activities for a specific project;

17.1.20 Corrective action reports;

17.1.21 Preventive action records;

17.1.22 Copies of internal and external audits including audit responses;

17.1.23 Copies of all current and historical laboratory SOPs, policies and Quality Manuals, both electronic and original hard copies;

17.1.24 Sample receiving records (including information on any inter laboratory transfers);

17.1.25 Sample storage records;

17.1.26 Data review and verification records;

17.1.27 Personnel qualification, experience and training records;

17.1.28 Archive records; and

17.1.29 Management reviews.

17.2 Records Management and Storage

These procedures are described in more detail in Laboratory SOPs HS-QS11 for Record Archival Procedures and HS-QS01, Documents and Records. Document Control and Laboratory Records. These procedures require that all records, as either hard copy or electronic, be maintained for a period of at least ten (10) years. The records are stored in secure storage to protect them from deterioration or damage and to protect client confidentiality. In the event that the laboratory transfers ownership or goes out of business, records are maintained or transferred according to the clients' instructions. All electronic records are backed-up daily by the IT Department. Access to protected records is limited to laboratory management or their designees to prevent unauthorized access or amendment.

17.3 Legal Chain of Custody Records are managed when projects request the use of internal chain of custody procedures as described in SOP HS-SM001 Sample Log-in Procedures.

18) Audits

Audits measure laboratory performance and verify compliance with accreditation/ certification and project requirements. Audits specifically provide management with an on-going assessment of the quality system. They are also instrumental in identifying areas where improvement in the quality system will increase the reliability of data. Audits are of four main types: internal, external, performance, and system.

18.1 Internal Audits – The laboratory periodically conducts internal audits in all areas of the laboratory to ensure that its operations continue to comply with the requirements of the Quality System as well as requirements of the standards on which the Quality System is based. The internal audit reviews laboratory conformance in two areas: quality system procedures and analytical method procedures. A quality system audit reviews general laboratory cleanliness, employee training documentation, support systems, equipment and facilities maintenance and repair records, sample handling and record-keeping practices. Analytical method evaluations include a review of how analysts perform preparation and analysis steps in conformance to approved laboratory standard operating procedures. All areas of the quality system must be conducted annually at a minimum, but any area assessments may be performed monthly or quarterly until all areas are performed. Should an area be found in nonconformance, a corrective action must be designated to the responsible individuals. Upon completion of the corrective action, re-auditing must be performed as verification.

It is the responsibility of the Quality Manager to plan and organize audits as required by the schedule and requested by management. These audits are carried out by trained and qualified personnel who are, wherever resources permit, independent of the activity to be audited.

18.1.1 Analytical method audits must be conducted in a manner such that each department is audited at least once annually for at least one analytical method that is routinely performed and is representative of the majority of methods performed by that department. After an audit is performed, a report is generated and given to management and each supervisor of the department audited. This report includes the findings and observations and the recommendations for improvement or correction. Time-lines for responses and corrections are provided so they may be addressed in a timely fashion. The supervisors of each area provide responses to any findings with demonstration of corrections as needed.

18.1.2 An annual inspection/audit of the LIMS is performed by the quality manager or designee to ensure the quality of electronic data. Checks are done by hand calculating data, with the objective of arriving at at the same result as LIMS. This calculation report is signed and stored by the QA department.

18.1.3 When an audit finding casts doubt on the effectiveness of the operation or on the correctness or validity of test results, the laboratory shall notify affected clients in writing within seven days.

18.1.4 All investigations that result in findings of inappropriate activity are documented and include any disciplinary actions, corrective action and appropriate notifications of clients.

18.2 External Audits - It is the laboratory's policy to cooperate and assist with all external audits, whether performed by a client or an accrediting authority. All external audits are

fully documented and tracked to closure. Management ensures that all areas of the laboratory are accessible to auditors as applicable and that appropriate personnel are available to assist in conducting the audit. Any findings related to an external audit follow corrective action procedures. Management ensures that corrective actions are carried out within the timeframe specified by the auditor(s).

18.3 Performance Audits - Performance audits may be Proficiency Test Samples, double-blind samples through a provider or client, or anything that tests the performance of the analyst and method.

18.3.1 TNI Proficiency Test (PT) samples are scheduled twice annually for each TNI field of accreditation per matrix. The PT samples tested are purchased from a TNI approved PT provider. The results assess analyst proficiency when conducting analyses for specific analyte(s) on a matrix specific basis. PT sample management, analysis and reporting of PT sample results are to be conducted in the same manner as real environmental samples utilizing the same staff and methods as used for routine analysis. This requires use of the same procedures, equipment, facilities, and frequency of analysis.

18.3.2 PT sample results are forwarded by QA Manager or designee to the PT provider via the provider supplied reporting format (i.e. fax, mail or internet reporting). After closing of a PT study, results are evaluated by the provider and reported directly to the primary TNI Accrediting Authority (TCEQ) and secondary TNI Accrediting Authorities when required (e.g. LDEQ), to other non-TNI State Accrediting Authorities as required, and to the laboratory. All recent results of the PT studies are posted in the laboratory and made available to the staff and interested clients. For those results that deviate from the accepted values, a nonconformance corrective action (NCAR) must be issued to the appropriate departmental supervisor or analyst to investigate and report the findings. The NCAR process typically requires analysis of another PT to verify the adequacy of the corrective action. The QA Department maintains records of the corrective action PT and related documents. The results of PT corrective actions and corrective action PT are reported to the accrediting authority as required by the respective program. Corrective PT studies are sent directly to all respective accrediting authorities

18.4 System Audits

The Laboratory's management system is audited though annual management reviews. Refer to Sections 19 – "Management Review" and SOP CE-QA001 Internal Audits for further discussion of systems audits.

18.5 Handling Audit Findings

18.5.1 Internal or external audit findings are responded to within the time frame agreed to at the time of the audit. The response may include action plans that could not be completed within the response time frame. A completion date is established by management for each action item and included in the response.

18.5.2 The responsibility for developing and implementing corrective actions to findings is the responsibility of the Quality Assurance Manager or the

Technical Director. Corrective actions are documented through the corrective action process described in Section 16 – "Corrective Actions".

18.5.3 Audit findings that cast doubt on the effectiveness of the laboratory operation to produce data of known and documented quality or that question the correctness or validity of sample results must be investigated. Corrective action procedures described in SOP HS-QS003 Nonconformance Corrective Action Reporting must be followed. Clients must be notified in writing if the investigation shows the laboratory results have been negatively affected and the client's requirements have not been met. The client must be notified within one business day after the laboratory discovers the issue. Laboratory management will ensure that this notification is carried out within the specified time frame.

18.5.4 All investigations that result in findings of inappropriate activity are documented and include any disciplinary actions involved, corrective actions taken, and all appropriate notifications of clients

19) Management Review

Top management reviews the management system on an annual basis and maintains records of review findings and actions.

19.1 Management Review Topics

The following are reviewed to ensure their suitability and effectiveness:

- Changes in internal and external issues that are relevant to the laboratory
- Fulfilment of objectives
- The suitability of policies and procedures;
- Status of actions from previous management reviews
- Reports from managerial and supervisory personnel;
- The outcome of recent internal audits;
- Corrective and preventive actions;
- Assessments by external bodies;
- The results of inter laboratory comparisons or proficiency tests;
- Changes in the volume and type of the work;
- Customer and personnel feedback;
- Complaints;
- Recommendations for improvement;
- Effectiveness of any implemented improvements
- Results of risk identification
- Outcomes of he assurance of the validity of results
- Other relevant factors, such as quality control activities, resources, and staff training.

19.2 Procedure

The procedure for Management Review can be found in SOP HS-QS017. Findings and follow-up actions from management reviews are recorded. Management will determine

appropriate completion dates for action items and ensure they are completed within the agreed upon time frame.

20) Personnel

ALS employs competent personnel based on education, training, experience and demonstrated skills as required. The laboratory's organization chart can be found in Appendix B.

20.1 Overview

20.1.1 All personnel are responsible for complying with all quality and data integrity policies and procedures that are relevant to their area of responsibility.

20.1.2 All personnel who are involved in activities related to sample analysis, evaluation of results or who sign test reports, must demonstrate competence in their area of responsibility. Appropriate supervision is given to any personnel in training and the trainer is accountable for the quality of the trainees work. Personnel are qualified to perform the tasks they are responsible for based on education, training, experience and demonstrated skills as required for their area of responsibility.

20.1.3 The laboratory provides goals with respect to education, training and skills of laboratory staff. Training needs are identified at the time of employment and when personnel are moved to a new position or new responsibilities are added to their job responsibilities. Ongoing training, as needed, is also provided to personnel in their current jobs. The effectiveness of the training must be evaluated before the training is considered complete.

20.1.4 An overview of top management's responsibilities are included in Section 3 – "Management". Job descriptions include the specific tasks, minimum education and qualifications, skills, and experience required for each position. Job description for staff not in management can be found in their individual personnel folder.

20.2 Training

Employees are required to understand that any infractions of the laboratory data integrity procedures shall result in a detailed investigation that could lead to very serious consequences including immediate termination, debarment or civil/criminal prosecution. This is discussed in the Ethics and Data Integrity Policy that every employee is required to sign annually. Attendance for required training is monitored through a signature attendance sheet.

The following topics are covered:

- Organizational mission and its relationship to the critical need for honesty and full disclosure in all analytical reporting
- How and when to report data integrity issues
- Record keeping
- Training, including discussion regarding all data integrity procedures
- Data integrity training documentation
- In-depth data monitoring and data integrity procedure documentation
- Specific examples of breaches of ethical behavior such as improper data manipulations, adjustments of instrument time clocks, and inappropriate changes in concentrations of standards.

20.2.1 SOP-HS-QS013 Employee Training requires all analysts to be trained in the elements of this QA Manual, and that they must sign a method qualification statement that they have read, understand and agree to follow the technical SOPs they perform.. This information must be on file in the QA department after completion and it the responsibility of each departmental supervisor that these items are completed and approved.

20.2.2 All personnel are appropriately trained and competent in their assigned tasks before they contribute to functions that can affect data quality. It is management's responsibility to assure personnel are trained. Training records are used to document management's approval of personnel competency. The date on which authorization and/or competence is confirmed is included.

Training records are maintained by the Quality Assurance Manager and include Demonstrations of Capability (Initial and Continuing), Experience Documentation, and Ongoing Training. Ongoing Training

Staff members are given the following ongoing training:

20.2.2.1 All staff members are given refresher data integrity training and are required to sign off on the Ethics and Data Integrity Policy. The training is documented on a training attendance sheet that outlines what was covered during the training.

20.2.2.2 The employee attests, through signature, that they have read, understood, and agree to perform the latest version of the Quality Manual and any SOPs or policies that the analyst is responsible for following.

20.2.2.3 Annually, the analyst shows continued proficiency in each method they perform by Continuing Demonstration of Capability or by passing a Performance Evaluation Sample, see Section 12.2

20.3 Ethics and Data Integrity Training

20.3.1 Data integrity and ethics training, signed, and dated integrity documentation for all laboratory employees, periodic monitoring of data integrity, and documented data integrity procedures.

20.3.2 SOP CE-GEN001 Laboratory Ethics and Data Integrity Procedures- provides

guidance and direction for employees when generating laboratory data and a thorough understanding of what constitutes an improper, unethical or illegal action and consequences of such action. The ethics policy specifically defines employee responsibility and accountability with the following being required of all personnel:

20.3.2.1 ALS Group USA, Corp employees shall at all times conduct themselves and the business of the Company in an honest and ethical manner.

20.3.2.2 ALS Group USA, Corp employees shall comply with the terms of the ethics agreement, and as a condition of employment is required to sign the Ethics Agreement.

20.3.2.3 The willful act of improper manipulation or falsification of data will not be tolerated and is subject to punitive measures up to and including dismissal and subsequent legal action.

20.3.2.4 Observance of unethical behavior shall be immediately reported to a supervisor, a manager, or the QA Manager. Failure to report such activity is considered to be in support of the unethical activity and shall be dealt with in those terms.

20.3.2.5 The ethics agreement shall be posted in a common area.

20.3.2.6 Unauthorized release of confidential information about the Company or its customers shall be subject to disciplinary action, up to and including dismissal and subsequent legal action.

20.3.3 Employees are trained to understand that improper or unethical actions are serious matters that can have a very negative effect on the laboratory. The actions can result in any of the following: potential civil or criminal liability for ALS Group USA, Corp and employees; cost in time and resources of defending data before auditors; loss of client trust; loss of business and potential fines and imprisonment of employees involved. In order to maintain the integrity and reputation of ALS Group USA, Corp, it is most important that all the data released in projects be as factual as possible. Therefore, misrepresentation of any data by an ALS Group USA, Corp employee is not allowed. Any employee who knowingly releases false data values will be subject to disciplinary action, up to an including possible termination of employment and legal action.

20.3.4 Periodic monitoring of data integrity is performed by the QA department when performing laboratory data audits as part of SOP HS-QS012 Internal Audits or at any time by the QA Department should an inappropriate action be suspected or a lack of proper training be evident. In addition to periodic monitoring QA will on a periodic based perform an in-depth monitoring following the procedure in the process that includes items such as preparation, equipment, software, calculations and quality control.

20.3.5 Documented data integrity procedures are part of training provided in SOP HS-QS016 Manual Integration Policy and SOP HS-QS009 Data Reduction, Review and Validation.

21) Reporting of Results

Data are reported without qualification if they are greater than the lowest calibration standard, lower than the highest calibration standard, and without compromised sample or method integrity (all supporting QC assessments meet stated requirements per method).

21.1 Test Reports - The report format has been designed to accommodate each type of test performed and to minimize the potential for misunderstanding or misuse. Each test report generated contains the following information:

21.1.1 Report Cover Letter, includes the following: client name, address, date of issue for the cover letter, project reference,

21.1.1.1 The ALS Laboratory Work Order Number

21.1.1.2 Report introduction for samples submitted, stating the number of samples received and date(s) of receipt, for the analysis presented in the report

21.1.1.3 The statement like "the analytical data provided relates directly to the samples received at ALS Group USA, Corp and for only the analysis requested"

21.1.1.4 The statement like "Results are expressed "as received" unless otherwise noted."

21.1.1.5 The statement like "QC sample results for this data met laboratory specifications except as noted in the Case Narrative or as noted with qualifiers in the QC batch information. Should this laboratory report need to be reproduced, it should be reproduced in full unless written approval has been obtained by ALS Group USA, Corp. Samples will be disposed in 30 days unless storage arrangements are made. The total number of pages in this report is 16".

21.1.1.6 Signature of the Project Manager (this may be electronic)

21.1.1.7 TNI Accreditation ID (e.g. Texas TNI Certificate Number or other applicable state accreditation ID)

21.1.1.8 Non-accredited tests and analytes must be clearly identified in reports.

21.1.1.9 Lab Name as ALS Group USA, Corp, full physical address (same as on QA Manual)

21.1.1.10 Lab Phone and Fax Number (same as on the QA Manual)

21.1.1.11 ALS Group USA, Corp world wide web site address

21.1.2 Sample Summary Table

- Client Name
- Project Name
- ALS Laboratory Work Order Number
- Date of issue for the Summary Table
- TNI Accreditation ID or other applicable state accreditation ID
- Work Order Sample Summary to indicate for each sample received -

- Lab Sample ID
- Client Sample ID
- Date & Time of Sample Collection
- Date & Time of Sample Receipt
- Sample Analysis Hold Status (check as either yes or no)

21.1.3 Case Narrative, or client required laboratory data review checklist, if required to further describe any qualified data reported – the narrative references the following:

- Client Name
- Project Name
- ALS Laboratory Work Order Number
- Date of issue for the Narrative Report
- TNI Accreditation ID or other applicable state accreditation ID
- A discussion of the qualified data reported

21.1.4 Each Analytical Report includes the following information:

- Client Name
- Project Name
- ALS Laboratory Work Order Number
- Date of issue for the Analytical Report
- Client Sample ID
- ALS Laboratory Sample ID
- Date & Time of Sample Collection
- Sample matrix identification
- Analytical Report paginated as "AR page X of Y"
- Identification of each test performed and name of analyte reported for that test
  - Method Reference
  - Analyte Name(s)
  - Test Result and unit
  - Reporting Limit (aka LOQ) for analyte
  - LOD for analyte if required in client reporting format
  - Dilution factor(s) associated with reported result(s)
  - Surrogate result and % recovery, if applicable
  - Date of test preparation, if applicable
  - Date of test analysis
  - Initials of Analyst
  - Data Qualifiers defined on Analytical Report - ND, J, B, *, S, P, E, H, where:
    - ND = not detected at Reporting Limit
    - J = analyte detected below quantitation limits
    - B = analyte detected in the associated method blank
    - * = value exceeds Maximum Contaminant Level
    - S = Spike Recovery outside accepted recovery limits
    - P = Dual column results percent difference > 40%
    - E = Value above quantitation range
    - H = Analyzed outside Hold Time
    - a = accredited by the applicable State Authority (optional)

- n = accreditation not offered by the State Authority (optional)

21.1.5 QC Batch Report - a report of applicable batch QC samples (method blank, LCS, MS, Duplicate, etc.) by batch ID, test method and matrix

- Client Name
- Project Name
- ALS Laboratory Work Order Number
- Date of issue for the QC Batch Report
- Batch ID, Instrument ID and Method – the following are reported
  - QC sample ID (method blank, LCS, MS, etc.)
  - QC sample PQL (reporting limit)
  - QC sample result (value of a blank, LCS or MS)
  - QC sample reference value (e.g. background sample result for and MS)
  - QC sample dilution factor
  - QC Spike Level (e.g. applicable to LCS, MS, MSD sample types)
  - Calculated % Recovery for LCS or MS, MSD
  - Applicable control limits for LCS or MS & MSD or Duplicate (as RPD)
  - IDs of samples associated with the Batch ID (sequentially assigned by LIMS)
  - Applicable Batch QC data qualifiers - ND, J, B, *, S, P, E, H, O & R
  - ND = not detected at Reporting Limit
  - J = analyte detected below quantitation limits
  - B = analyte detected in the associated method blank
  - * = value exceeds a regulatory limit (e.g. an MCL or client permit value)
  - S = Spike Recovery outside accepted recovery limits
  - P = Dual column results percent difference > 40%
  - E = Value above quantitation range
  - H = Analyzed outside Hold Time
  - O = Referenced analyte is >4 times amount spiked
  - R = RPD outside accepted limits

21.1.6 Chain of Custody documents –see example in SOP HS-SM001 Appendix 22.1

21.1.7 Sample Receipt Checklist – see example in SOP HS-SM001 Appendix 22.2

21.1.8 Subcontractor analytical results are presented, in their entirety, as an attachment to the final report.

21.1.9 Amending Report for Correction or Additional Testing.

21.1.9.1 Amended reports must be clearly identified as an amended report and which revision on each page of the final report.

21.1.9.2 Case narrative must include reason for amending the report, see SOP HS-ADM003 Work Order Reporting.

21.2 Supplemental Test Report Information

When necessary for interpretation of the results or when requested by the client, test reports include the following additional information:

21.2.1 deviations from, additions to, or exclusions from the test method, information on specific test conditions, such as environmental conditions, and any non-standard conditions that may have affected the quality of the results, and any information on the use and definitions of data qualifiers;

21.2.2 a statement of compliance/non-compliance when requirements of the management system are not met, including identification of test results that did not meet the laboratory and regulatory sample acceptance requirements, such as holding time, preservation, etc.;

21.2.3 where applicable and when requested by the client, a statement on the estimated uncertainty of the measurement;

21.2.4 where appropriate and needed, opinions and interpretations. When opinions and interpretations are included, the basis upon which the opinions and interpretations are documented. Opinions and interpretations are clearly marked as such in the test report.

21.2.5 additional information which may be required by specific methods or client;

21.2.6 qualification of results with values outside the calibration range as appropriate.

21.3 A statement of compliance/non-compliance when requirements of the quality systems are not met, including identification of test results that do not meet TNI sample acceptance requirements, such as holding time, preservation, etc., are included in the project narrative;

21.3.1 When requested by the client, a statement on the estimated uncertainty of the measurement is included in the project narrative as per SOP HS-QS019 Estimation of Measurement Uncertainty .

21.4 Electronic Transmission of Results

All test results transmitted by telephone, fax, telex, e-mail, or other electronic means comply with the requirements of the TNI Standard and associated procedures to protect the confidentiality and proprietary rights of the client. Electronic Data Deliverables are provided to the client as needed and as defined by the client.

21.5 Advertising Policy

21.5.1 ALS's TNI accredited laboratories can use the TNI accredited logo by adherence to the following:

21.5.1.1 Where the TNI name and/or logo is used on general literature such as letterhead and advertisement, it shall always be accompanied by the word "accredited".

21.5.1.2 While there are no restrictions on the size and color of the TNI accredited logo reproduction, the logo must maintain its form.

21.5.1.3 The TNI accredited logo may be generated electronically provided that the prescribed formats and forms are retained.

21.5.1.4 When promoting or providing proof of accreditation, accredited laboratories should use the scope(s) of accreditation, as this document details the specific tests which are accredited. The certificate should be used for display purposes and may also accompany the scope.

21.5.1.5 When the TNI accredited logo is used to endorse test results, it shall always be accompanied by the TNI accreditation number(s).

21.5.1.6 When the TNI accredited logo is used on a business solicitation document such as a proposal or quotation form, the laboratory has the responsibility to distinguish between those proposed tests that fall within the laboratory's scope of accreditation and those that do not. This is done by attaching a copy of the current TNI Scope of Accreditation sheet and Supplement to the Scope, if appropriate, or by noting which tests or calibration is non-accredited.

21.5.1.7 The TNI accredited logo and/or reference to the laboratory's accreditation may be made in advertisements provided the requirements of this document are strictly followed.

21.5.1.8 Upon suspension or termination of accreditation, a laboratory must immediately cease to issue test reports displaying the logo and shall cease publishing documents containing the logo.

21.5.2 ALS's PJLA accredited laboratories can use the PJLA accredited logo by adherence to the following:

21.5.2.1 ALS must fully comply with the most current revision of PJLA SOP-3 Accreditation Symbol Procedure.

21.5.2.2 Upon suspension or termination of accreditation, a laboratory must immediately cease to issue test reports displaying the logo and shall cease publishing documents containing the logo.

22) Continuous Improvements

22.1 ALS Environmental routinely engages in quality improvement through ongoing use of internal systems and evaluation of external feedback. Senior management supports this policy by making continuous improvement one of the ALS Core Values, see SOP CE-GEN 016 Continuous Quality Improvement Policy.

22.1.1 Management Role

ALS management is committed to improvement of the management and quality systems through compliance with its own policies and procedures; and evolving these policies and procedures as needed.

Senior management, Laboratory Directors, and laboratory management teams support improvement activities and processes. Improvement is effected through ongoing management review and evaluation of improvement opportunities and using available input.

22.1.2 Quality System Role

Quality systems are designed to meet the requirements of various certification and accreditation protocols and standards, as well as various program and project requirements. As these requirements change or new ones become

applicable, ALS will pursue improvements to the quality systems and protocols as warranted.

As part of the quality system several procedures and policies are in place which include a component of improvement. Quality programs at ALS laboratories will ensure that these procedures and policies are implemented.

22.2 Improvement in the overall effectiveness of the laboratory management system is a result of the implementation of the various aspects of the laboratory's management system: quality policy and objectives (QAM Section 3 – "Management"); internal auditing practices (SOP HS-QS012 Internal Audits); the review and analysis of data (SOPHS-QS009 S Data Reduction, Review and Validation); the corrective action (SOP HS-QS003Nonconformance Corrective Action Reporting) and preventive action (QAM Section 16 – "Preventative Action") process; and the annual management review of the quality management system (SOP HS-QS017 Management Review) where the various aspects of the management/quality systems are summarized, and evaluated and plans for improvement are developed.

23) Management of Change

23.1 This procedure is to be utilized by ALS-Environmental USA laboratories where required by certification or accreditation, project specifications, or contract to make changes in a planned or systematic way, to reduce negative impacts upon the organization, staff, and clients. See SOP CE-GEN015 Management of Change for policy and produces.

23.1.1.1 Changes to be managed may lie within the organization and controlled by the organization; or may be internal changes that have been triggered by external events originating outside the organization, over which we have little or no control (e.g. regulatory changes, actions of competitors, or technological changes)..

23.1.1.2 The scale and potential impact of the proposed change will indicate whether or not the use of this procedure is required. For example, purchase and introduction of a new pH meter would have little impact on the laboratory; whereas purchase and introduction of instrumentation not previously used could have a major impact on the laboratory (i.e. training required, allocation of laboratory space, changes to sample preparation and work procedures etc.) and therefore would require implementation of this procedure.

24) Summary of Changes and Document History

Revision Number	Effective Date	Document Editor	Description of Changes
11.6	09/11/2020	E. Marinez	Update subsections for 21.5 Advertizing Policy to remove references to L-A-B and replace with proper references to PJLA.
11.6	09/11/2020	E. Marinez	Appendix J Laboratory Accreditations and Scopes Update Certificate numbers, where

Revision Number	Effective Date	Document Editor	Description of Changes
			applicable. Remove ANAB certificate and scope. Replace with PJLA certificate and scope.
11.6	9/11/2020	E. Marinez	Section 25 References Update references to current versions where applicable. Remove any references to ANAB. Insert references to PJLA.
11.6	9/11/2020	E. Marinez	Appendices updated to most current lists and information, where applicable.
11.5	12/21/2019	G. Moulton	Sec 8.1: The laboratory collaborates with clients and/or their representatives in clarifying their requests and in monitoring of the laboratory performance related to their work. Each request is reviewed to determine the nature of the request and the laboratory's ability to comply with the request within the confines of prevailing statutes and/or regulations without risk to the confidentiality of other clients.
11.5	12/21/2019	G. Moulton	Sec 8.1.1: The laboratory actively seeks client feedback, both positive and negative, to identify areas of improvement within the quality system, testing activities and service to the client.
11.5	12/21/2019	G. Moulton	Sec 8.1.2: The laboratory will clarify requests if the customer has specified incorrect, obsolete, or improper methods.
11.5	12/21/2019	G. Moulton	Sec 8.1.3: The laboratory will notify customers when methods require modifications to ensure achievement of project-specific objectives contained in planning documents (e.g., difficult matrix, poor performing analyte).
11.5	12/21/2019	G. Moulton	Sec 8.1.4: The laboratory will communicate with customers when project planning documents (e.g., QAPP or Sampling and Analysis Plan (SAP)) are missing or requirements (e.g., action levels, detection and quantification capabilities) in the documents require clarification.
11.5	12/21/2019	G. Moulton	Sec 8.1.5: The laboratory will notify customers when a problem has been encountered with sampling or analysis that may impact results (e.g., improper preservation of sample).
11.5	12/21/2019	G. Moulton	Sec 19.1 Updated elements of a management review added new elements from ISO 17025.
11.4	12/21/2018	G. Moulton	Updated cover and quality manager
11.4	12/21/2018	G. Moulton	Split QAM into two sections to allow for the Appendices to be upldated regularly without affecting the body of the QAM.

Revision Number	Effective Date	Document Editor	Description of Changes
11.4	12/21/2018	G. Moulton	Revised numbering for sections 1.3.1 to 1.3.3, 2.1.1 to 2.1.3, 3.1.1 to 3.1.11.6, 3.5.2.1 to 3.5.2.5, 3.5.3.1 to 3.5.5.1, 3.7.1 to 4.2, 4.7.1 to 4.7.2, 5.1 to 10.4, 11.2.2.1 to 11.2.2.12.1, 11.2.4.2 to 11.4.1 , 12.3.3.1TO 12.3.3.4, 12.5.4.1 to 12.5.4.3, 12.8.1.1 to 12.8.2.6, 12.8.3.1 to 12.8.3.1.2. 13.1.9.1 to 13.1.9.3, 14.1.8.1 to 14.4.1.6, 16.1 to 16.1.2, 16.2 to 16.2.3, 17.1.1 to 17.1.29, 18.5.1 to 18.5.4, 20.1.1 to 20.1.4, 20.2.2.1 to 20.2.2.3, 20.3.2.1 to 20.3.2.6, 21.1.1.1 to 21.1.1.11, 25.1 to 25.1.22.
11.4	12/21/2018	G. Moulton	Appendices: Removed resumes, Updated Org chart, Added signatories for reports, Updated External documents list, Updated SOP list, Added certs with expiration dates. 18.1.2 Added LIMS inspection.
11.4	12/21/2018	G. Moulton	Modified sec. 2.2 (added responsible individual Hoai Van). 2.4: agreements and impartiality. sec: 3.2.7 (sample management Supervisor). Modified 3.4 Quality policy. 3.5.4.5, modified 3.7.(elements of a SOP). Modified sec 4.5, and 4.6.1 update and location of controlled doc.Modified sec 5.3 add SOP HS-GEN009 and current version of DOD QSM, Modified sec 9.2, 9.3 and 9.4 To improve complaint resolution. Modified 10.5: added sec 10.5, sec 11.1 (coc for evidentiary purpose), Inserted SOP HS-HS019, 12.5.2 (Inserted sop HS-QS009). 12.5.4 (Inserted sop HS-IT007), Modified 12.6.6 IT Secutity. Modified sec 13.1.9.1 (bracketing range of use, weights certified every year). Sec 20.1.4: included where staff job descriptions can be found.
11.4	12/21/2018	G. Moulton	Reworded sec 10.3 (power loss), reworded last line of sec 12.2 (IDOC requirement). 12.3.1 and 12.3.2 (LODs/LOQ analyzed on a quarterly basis)
11.4	12/21/2018	G. Moulton	Added sec 8.2.6 and 8.2.7 – Client confidentiality.
11.4	12/21/2018	G. Moulton	Removed last two sentences of 10.4
11.4	12/31/17	T. Yen	3.5.4 - 3.5.5 Ethics and Data Integrity Investigation and Notification.

Revision Number	Effective Date	Document Editor	Description of Changes
11.3	06/19/2017	T. Yen	General review.
11.3 – Section 4.4.3	06/19/2017	T. Yen	Preparation and Management of SOP
11.3 – Section 6	06/19/2017	T. Yen	Subcontracted testing procedure consolidated
11.3 – Section 11	06/19/2017	T. Yen	Sample Management procedures
11.3 – Sections 20.3 & 3.5	06/19/2017	T. Yen	Ethic and Data Integrity moved to Section 20.3 and 3.5.
11.3 Section 12.6.5	06/19/2017	T. Yen	Validation of New Equipment Identification
11.3 Sections 12.6.7 & 12.6.8	06/19/2017	T. Yen	Out of Service Equipment
11.3 – Section 12.6.9	06/19/2017	T. Yen	Equipment status documentation.
11.3 – Section 12.8.2	06/19/2017	T. Yen	Continuing Calibration Blanks (CCB)
11.3 – Sections 17.1 & 17.2	06/19/2017	T. Yen	Record retention standardized to 10 years
11.3 – Section 21.1.9	06/19/2017	T. Yen	Procedure of amending report for correction or additional testing.
11.3 – Section 25	06/19/2017	T. Yen	References update.
11.3 – Section Appendix G 11.3 Appendix A	06/19/2017 06/19/2017	T. Yen T. Yen	Master SOP update. Acronym Update-Add Management of Change
11.3 – Section 22	06/19/2017	T. Yen	New section on Continuous Improvements

Revision Number	Effective Date	Document Editor	Description of Changes
11.3-Section 23	06/19/2017	T. Yen	New Section on Management of Change
11.2	11/30/2016	T. Yen	Minor revision, update to certificates, staff and equipment list.
11.2 – Section 9.0	11/30/2016	T. Yen	Online survey procedure.
11.2 – Appendices	11/30/2016	T. Yen	Appendices updated.
11.1	7/31/2015	T. Yen	Minor revision, update to certificates, staff and equipment list.
11.1- Section 2.2	7/31/2015	T. Yen	SOP HS-GEN002 changed to CE-GEN001
11.1- Appendix J	7/31/2015	T. Yen	TX Cert updated to new version T104704231-15-15.
11.1- Appendix J	7/31/2015	T. Yen	LDEQ Cert update July1, 2015 – June 30, 2016.
11.0	2/28/2015	T. Yen	Minor revision, update to certificates, staff and equipment list.
10.0	2/28/2015	T. Yen	QAM format and sections.
10.0	2/28/2015	T. Yen	References for TCEQ QAPP 2014, DOD QSM 5.0, TNI 2009 updated
10.0 – Section 4.5	2/28/2015	T. Yen	Electronic Signature Policy added to QAM.
10.0 – Section 16.14.3	2/28/2015	T. Yen	QA in depth data monitoring.
10.0 – Section 21.1.1	2/28/2015	T. Yen	Non-accredited tests and analytes must clearly identified in reports.
10.0 Appendix J	2/28/2015	T. Yen	Primary TNI certificate insert to document accredited testing methods and compounds.
09.2 09.1	11/19/2012 07/15/2012	T. Yen J. Cady	Management of Change in Appendix G Minor Revision – Utilized updated TNI acronym. Updated Organizational chart, Equipment list, SOP list, and Accreditation list. Logo policy included.
09.0	08/05/2011	J. Cady	Major Format Revision to 2009 TNI Standard
08.1	03/31/2011	I. Williams	Applied new document format. Deleted the following appendices: F-MDL/PQL G-LCS Limits

25) References for Quality System Standards, External Documents, Manuals, and Test Procedures

25.1 The following list represents key references for the laboratory quality program and systems.

25.1.1 TNI Standard – Environmental Laboratory Sector, Volume 1, Modules 1- Modules 7, Management and Requirements for Laboratories Performing Environmental Analysis, EL-V1M1-2011 thru EL-V1M7-2011, 2009/2016

25.1.2 International Standard – General Requirements for the Competence of Testing and Calibration Laboratories, ISO/IEC 17025:2017(E)

25.1.3 Selected USEPA Approved Methods, 40 CFR, Part 136 including changes incorporated in the Methods Update Rule (MUR) published February 19, 2015.

25.1.4 USEPA Methods published in Appendix A, B and C of 40 CFR, Part 136.

25.1.5 Standard Methods for the Examination of Water and Wastewater, 18th through Current Editions, Hard copy and/or Electronic Version.

25.1.6 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition, through Updates III (December 1996) and Update IV (February 2007), and new published methods online at http://www.epa.gov/epaoswer/hazwaste/test/sw846.htm.

25.1.7 Selected USEPA Drinking Water methods published by the USEPA Office of Ground Water and Drinking Water

25.1.8 Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, (Revised March 1983).

25.1.9 Methods for the Determination of Inorganic Substances in Environmental Samples, EPA/600/R-93/100 (August 1993).

25.1.10 USEPA SW-846 Test Methods for Evaluating Solid Waste, 3rd Edition, through Updates III and VI, and published new methods from SW-846 (e.g. SW8270E).

25.1.11 *Methods for the Determination of Metals in Environmental Samples*, EPA/600/4-91/010 (June 1991) and Supplements.

25.1.12 *Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater*,

25.1.13 EPA 600/4-82-057.

25.1.14 *Methods for the Determination of Organic Compounds in Drinking Water*,

25.1.15 EPA/600/4-88/039 and Supplements.

25.1.16 Selected APHA, AWWA, and ASTM methods.

25.1.17 *DoD Quality Systems Manual for Environmental Laboratories,* Current version

25.1.18 *Manual for the Certification of Laboratories Analyzing Drinking Water*, 5th Edition, EPA 815-B-97-001 (January 2005).

25.1.19 US EPA Region 9 QC Database, epa.gov/region9/qa/datatables.html.

25.1.20 State approved UST methods for TPH (e.g. TPH by TCEQ1005, Rev 3, June 2001).

25.1.21 TCEQ Quality Assurance Project Plan For Environmental Monitoring and Measurement Activities Relating to the Resource Conservation and Recovery Act (RCRA) & Underground Injection Control (UIC), Current Fiscal Year.

25.1.22 Perry Johnson Laboratory Accreditation, Inc. (PJLA), SOP-3 Accreditation Symbol Procedure Revision 1.7, October 2019.

26) Appendices

APPENDIX A – Glossary

The following are a list of acronyms used in this document and their definitions

AB	-	Accrediting Body
ANSI	-	American National Standards Institute
ASQC	-	American Society for Quality Control
ASTM	-	American Society for Testing and Materials
Blk	-	Blank
˚C	-	Degrees Celsius
cal	-	Calibration
CAS	-	Chemical Abstract Service
CCV	-	Continuing Calibration Verification
CoA	-	Certificate of Analysis
COC	-	Chain of Custody
DO	-	Dissolved Oxygen
DOC	-	Demonstration of Capability
DoD	-	Department of Defense
EPA	-	Environmental Protection Agency
g/L	-	Grams per Liter
GC/MS	-	Gas Chromatography/Mass Spectrometry
ICAL	-	Initial Calibration
ICP-MS	-	Inductively Coupled Plasma-Mass Spectrometry
ICV	-	Initial Calibration Verification
ISO/IEC	-	International Organization for Standardization/International Electrochemical Commission
lb/in2	-	Pound per Square Inch
LCS	-	Laboratory Control Sample
LCDS	-	Laboratory Control Duplicate Sample
LFB	-	Laboratory Fortified Blank
LOD	-	Limit of Detection
LOQ	-	Limit of Quantitation
MOC	-Management of Change	

MDL	-	Method Detection Limit
mg/kg	-	Milligrams per Kilogram
mg/L	-	Milligrams per Liter
MS	-	Matrix Spike
MSD	-	Matrix Spike Duplicate
NELAC	-	National Environmental Laboratory Accreditation Conference
NELAP	-	National Environmental Laboratory Accreditation Program
NIST	-	National Institute of Standards and Technology
PT	-	Proficiency Test(ing)
PTP	-	Proficiency Testing Provider
PTPA	-	Proficiency Testing Provider Accreditor
QA	-	Quality Assurance
QAD	-	Quality Assurance Department
QAM	-	Quality Assurance Manager
QC	-	Quality Control
QM	-	Quality Manual
RL	-	Reporting Level
RPD	-	Relative Percent Difference
RSD	-	Relative Standard Deviation
SOPs	-	Standard Operating Procedures
SPK	-	Spike
STD	-	Standard
SV	-	Semi-Volatile (Organic Compound)
TNI	-	The NELAC Institute
ug/L	-	Micrograms per Liter
UV	-	Ultraviolet
VOC	-	Volatile Organic Compound

For the purpose of this Standard, the relevant terms and definitions conform to ISO/IEC 17011:2004 and ISO/IEC 17025: 2017. Additional relevant terms are defined below.

Accreditation Body: The territorial, state or federal agency having responsibility and accountability for environmental laboratory accreditation and which grants accreditation.
Accreditation Field of Proficiency Testing: Same as "Field of Proficiency Testing".
Analysis Date: The calendar date of analysis associated with the analytical result reported for an accreditation or experimental field of proficiency testing.

Experimental Field of Proficiency Testing (Experimental FoPT): Analytes for which a laboratory is required to analyze a PT sample if they seek or maintain accreditation for the field of accreditation but for which successful analysis is not required in order to obtain or maintain accreditation.
Field of Accreditation: Those matrix, technology/method, and analyte combinations for which the accreditation body offers accreditation.
Field of Proficiency Testing (FoPT): Analytes for which a laboratory is required to successfully analyze a PT sample in order to obtain or maintain accreditation, collectively defined as: matrix, technology/method, analyte.
Primary Accreditation Body (Primary AB): The accreditation body responsible for assessing a laboratory's total quality system, on-site assessment, and PT performance tracking for fields of accreditation.
Proficiency Testing (PT): A means to evaluate a laboratory's performance under controlled conditions relative to a given set of criteria, through analysis of unknown samples provided by an external source.
Proficiency Testing Program (PT Program): The aggregate of providing rigorously controlled and standardized environmental samples to a laboratory for analysis, reporting of results, statistical evaluation of results and the collective demographics and results summary of all participating laboratories.
Proficiency Testing Provider (PTP): A person or organization accredited by the TNI-approved Proficiency Testing Provider Accreditor to operate a TNI-compliant PT program.
Proficiency Testing Provider Accreditor (PTPA): An organization that is approved by TNI to accredit and monitor the performance of proficiency testing providers.
Proficiency Testing Sample (PT Sample): A sample, the composition of which is unknown to the laboratory and is provided to test whether the laboratory can produce analytical results within the specified acceptance criteria.
Proficiency Testing Study (PT Study): A single complete sequence of circulation of proficiency testing samples to all participants in a proficiency test program.
PT Study Closing Date: The calendar date for which analytical results for a PT sample shall be received by the PT provider from the laboratory.
PT Study Opening Date: The calendar date that a PT sample is first made available to any laboratory by a PT provider.
Revocation: The total or partial withdrawal of a laboratory's accreditation by an accreditation body.
Study: This term refers to a PT Study or Supplemental PT Study.
Supplemental Proficiency Testing Study (Supplemental PT Study): A PT sample that may be from a lot previously released by a PT Provider that meets the requirements for supplemental PT samples given in Volume 3 of this Standard but that does not have a pre-determined opening date and closing date.
Suspension: The temporary removal of a laboratory's accreditation for a defined period of time, which shall not exceed six (6) months or the period of accreditation, whichever is longer, in order to allow the laboratory time to correct deficiencies or area of non-conformance with the Standard.
TNI PT Board: A board consisting of TNI members or affiliates, appointed by the TNI Board of Directors, which is responsible for the successful implementation and operation of the TNI Proficiency Testing Program. The duties of the TNI PT Board are defined in the TNI PT Board Charter.
Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.
Accreditation: The process by which an agency or organization evaluates and recognizes a laboratory as meeting certain predetermined qualifications or standards, thereby accrediting the laboratory.
Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components that are due to sampling and analytical operations; a data quality indicator.

Analyst: The designated individual who performs the "hands-on" analytical methods and associated techniques and who is the one responsible for applying required laboratory practices and other pertinent quality controls to meet the required level of quality.
Analytical Uncertainty: A subset of Measurement Uncertainty that includes all laboratory activities performed as part of the analysis.
Assessment: The evaluation process used to measure or establish the performance, effectiveness, and conformance of an organization and/or its systems to defined criteria (to the standards and requirements of laboratory accreditation).
Audit: A systematic and independent examination of facilities, equipment, personnel, training, procedures, record-keeping, data validation, data management, and reporting aspects of a system to determine whether QA/QC and technical activities are being conducted as planned and whether these activities will effectively achieve quality objectives.
Batch: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one (1) to twenty (20) environmental samples of the same quality systems matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be twenty-four (24) hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.
Bias: The systematic or persistent distortion of a measurement process, which causes errors in one direction (i.e., the expected sample measurement is different from the sample's true value).
Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results. Blanks include:
Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.
Calibration: A set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring instrument or measuring system, or values represented by a material measure or a reference material, and the corresponding values realized by standards.

1) In calibration of support equipment the values realized by standards are established through the use of reference standards that are traceable to the International System of Units (SI).
2) In calibration according to methods, the values realized by standards are typically established through the use of Reference Materials that are either purchased by the laboratory with a certificate of analysis or purity, or prepared by the laboratory using support equipment that has been calibrated or verified to meet specifications.

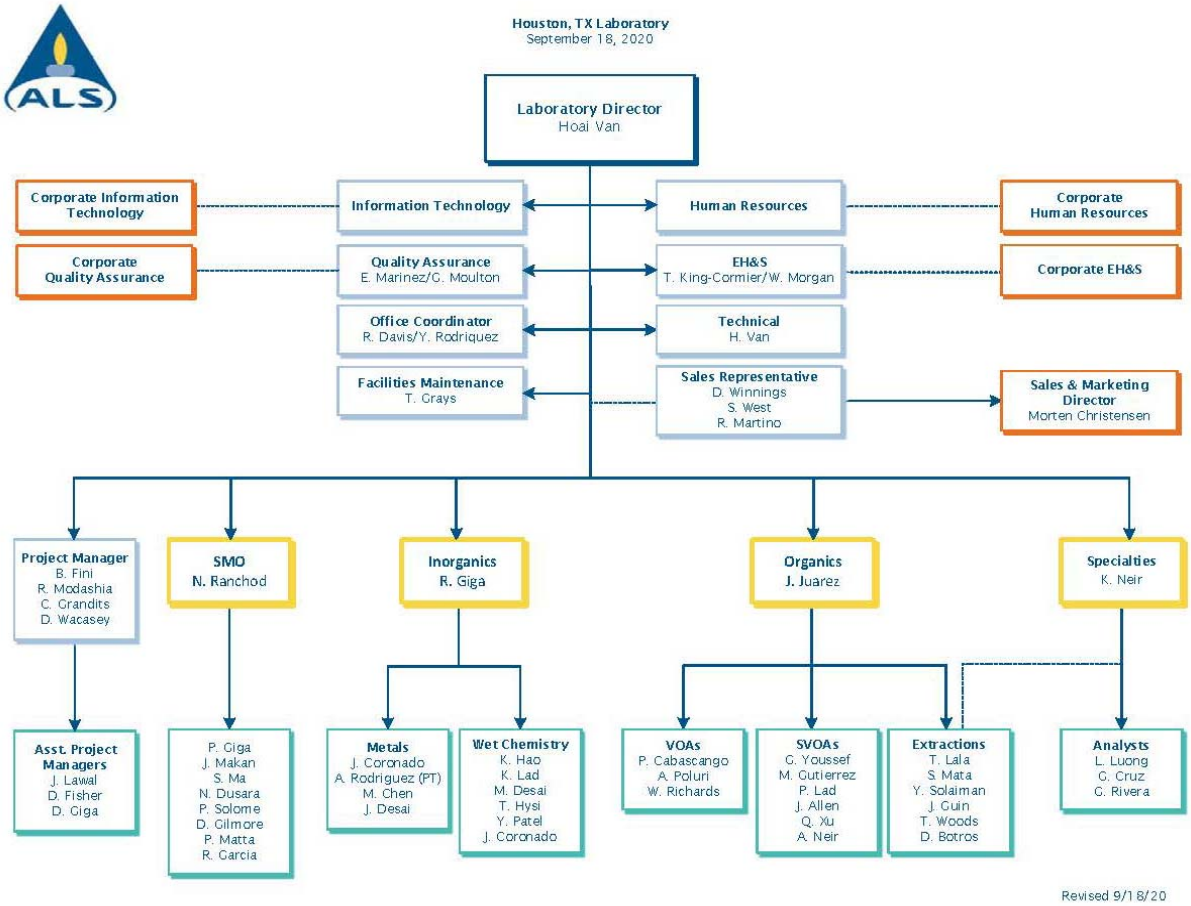
Calibration Curve: The mathematical relationship between the known values, such as concentrations, of a series of calibration standards and their instrument response.
Calibration Standard: A substance or reference material used for calibration.
Certified Reference Material (CRM): Reference material accompanied by a certificate, having a value, measurement uncertainty, and stated metrological traceability chain to a national metrology institute.
Chain of Custody Form: Record that documents the possession of the samples from the time of collection to receipt in the laboratory. This record generally includes: the number and types of containers; the mode of collection; the collector; time of collection; preservation; and requested analyses.
Confirmation: Verification of the identity of a component through the use of an approach with a different scientific principle from the original method. These may include, but are not limited to:

Second column confirmation, Alternate wavelength, Derivatization, Mass spectral interpretation, Alternative detectors, or Additional cleanup procedures.
Data Reduction: The process of transforming the number of data items by arithmetic or statistical calculation, standard curves, and concentration factors, and collating them into a more useful form.
Demonstration of Capability: A procedure to establish the ability of the analyst to generate analytical results of acceptable accuracy and precision.
Field of Accreditation: Those matrix, technology/method, and analyte combinations for which the accreditation body offers accreditation.
Finding: An assessment conclusion referenced to a laboratory accreditation standard and supported by objective evidence that identifies a deviation from a laboratory accreditation standard requirement.
Holding Times: The maximum time that can elapse between two specified activities.
Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.
Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes and taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a reference method. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system.
Legal Chain of Custody Protocols: Procedures employed to record the possession of samples from the time of sampling through the retention time specified by the client or program. These procedures are performed at the special request of the client and include the use of a Chain of
Custody Form that documents the collection, transport, and receipt of compliance samples by the laboratory. In addition, these protocols document all handling of the samples within the laboratory.
Limit(s) of Detection (LOD): A laboratory's estimate of the minimum amount of an analyte in a given matrix that an analytical process can reliably detect in their facility.
Limit(s) of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence.
Matrix: The substrate of a test sample.
Matrix Duplicate: A replicate matrix prepared in the laboratory and analyzed to obtain a measure of precision.
Matrix Spike (spiked sample or fortified sample): A sample prepared, taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a referenced method, by adding a known amount of target analyte to a specified amount of sample for which an independent test result of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.
Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.
Measurement System: A method, as implemented at a particular laboratory, and which includes the equipment used to perform the test and the operator(s).
Method: A body of procedures and techniques for performing an activity (e.g., sampling, chemical analysis, quantification), systematically presented in the order in which they are to be executed.
Mobile Laboratory: A portable enclosed structure with necessary and appropriate accommodation and environmental conditions for a laboratory, within which testing is performed by analysts. Examples include but are not limited to trailers, vans, and skid-mounted structures configured to house testing equipment and personnel.
National Institute of Standards and Technology (NIST): A federal agency of the US Department of Commerce's Technology Administration that is designed as the United States national metrology institute (NMI).

Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.
Preservation: Any conditions under which a sample must be kept in order to maintain chemical and/or biological integrity prior to analysis.
Procedure: A specified way to carry out an activity or process. Procedures can be documented or not.
Proficiency Testing: A means of evaluating a laboratory's performance under controlled conditions relative to a given set of criteria through analysis of unknown samples provided by an external source.
Proficiency Testing Program: The aggregate of providing rigorously controlled and standardized environmental samples to a laboratory for analysis, reporting of results, statistical evaluation of the results and the collective demographics and results summary of all participating laboratories.
Proficiency Test Sample (PT): A sample, the composition of which is unknown to the laboratory and is provided to test whether the laboratory can produce analytical results within the specified acceptance criteria.
Protocol: A detailed written procedure for field and/or laboratory operation (e.g., sampling, analysis) which must be strictly followed.
Quality Assurance: An integrated system of management activities involving planning, implementation, assessment, reporting, and quality improvement to ensure that a process, item, or service is of the type and quality needed and expected by the client.
Quality Control: The overall system of technical activities that measures the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by the customer; operational techniques and activities that are used to fulfill requirements for quality; also the system of activities and checks used to ensure that measurement systems are maintained within prescribed limits, providing protection against "out of control" conditions and ensuring that the results are of acceptable quality.
Quality Control Sample: A sample used to assess the performance of all or a portion of the measurement system. One of any number of samples, such as Certified Reference Materials, a quality system matrix fortified by spiking, or actual samples fortified by spiking, intended to demonstrate that a measurement system or activity is in control.
Quality Manual: A document stating the management policies, objectives, principles, organizational structure and authority, responsibilities, accountability, and implementation of an agency, organization, or laboratory, to ensure the quality of its product and the utility of its product to its users.
Quality System: A structured and documented management system describing the policies, objectives, principles, organizational authority, responsibilities, accountability, and implementation plan of an organization for ensuring quality in its work processes, products (items), and services. The quality system provides the framework for planning, implementing, and assessing work performed by the organization and for carrying out required quality assurance (QA) and quality control (QC) activities.
Quality System Matrix: These matrix definitions are to be used for purposes of batch and quality control requirements:
Air and Emissions: Whole gas or vapor samples including those contained in flexible or rigid wall containers and the extracted concentrated analytes of interest from a gas or vapor that are collected with a sorbent tube, impinger solution, filter, or other device.
Aqueous: Any aqueous sample excluded from the definition of Drinking Water or Saline/Estuarine. Includes surface water, ground water effluents, and TCLP or other extracts.
Biological Tissue: Any sample of a biological origin such as fish tissue, shellfish, or plant material. Such samples shall be grouped according to origin.
Chemical Waste: A product or by-product of an industrial process that results in a matrix not previously defined.

Drinking Water: Any aqueous sample that has been designated a potable or potential potable water source.
Non-Aqueous Liquid: Any organic liquid with <15% settleable solids.
Saline/Estuarine: Any aqueous sample from an ocean or estuary, or other salt water source such as the Great Salt Lake.
Solids: Includes soils, sediments, sludges and other matrices with >15% settleable solids.
Raw Data: The documentation generated during sampling and analysis. This documentation includes, but is not limited to, field notes, electronic data, magnetic tapes, untabulated sample results, QC sample results, print outs of chromatograms, instrument outputs, and handwritten records.
Reference Material: Material or substance one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials.
Reference Standard: Standard used for the calibration of working measurement standards in a given organization or at a given location.
Sampling: Activity related to obtaining a representative sample of the object of conformity assessment, according to a procedure.
Selectivity: The ability to analyze, distinguish, and determine a specific analyte or parameter from another component that may be a potential interferent or that may behave similarly to the target analyte or parameter within the measurement system.
Sensitivity: The capability of a method or instrument to discriminate between measurement responses representing different levels (e.g., concentrations) of a variable of interest.
Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of standard setting and meets the approval requirements of standard adoption organizations procedures and policies.
Standard Operating Procedures (SOPs): A written document that details the method for an operation, analysis, or action, with thoroughly prescribed techniques and steps. SOPs are officially approved as the methods for performing certain routine or repetitive tasks.
Technology: A specific arrangement of analytical instruments, detection systems, and/or preparation techniques.
Traceability: The ability to trace the history, application, or location of an entity by means of recorded identifications. In a calibration sense, traceability relates measuring equipment to national or international standards, primary standards, basic physical constants or properties, or reference materials. In a data collection sense, it relates calculations and data generated throughout the project back to the requirements for the quality of the project.
Verification: Confirmation by examination and objective evidence that specified requirements have been met. NOTE: In connection with the management of measuring equipment, verification provides a means for checking that the deviations between values indicated by a measuring instrument and corresponding known values of a measured quantity are consistently smaller than the maximum allowable error defined in a standard, regulation or specification peculiar to the management of the measuring equipment. The result of verification leads to a decision either to restore in service, to perform adjustment, to repair, to downgrade, or to declare obsolete. In all cases, it is required that a written trace of the verification performed shall be kept on the measuring instrument's individual record.

APPENDIX B – Organization Charts and Approved Signatories for Reports



Approved Signatories for Reports

Hoai Van	Technical Manager/Lab Director
Erica Marinez	Quality Manager
Bernadette Fini	Project Manager
Raj Modashia	Project Manager
Dane Wacasey	Project Manager
Corey Grandits	Project Manager

APPENDIX C – Ethics and Data Integrity Agreement

ETHICS AND DATA INTEGRITY AGREEMENT

I state that I understand the high standards of integrity required of me with regard to the duties I perform and the data I report in connection with my employment at ALS.

I agree that in the performance of my duties at ALS:

1. I shall not intentionally report data values that are not the actual values obtained;

2. I shall not intentionally report the dates, times and method citations of data analyses that are not the actual dates, times and method citations of analyses;

3. I shall not intentionally represent another individual's work as my own;

4. I shall not intentionally report data values that do not meet established quality control criteria as set forth in the Method and/or Standard Operating Procedures, or as defined by company policy.

5. I agree to inform ALS of any accidental or intentional reporting of non-authentic data by other employees.

6. I have read this ethics and data integrity agreement and understand that failure to comply with the conditions stated above will result in disciplinary action, up to and including termination.

7. I agree to adhere to the following protocols and principals of ethical conduct in my work at ALS. All work assigned to me will be performed using ALS approved methods and procedures and in compliance with the quality assurance protocols defined in the ALS Quality System.

8. I will not intentionally falsify nor improperly manipulate any sample or QC data in any manner. Furthermore, I will not modify data values unless the modification can be technically justified through a measurable analytical process or method acceptable to ALS. All such modifications and their justification will be clearly and thoroughly documented in the raw data and appropriate laboratory record, and will include my initials or signature and the date.

9. I will not make false statements to, or seek to otherwise deceive ALS staff, managers or clients. I will not knowingly, through acts of commission, omission, erasure or destruction, improperly report any test results or conclusions, be they for client samples, QC samples, or standards.
10. I will not condone any accidental or intentional reporting of unauthentic data by other ALS staff and will immediately report such occurrences to my Supervisor, Lab Director, Quality Assurance Manager, or Human Resources. I understand that failure to report such occurrences may subject me to immediate discipline, including termination.

11. If a supervisor, manager, director or other member of the ALS leadership group requests me to engage in or perform an activity that I feel is compromising data validity or defensibility, I have the right to not comply with the request. I also have the right to appeal this action through an ALS local Quality Staff, Corporate Quality Assurance or Human Resources.

12. I understand that if my job includes supervisory responsibilities, I will not instruct, request or direct any subordinate to perform any unethical or non-defensible laboratory practice. Nor will I discourage, intimidate or inhibit a staff member who may choose to appropriately appeal my supervisory instruction, request or directive that may be perceived to be improper, nor retaliate against those who do so.

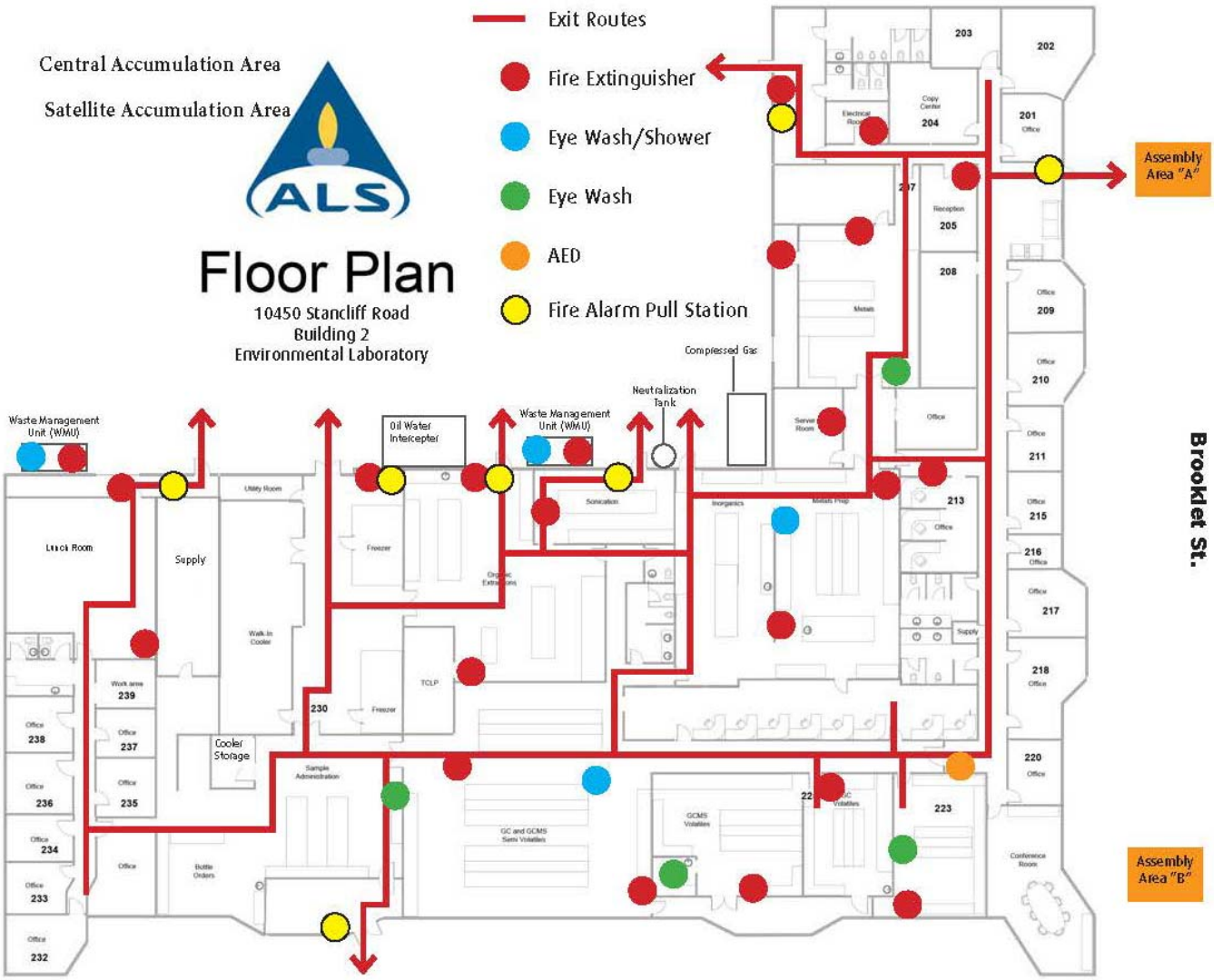
13. I understand that employees who report violations of this policy will be kept free from intimidation and recrimination arising from such reporting.

I have read, and understand the above policy and realize that failure to adhere to it may result in disciplinary action, up to and including termination. Compliance with this policy will be strictly enforced with all personnel employed by the company.

Employee Name _____ Signature _____

ALS Location_____ Date _____

APPENDIX D – Laboratory Floor Plan



APPENDIX E – Analytical Equipment

Equipment	Manufacturer	Model	Year Purchased	Location	Condition
10' x 15' Walk-in Freezer	Hussmann/Tappan	Walk-in Freezer	12/1999	CS	Good
10' x 35' Walk-in Refrigerator		Walk-in Refrigerator	07/2005	CS	Good
13' x 40' Walk-in Refrigerator	Thermo-Kool	Walk-in Refrigerator	04/2007	CS	Good
6' x 10' Walk-in Refrigerator	NorLake	Walk-in Refrigerator	12/1999	CS	Good
Freezer		Freezer	2009	CS	Good
Refrigerator		Refrigerator	01/2000	CS	Good
3-D Shaker	Glass-col	3-D Shaker	01/2002	EXT	Good
Centrifuge	Beckman-Coulter	Avanti JHC	09/2014	EXT	Good
Centrifuge	International Equip. Corp	Clinical Centrifuge	01/2000	EXT	Good
Drying Oven	Fisher Scientific	Drying Oven	2009	EXT	Good
Furnace	Thermodyne	Furnace	07/2008	EXT	Good
GPC	OI	Analytical Autoprep 2000	06/2002	EXT	Good
Heating Stir Plate	Corning	PC420D		EXT	Good
Magnetic Stirrer (1 units)	VWR	Standard High Volume Stirrer		EXT	Good
Magnetic Stirrer (2 units)	Labline	Multi Magnetic	01/2000	EXT	Good
Microwave Extractor	CEM	Mars 6	03/2014	EXT	New
Multi Tube Vortex	Fisher Scientific	Muti Tube Vortex	01/2010	EXT	Good
Nitrogen Evaporator (2 units)	Organomation	N-Evap	01/2001	EXT	Good
pH Meter	Mettler Toledo	FiveEasyPlus		EXT	Good
Pressure Filter (3 units)	Millipore	Pressure Filter		EXT	Good
Refrigerator/Freezer	GE	Refrigerator/Freezer	02/2003	EXT	Good
Refrigerators (2 units)	Various	Various	06/2001	EXT	Good
Sonicator, Ultrasonic with Sonabox	Misonix / Sonabox	Ultrasonic Processor, XL2020 / Sound Enclosure	02/2011	EXT	Excellent
Soxtec Extraction (1 unit)	Soxtec	Model 2055 (Tot. Ext. Capacity = 6)	06/2002	EXT	Good
Soxtec Extraction (3 units)	Soxtec	Model 2055 (Tot. Ext. Capacity = 6)	07/2008	EXT	Good
TCLP Tumbler (4 units)	Environmental Express	ZHE Extractor	01/2002	EXT	Good
Top Loading balance (3 units)	Ohaus	ScoutPro 200g	11/2008	EXT	Good
Turbo Vap II (1 unit)	Caliper Life Sciences	Turbo Vap II	03/2010	EXT	Good
Turbo Vap II (1 unit)	Caliper Life Sciences	Turbo Vap II	10/2011	EXT	Excellent
Turbo Vap II (1 unit)	Caliper Life Sciences	Turbo Vap II	04/2013	EXT	Excellent

Equipment	Manufacturer	Model	Year Purchased	Location	Condition
Turbo Vap II (1 unit)	Caliper Life Sciences	Turbo Vap II	03/2006	EXT	Good
Ultra Sonic Bath	VWR	Ultra Sonic Bath	10/2010	EXT	Good
Ultra sonic Bath	Branson	2200	12/1999	EXT	Good
Vortex Mixer	Thermolyne	MaxiMin		EXT	Good
Water Bath	Precision	Water Bath	01/2000	EXT	Good
ZHE Extractors (32 units)	Millipore	ZHE	02/2009	EXT	Good
Analytical balance	Mettler	AE 200	01/2000	GCSV	Good
Centrifuge	Beckman-Coulter	Allegra X-12	01/5005	GCSV	Good
ECD Detector (2 Spare)	Agilent			GCSV	Good
ECD Micro Detector (2 Spare)	Agilent			GCSV	Good
Freezer	GE	Freezer	10/2010	GCSV	Good
Freezer	Kenmore	Freezer	04/2002	GCSV	Good
GC Dual ECD (ECD 5 & 6)	HP / HP	5890 Series II / 7673 Injectors	07/2000	GCSV	Good
GC Dual ECD (ECD 7 & 8)	Agilent / Agilent	6890N, dual micro ECDs / 7683B Injector	05/2005	GCSV	Good
GC Dual ECD (ECD 9 &10)	HP / HP	5890 Series II / 7673 Injector	05/2007	GCSV	Good
GC Dual ECD (ECD 11 &12)	Agilent / Agilent	7890N, dual micro ECDs / 7683B Injector	11/2014	GCSV	Good
GC with FID/FPD (FID #1)	HP / HP	5890A / Cobra L/S Injector	11/1999	GCSV	Good
GC with FID (FID #4)	HP	5890A Series II	Feb-01	GCSV	Good
GC with FID, Dual Thu-put (FID#7 / #8)	Agilent	6890N, Dual Column/FID / 7683 Injectors (s)	02/2006	GCSV	Good
GC with FID, Dual Thu-put (FID#10 / #11)	Agilent	6890N, Dual Column/FID / 7683 Injectors (s)	02/2006	GCSV	Good
GC with FID Dual Thru Put #12/#13	Agilent	6890N Dual Column FID / 7683 Injectors (s)	05/2010	GCSV	Good
GC with FID (FID #16)	Agilent	7890 Series / 7693 Injector	2007	GCSV	Good
GC with FID (FID #17)	Agilent	7890 Series	2007	GCSV	Good
HPLC1 w/ UV & Fluorescence Det.	Agilent	1100 Series HPLC w auto sampler	10/2003	GCSV	Good
HPLC2 w/ UV & Fluorescence Det.	Agilent	1100 Series HPLC w auto sampler	10/2010	GCSV	Good
HPLC3 w/ UV & Fluorescence Det.	Agilent	1100 Series HPLC w auto sampler	10/2010	GCSV	Good
Mixer	Barnstead	MaxQ		GCSV	Good
Mixer	VWR	OS500		GCSV	Good
Refrigerator	Frigidaire	Refrigerator	10/2010	GCSV	Good
Refrigerator		Refrigerator (Explosion Proof)	10/2005	GCSV	Good
Balance	Highland	HBC302	11/2012	GCVOA	Good

Equipment	Manufacturer	Model	Year Purchased	Location	Condition
BTEX 1&2 (Dual PID)	HP/Varian/Tekmar	5890 Series II/Tekmar 3000 PT/ Archon Autosampler	09/2000	GCVOA	Good
BTEX 3&4 (Dual PID)	HP/Varian/Tekmar	5890 Series II/Tekmar 3000 PT/ Archon Autosampler	02/2001	GCVOA	Good
BTEX 5&6 (Dual PID)	HP/Tekmar/Tekmar	5890 Series II/Tekmar 3000 PT/ Tekmar SolaTek Autosampler	02/2001	GCVOA	Good
FID#14/15 VPH (PID & FID)	Agilent/Tekmar	7890A GC /Tekmar Atomix PT & Autosampler	10/2011	GCVOA	Excellent
FID#9 GRO	Agilent/Tekmar/OI	6890 GC /Tekmar 3100 PT/OI Archon Autosampler	09/2006	GCVOA	Good
Refrigerator/Freezer	Kenmore	Refrigerator/Freezer	02/2009	GCVOA	Good
Refrigerators (3)	True Mfg. (2), Pharmacy (1)	Refrigerators	06/2001	GCVOA	Good
Top Loading balance	Ohaus	ScoutPro 200g	11/2008	GCVOA	Good
Computer Server (2 Target servers)	HP and Compaq	Servers	07/2005	IT	Good
Computer Servers (4 servers)	HP and Compaq	Servers	12/1999	IT	Good
LIMS Database	LIMS	Database	07/2004	IT	Good
SQL Server (Alpha LIMS) (2 server)	HP and Compaq	Servers	07/2005	IT	Good
Analytical balance	Mettler	Toledo XS105	07/2007	MET	Good
Hot Block Digesters - Metals (2 units)	Environmental Express	Hot Block Digester	01/2000 & 07/2001	MET	Good / Good
Hot Block Digesters - Mercury	Environmental Express	Hot Block Digester	04/2007	MET	Good
ICP/MS	Agilent	7500 Series C/ASX510 Autosampler	08/2003	MET	Good
ICP/MS	Agilent	7500 Series ORS/ASX500 Autosampler	03/2007	MET	Good
ICP/MS	Agilent	7700 Series ORCE/ASX500 Autosampler	03/2009	MET	Good
ICP/MS	Agilent	7700 Series ORS/ASX520 Autosampler	06/2011	MET	Excellent
Mercury Analyzer	CETAC	Technologies M-7600A	03/2013	MET	Excellent
Mercury Analyzer	CETAC	Technology M7500A	01/2010	MET	Good
GC/MSD III (SV3)	Agilent	6890 GC/ 5973 MSD/7683 Autosampler	03/2002	MSSV	Good
GC/MSD IV (SV4)	Agilent	6890 GC/ 5973 MSD/7682 Autosampler	08/2004	MSSV	Good
GC/MSD V (SV5)	Agilent	6890 GC/ 5975 MSD/7683 Autosampler	06/2006	MSSV	Good
GC/MSD V11 (SV7)	Agilent	7890A GC/ 5975C MSD/7693 Autosampler	06/2010	MSSV	Good

Equipment	Manufacturer	Model	Year Purchased	Location	Condition
GC/MSD VI (SV6)	Agilent	7890A GC/ 5975C MSD/7693 Autosampler	05/2010	MSSV	Good
8' x 10' Walk-in Refrigerator	NorLake	Walk-in Refrigerator	06/2002	MSVOA	Good
Analytical balance	Mettler	AE 200	01/2000	MSVOA	Good
Centrifuge	IEC	Clinical Centrifuge		MSVOA	Good
Centrifuge	IEC	HNSII		MSVOA	Good
Freezer	GE	Freezer	10/2005	MSVOA	Good
Freezer	Kenmore	Freezer	11/2007	MSVOA	Good
MSVOA1	HP/Tekmar/Varian	5890 Series II / 5972A MSD/EST Encon PT/EST Centurion Autosampler	12/1999	MSVOA	Good
MSVOA2	HP/Tekmar/Varian	6890 GC / 5973A MSD /Tekmar Atomix PT & Autosampler	07/2000	MSVOA	Out of Service
MSVOA3	HP/Tekmar/Varian	5890 Series II/HP5972A MSD / Tekmar Velocity XPT PT/Varian Archon Autosampler	12/1999	MSVOA	Good
MSVOA4	HP/Tekmar/Varian	6890 GC /5973 Inert MSD / Tekmar Velocity XPT PT/Varian Archon Autosampler	04/2005	MSVOA	Excellent
MSVOA5	Agilent/Tekmar/Tekmar	6890 GC / 5975 Inert MSD /Tekmar Velocity XPT PT/Tekmar SolaTek Autosampler	03/2007	MSVOA	Excellent
MSVOA6	Agilent/Tekmar/Varian	7890A GC / 5975 Inert MSD / Tekmar Velocity XPT PT/Varian Archon Autosampler	02/2009	MSVOA	Excellent
MSVOA7	Agilent/Tekmar	7890A GC/ 5975C MSD/Tekmar Atomix PT & Autosampler	06/2010	MSVOA	Excellent
MSVOA8	Agilent/Tekmar	7890A GC/ 5975C MSD/Tekmar Velocity EXP PT /Varian Archon Autosampler	06/2010	MSVOA	Excellent
MSVOA9	Agilent/Tekmar	7890B GC/ 5997B MSD/Tekmar Atomix PT & Autosampler	01/2018	MSVOA	New
Top Loading Balance	OHAUS	Adventurer Pro #B430842121	8/4/2014	MSVOA	NEW
Glass Crusher	C. Bell Co.	Glass Crusher	03/2013	Waste	Excellent
Plastic Shredder	Prodeva Co	Plastic Shredder	04/2014	Waste	New
1664 Solid Phase Extraction System – 6 units	Environmental Express	Step Saver System	08/2006	WC	Good
Analytical balance	Mettler	Toledo XS105	09/2011	WC	Excellent
Analytical balance	Shimadzu	AUX220	02/2006	WC	Good

Equipment	Manufacturer	Model	Year Purchased	Location	Condition
Blender	Waring	Blender	10/2011	WC	Excellent
BOD Incubator	VWR	Incubator		WC	Good
BOD/CBOD/Alkalinity/pH Autoanalyzer	Mantech	AutoMax 122	06/2011	WC	Excellent
COD Analyzer	Thermo Scientific	Orion AQ2040 COD Analyzer		WC	Good
COD Digestor	Bioscience	COD Digestor	02/2001	WC	Good
COD Digestor	Hach	DRB 200	10/2011	WC	Excellent
Cyanide/Phenolics/Ammonia Distillation (2 units)	Environmental Express	54 Position Hot Block Heater	01/2013	WC	Excellent
Dessicators (2 units)	Fisher	Dessicators	11/2011	WC	Excellent
Dessicators (3 units)	Various	Dessicators	05/2005	WC	Good
DO meter	Thermo	Orion 850+	09/2007	WC	Good
Drying Oven (1 unit)	Binder	Binder	02/2014	WC	Excellent
Drying Ovens (2 units)	VWR	Model 1326	12/2005	WC	Excellent
Drying Ovens (2 units)	VWR	Model 414004-552	09/2011	WC	Excellent
Hach COD Analyzer	Hach	DR 3900	10/2011	WC	Excellent
Hot Plates 1	VWR	VHP-C10	02/2010	WC	Good
Hot Plates 2	VWR	Dylathern		WC	Good
Hot Plates 3	Ika-Werk	RT-10		WC	Good
Ion Chromatograph	Dionex	ICS – 3000, Dual IC System	01/2006	WC	Good
Ion Chromatograph	Dionex	ICS – 2100	01/2010	WC	Good
Midi Cyanide/Phenolics/Ammonia Distillation (2 units)	Environmental Express	10 position Cyanide Distillation Unit	06/2002	WC	Good
Pensky-Martens Closed Cup Flashpoint	Koehler	Pensky-Martens Closed Cup Flashpoint	03/2014	WC	Excellent
Refrigerator	Kelvinator	Refrigerator	01/2000	WC	Good
Specific Ion/pH Meter	Fisher	Accumet XL-60	06/2011	WC	Excellent
Specific Ion/pH Meter	Thermo	Orion Versa Star	04/2014	WC	Excellent
Stirrer (2 units)	Thermo Scientific	Stirrer	10/2010	WC	Good
Stirrer (2 units)	VWR	VWR ColorSquid Stirrer		WC	Good
TKN Digester Unit	Aim Lab	600 Dig System	08/2008	WC	Good
TOC Analyzer (for soils and waters)	Element	Vario TOC	09/2014	WC	Good
TOC Analyzer (for soils and waters)	Shimadzu	5020S; soils –SSM 500A, waters-TOC _VCSH & Autosampler	08/2010	WC	Good
Turbidimeter	Thermo Scientific	Orion AQ4500	07/2014	WC	Good
UV/VIS	Shimadzu	UV-2450	02/2006	WC	Good
UV/VIS -Auto	Thermo Scientific	Gallery	06/2012	WC	Excellent
Vortex Mixer (2 units)	VWR	VWR Analog Vortex Mixer		WC	Good

APPENDIX F – Containers, Preservation and Holding Times

Parameter	Containers [1]	Preservative	Holding Time [2]
Acidity / E305.1	P, G - 250 mL	>0 to 6 ° C	14 days
Alkalinity / SM 2320B – E310.1	P, G - 250 mL	>0 to 6 ° C	14 days
Ammonia as N	P, G – 250 or 500 mL	>0 to 6 ° C; H_2SO_4 to pH<2	28 days
Bacterial Tests (Coliform, Total, Fecal and *E. Coli*)	PA, G – 125-mL	Cool <10 ° C; 0.008% $Na_2S_2O_3$ if Cl_2 present	8 hours
Biological Oxygen Demand (BOD)	P, G – 1000 mL	>0 to 6 ° C	48 hours
(Carbonaceous) Biological Oxygen Demand (CBOD)	P, G – 1000 mL	>0 to 6 ° C	48 hours
Bromide	P, G – 500 mL	None required	28 days
(Total Organic) Carbon (TOC) / SW 9060	P, G – 125 amber mL or 40 mL amber vial	>0 to 6 °C; HNO_3 or H_2SO_4 to pH<2	28 days
Chemical Oxygen Demand (COD)	P, G – 250 mL	>0 to 6 ° C; H_2SO_4 to pH<2	28 days
Chloride	P, G – 250 mL	None required	28 days
Chlorine, Residual	P, G – 120 mL	>0 to 6 ° C	15 minutes
Color	P, G – 250 mL	>0 to 6 ° C	48 hours
Conductivity (Spec. Conductance)	P, G – 250 mL	>0 to 6 ° C	28 days
(Reactive) Cyanide	P, G – 4 oz wm	None required	14 days
Cyanide (Total and Amenable to Chlorination)	P, G - 500 mL	>0 to 6 ° C; NaOH to pH>12; 0.6g ascorbic acid	14 days
Cyanide (Total or Reactive) / Soil	P, G – 100 g in 250-ml wm bottle.	>0 to 6 ° C	14 days
Fluoride	P – 250 mL	None required	28 days
Hardness	P, G – 250 mL	HNO_3 or H_2SO_4 to pH<2	6 months
Nitrate as N	P, G – 250 mL	>0 to 6 ° C	48 hours
Nitrate-Nitrite as N	P, G – 250 mL	>0 to 6 ° C; H_2SO_4 to pH<2	28 days
Nitrite as N	P, G – 250 mL	>0 to 6 ° C	48 hours
(Total Kjeldahl) Nitrogen	P, G – 250 mL	>0 to 6 ° C; H_2SO_4 to pH<2	28 days
Oil and Grease	G – 1000 mL wm	>0 to 6 ° C; H_2SO_4 to pH<2	28 days
Oxygen, Dissolved	P, G – 1000 mL	>0 to 6 ° C	15 minutes
pH (hydrogen ion)	P, G – 250 mL	>0 to 6 ° C	15 minutes
(Total) Phenols (wet method)	G / amber – 1000 mL	>0 to 6 ° C; H_2SO_4 to pH<2	28 days
(*ortho*-) Phosphate	P, G – 250 mL	Filter immediately; >0 to 6 ° C	48 hours
(Total) Phosphate	P, G – 250 mL	>0 to 6 ° C; H_2SO_4 to pH<2	28 days
Residue (Total Solids)	P, G – 500 mL	>0 to 6 ° C	7 days
Residue (Dissolved Solids) (TDS)	P, G – 500 mL	>0 to 6 ° C	7 days
Residue (Suspended Solids) (TSS)	P, G – 1000 mL	>0 to 6 ° C	7 days
Residue (Settleable)	P, G – 1000 mL	>0 to 6 ° C	48 hours
Residue (Total Volatile) (TVS)	P, G – 500 mL	>0 to 6 ° C	7 days

Parameter	Containers [1]	Preservative	Holding Time [2]
Residue (Volatile Suspended) (TVSS)	P, G – 1000 mL	>0 to 6 ° C	7 days
Silica	P – 500 mL	>0 to 6 ° C	28 days
Sulfite	P, G – 250 mL	>0 to 6 ° C	15 minutes
Chromium VI	P, G – 250 mL	>0 to 6 ° C	24 hours
Chromium VI (soil)	P, G – 4 oz wide mouth	>0 to 6 ° C	24 hours
Mercury	P, G – 500 mL	HNO_3 to pH<2	28 days
Mercury (soil)	P, G – 4 oz wm bottle	None	28 days
Metals (except Chromium IV and Hg)	P, G – 500 mL	HNO_3 to pH<2	6 months
Metals (except CrVI and Hg)/ (soil)	P, G – 50 g in 120 mL bottle	None	6 months
TCLP Mercury	P, G – 1000 mL	>0 to 6 ° C	28 days to extract; 28 days after extraction to analysis
TCLP Metals (except Mercury)	P, G – 1000 mL	>0 to 6 °C	180 days to extract; 180 days after extraction to analysis
Dioxins (TCDD)	G – 2 x 1L amber	>0 to 6 ° C; 0.008% $Na_2S_2O_3$ if Cl_2 is present	7 days to extract; 40 days after extraction to analysis
Pesticides in Soil (Organochlorine) 8081B	G, 4 oz wide mouth	>0 to 6 °C	14 days to extract; 40 days after extraction to analysis
Pesticides – water (Organochlorine)/8081B	Amber G, 2 x 1L	>0 to 6 °C; adjust pH to 4-5	7 days to extract; 40 days after extraction to analysis
PCBs in Soil [4] SW 8082A	G, 4 oz wide mouth	>0 to 6 ° C	14 days to extract; 40 days after extraction to analysis
PCBs in water[4,5] SW 8082A / EPA 608	Amber G; 2 x 1L	>0 to 6°C; adjust pH to 4-5	7 days to extract; 40 days after extraction to analysis
(Total) Petroleum Hydrocarbons (TPH) Water – by TX 1005	G – 2 x 40 mL with no headspace	>0 to 6 °C; HCl to pH<2	14 days to extract; 14 days after extraction to analysis
(Total) Petroleum Hydrocarbons (TPH) Water – by TX 1005	2 - 5 gram samples in pre-tared 40 ml VOA vial	>0 to 6 ° C; freeze samples to –12 to -20 ° C within 48 hrs	14 days to extract; 14 days after extraction to analysis
Polynuclear Aromatic Hydrocarbons (PAHs) / (soil)	G, 4 oz wide mouth	>0 to 6 ° C; store in the dark	14 days to extract; 40 days after extraction to analysis
Polynuclear Aromatic Hydrocarbons (PAHs) by 8270 (water)	Amber G; 2 x 1L LVI: AG – 3 x 40 mL with no headspace	>0 to 6 ° C	7 days to extract; 40 days after extraction to analysis
Semi-Volatiles (BNAs) in soil	G, 4 oz wide mouth	>0 to 6 ° C	14 days to extract; 40 days after extraction to analysis
Semi-Volatiles (BNAs)	Amber G, 2 x 1L	>0 to 6 ° C	7 days to extract; 40 days after extraction to analysis

Parameter	Containers [1]	Preservative	Holding Time [2]
Semi-Volatiles (TCLP)	G, 4 o wide mouth	>0 to 6 ° C	14 days to TCLP extraction; 7 days from TCLP extraction to BNA extraction; 40 days after BNA extraction to analysis
Total Organic Halogens (TOX) / SW9020	Amber G, 250mL	>0 to 6 ° C; H_2SO_4 to pH<2	28 days
Volatiles (water) SW 8260B	G – 3 x 40 mL with no headspace	>0 to 6 ° C; HCl to pH<2	14 days
Volatiles (TCLP)	G, 2 x 4 oz wide mouth	>0 to 6 ° C	14 days to extract; 14 days after extraction to analysis
Volatiles (low level soil by 5035A, where soil likely contain VOCs < 200 ppb)	Collect sample using approved coring device (EnCore, etc) or field preserve 5 gram sample in pre-tared 40 ml VOA vial, containing 5ml of organic free water, 1g sodium bisulfate & stir bar	>0 to 6 ° C; or freeze[3] samples to –12 to -20 ° C as an alternative to preservation with sodium bisulfate as a means to inhibit biodegradation.	48 hrs to transfer contents of core device to a 40 ml VOA vial , containing 5ml of organic free water, 1g sodium bisulfate & stir bar; analyze transferred sample 14 days from collection
Volatiles (high level soil by 5035A, where soil may contain VOCs >200 ppb)	Collect sample using approved coring device (EnCore, etc) or field preserve samples in pre-tared 60 ml glass bottles with methanol	>0 to 6 ° C; or freeze[3] samples to –12 to –20 ° C as an alternative to preservation with methanol as a means to inhibit biodegradation.	48 hrs to transfer contents of core device to a 40 ml VOA vial , containing 10 ml of purge and trap grade methanol; analyze methanol preserved sample 14 days from collection
Volatiles (Soil)	G, 2 oz wide mouth[6]	>0 to 6 ° C	14 days
Alpha, Beta, and Radium	P, G – 1000 mL	HNO_3 to pH<2	6 months

[1] (P) polyethylene/plastic; (G) Glass; (PA) Autoclavable Plastic
[2] Recommended Holding Times from 40CFR136 and/or USEPA SW-846.
[3] Option to freeze core soil must be approved by regulatory agency or QA Project Plan.
[4] SW-846, Revision 4, February 2007, Chapter 4, Table 4-1, No Holding Time for PCBs.
[5] 40 CFR Part 136, (7-1-09 Edition), Table II, Maximum Holding Time1 year until extraction, 1 year after extraction.
[6] The prefer solid volatiles sampling method for TCEQ is 5035A and if sample in bulk jar, reports must be narrate as being receipt in improper containers.

APPENDIX G – Standard Operating Procedures

Department	SOP ID	SOP Title
Quality System	CE-GEN001	Laboratory Ethics and Data Integrity
Quality System	CE-GEN002	BP Laboratory Management Program SOP
Quality System	CE-GEN003	Records Management Policy
Quality System	CE-GEN004	Preventative Action
Quality System	CE-GEN005	Document Control
Quality System	CE-GEN006	Data Recall
Quality System	CE-GEN007	Procurement and Control of Laboratory Services and Supplies
Quality System	CE-GEN008	Method Development
Quality System	CE-GEN009	Establishing Standard Operating Procedures
Quality System	CE-GEN010	Handling Customer Feedback
Quality System	CE-GEN011	Assigning a TSR to a Project
Quality System	CE-GEN012	Policy For The USE of Accreditation Organization Names, Symbols and Logos
Quality System	CE-GEN013	Enterprise Product Laboratory Program SOP
Quality System	CE-GEN014	Spectra Energy Contract Laboratory Program SOP
Quality System	CE-GEN015	Management of Change
Quality System	CE-GEN016	Continuous Quality Improvement
Quality System	CE-QA001	Internal Audits
Quality System	CE-QA002	Manual Integration Policy
Quality System	CE-QA003	Training Policy
Quality System	CE-QA004	Qualification of Subcontract Laboratories
Quality System	CE-QA005	Laboratory Management Review
Quality System	CE-QA006	Proficiency Testing Sample Analysis
Quality System	CE-QA007	Making Entries Onto Analytical Records
Quality System	CE-QA008	Nonconformance and Corrective Actions
Quality System	CE-QA009	Control Limits
Quality System	CE-QA010	Estimation of Uncertainty of Analytical Measurements
Quality System	CE-QA011	Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation
Quality System	CE-QA012	Quality of Reagents and Standards
Quality System	CE-QA013	New Instrumentation Suitability and Validation
Admin	HS-ADM003	Work Order Reporting
Admin	HS-ADM004	Complaint Resolution
Extractions	HS-EXT001	Separatory Funnel Extraction of Aqueous Samples
Extractions	HS-EXT002	Automated Soxhlet Extraction of Solids/Soils – SW3541
Extractions	HS-EXT003	Sep. Funnel Extraction - Herbicides from Waters, SW 8151A
Extractions	HS-EXT004	Extraction- Herbicides-Soils, SW3550B/ 8151A
Extractions	HS-EXT005	Extraction of TPH from Waters and Soil - TX1005
Extractions	HS-EXT006	Fractionation of TPH from Waters and Soil - TX1006
Extractions	HS-EXT007	Organic Compounds and DRO in Water by Microextraction
Extractions	HS-EXT008	LL Automated Soxhlet Extraction – DRO - Soils - SW3541/8015M
Extractions	HS-EXT009	LL Extraction of DRO From Waters - SW3510C
Extractions	HS-EXT013	Extraction of Explosives (salting out) - Waters by 8330A
Extractions	HS-EXT014	Extraction of Explosives from Soils by 8330A

Department	SOP ID	SOP Title
Extractions	HS-EXT017	Mass EPH Extraction - Fractionation of Waters & Soil
Extractions	HS-EXT018	Oklahoma DRO Extraction in Waters
Extractions	HS-EXT019	Oklahoma DRO Extraction in Soils
Extractions	HS-EXT020	O & G (HEM) in Soil by SW9071B - EPA 1664A
Extractions	HS-EXT021	Sulfur Cleanup Using Copper - SW3660B
Extractions	HS-EXT022	Microwave Extraction of Solid by Method 3546
Extractions	HS-EXT025	Elutriate Preparation
Extractions	HS-EXT030	Kansas Method Determination of Mid-Range Hydrocarbons (MRH) and High-Ranger Hydrocarbons (HRH) - Extraction
Extractions	HS-LA006	Oil and Grease from 7 Day Leachate Test of Soil - LA DNR 29B
Extractions	HS-LA007	Oil and Grease from Soil - LA DNR 29B
Extractions	HS-LEACH001	TCEQ Seven Day Leachate Preparation
Extractions	HS-SPLP001	Synthetic Characteristic Leach. Procedure (SPLP) – SV/ Metals
Extractions	HS-SPLP002	Synthetic Characteristic Leaching Procedure (SPLP) – ZHE
Extractions	HS-TCLP001	Toxic Characteristic Leaching Procedure (TCLP) – SV/ Metals
Extractions	HS-TCLP002	Toxic Characteristic Leaching Procedure (TCLP) – ZHE
Extractions	HS-TCLP003	TCLP - Particle Size Reduction - Semi Volatiles and Metals
GCSemi	HS-GCECD001	Organochlorine Pesticides by GC/ECD – 8081A
GCSemi	HS-GCECD002	Polychlorinated Biphenyls (PCBs) by GC/ECD - 8082
GCSemi	HS-GCECD003	Herbicides by GC/ECD - 8151A
GCSemi	HS-GCECD004	EDB / DBCP waters - GCECD – SW8011- E504.1
GCSemi	HS-GCFID001	TCEQ 1005 -Total Petroleum Hydrocarbons
GCSemi	HS-GCFID003	DRO and ORO by GC/FID SW-8015C
GCSemi	HS-GCFID005	Nonhalogenated Organics by SW8015C - Direct Injection
GCSemi	HS-GCFID006	Fractionation Analysis of TPH by TX1006
GCSemi	HS-GCFID007	Oklahoma DRO in Waters and Soils
GCSemi	HS-GCFID009	Massachusetts EPH
GCSemi	HS-GCFID010	RSK-175 for dissolved methane, ethane and ethene
GCSemi	HS-GCFID015	Kansas Method Determination of Mid-Range Hydrocarbons (MRH) and High-Ranger Hydrocarbons (HRH)
GCSemi	HS-HPLC002	Acrylamide by SW 8316
GCSemi	HS-HPLC003	Explosives by HPLC - SW 8330B
GCVOA	HS-GRO001	GRO - Soil & Water, 8015C using P&T
GCVOA	HS-GRO002	Massachusetts VPH
GCVOA	HS-GRO004	Oklahoma GRO in Waters and Soils
GCVOA	HS-GRO005	Kansas Method Determination of Low Range Hydrocarbons (LRH)
IT	HS-IT001	LIMS Raw Data and Data Integrity
IT	HS-IT002	Computer Software Installation & Maintenance
IT	HS-IT003	IT System Security
IT	HS-IT004	Electronic Data Archival and Storage
IT	HS-IT006	LIMS Test Code Validation
IT	HS-IT007	Software Testing
IT	HS-IT008	Software Development Methodology
IT	HS-IT009	Software Change Control
Metals	HS-LA004	True Total Barium - LA DNR 29B

Department	SOP ID	SOP Title
Metals	HS-MET001	Hot Block Digest for Solids/Soil – SW3050B
Metals	HS-MET002	Hot Block Digestion of Aqueous Samples – SW3010A - E200.8
Metals	HS-MET003	ICP-MS Analysis by 6020A and 200.8
Metals	HS-MET004	Mercury Prep / Analysis - Aqueous - SW7470A - E245.1
Metals	HS-MET005	Mercury Prep / Analysis - Solids / Soil - SW7471B
Metals	HS-MET007	Paint Chips
Metals	HS-MET008	Soil Drying and Sieving
MSSemi	HS-MSSV001	Semivolatile Organics by GC/MS - SW8270D - EPA625
MSSemi	HS-MSSV003	Low Level SV Organic Compounds by GC/MS - 8270D
MSSemi	HS-MSSV006	Polynuclear Aromatics Hydrocarbons by GC/MS Selective Ion Monitoring by Method 8270D
MSVOA	HS-MSV001	VOCs -GC/MS Soil & Water - SW 8260C - EPA 624
QA	ALSHS-QAM	Quality Assurance Manual
QA	HS-EQ001	Use and Maintenance of Balances
QA	HS-EQ002	Thermometer Calibration and Temperature Monitoring
QA	HS-EQ003	Lab Volumetric Ware Calibration
QA	HS-EQ004	Preventative Maintenance
QA	HS-GEN001	Preparation / Management of SOPs
QA	HS-GEN003	Glassware Cleaning
QA	HS-GEN004	Client Confidentiality of Electronic Data Transfers
QA	HS-GEN005	Departures from Approved Procedures
QA	HS-GEN006	Resources Review
QA	HS-GEN007	Subcontract Sample Submittal
QA	HS-GEN008	QC Criteria Dev Where No Regulatory Criteria Exist
QA	HS-GEN009	DoD/DOE QSM Criteria for Testing
QA	HS-QS001	Chemical Purchase & Receipt; Chemical Prep. & Tracking
QA	HS-QS002	Changing Analytical Results
QA	HS-QS003	Nonconformance Corrective Action Reporting
QA	HS-QS004	Control Charting
QA	HS-QS005	Validation of New Instrumentation and New Methods
QA	HS-QS006	Limit of Detection (LOD) - Limit of Quantitation (LOQ)
QA	HS-QS007	Reagent Water
QA	HS-QS008	Container Sub-sampling-metals, inorganics, SV organics
QA	HS-QS009	Data Reduction, Review and Validation
QA	HS-QS010	Container Sub-sampling-volatile organics, SW5035A
QA	HS-QS011	Records Archival
QA	HS-QS012	Internal Audits
QA	HS-QS013	Employee Training
QA	HS-QS014	Document Control and Laboratory Records
QA	HS-QS016	Manual Integration Policy
QA	HS-QS017	Management Review
QA	HS-QS018	Sporadic Marginal Exceedance
QA	HS-QS019	Estimation of Measurement Uncertainty
QA	HS-QS020	Cross Contamination Monitoring
QA	HS-QS021	Quality Assurance Training and Orientation

Department	SOP ID	SOP Title
QA	HS-QS022	Method Modifications
QA	HS-QS023	Risks and Opportunities
SA	HS-SM001	Sample Receipt and Log-in
SA	HS-SM002	Bottle Orders
SA	HS-SM003	LIMS Login Procedures
SA	HS-SM004	Foreign Soil Receipt and Storage
SA	HS-SM005	Procedure for Sample Couriers
Safety	HS-CHSP	Chemical Hygiene and Safety Plan
Safety	SHWD-001	Sample Handling and Waste Disposal Procedures
Safety	HS-EMER	Houston Emergency Response Plan
WetChem	HS-BIO003	BOD - CBOD, SM5210B
WetChem	HS-IC001	Anions by Ion Chromatography, SW-9056A - EPA 300.0
WetChem	HS-LA001	Sample Preparation - LA DNR 29B
WetChem	HS-LA002	Cation Exchange Capacity - Exchangeable Cations - LA DNR 29B
WetChem	HS-LA003	Saturation Point of Soils - LA DNR 29B
WetChem	HS-LA005	Leachate Test of Soil - LA DNR 29B
WetChem	HS-LA006	Oil and Grease from 7 Day Leachate Test of Soil - LA DNR 29B
WetChem	HS-LA007	Oil and Grease from Soil - LA DNR 29B
WetChem	HS-LA008	1:1 Aqueous Ext Prep - Sodium Adsorption Ratio - LA DNR 29B
WetChem	HS-LA009	pH in Soil - LA DNR 29B
WetChem	HS-LA010	Electrical Conductivity for Soil - LA DNR 29B
WetChem	HS-WC001	Total Alkalinity by SM 2320B/310.1
WetChem	HS-WC002	pH (Aqueous SW9040C / soils SW 9045D)
WetChem	HS-WC003	Total Suspended Solids, TSS- SM 2540 D
WetChem	HS-WC008	Chrome VI Analysis, SW 7196A / 3500-Cr B
WetChem	HS-WC009	Chrome VI - Preparation of Soils , SW 3060A
WetChem	HS-WC010	Ferrous Iron, SM 3500 Fe B
WetChem	HS-WC011	Specific Conductivity, EPA120.1
WetChem	HS-WC012	Total Dissolved Solids, TDS- SM 2540 C
WetChem	HS-WC013	Total, Fixed and Volatile Solids, Aqueous Samples- SM 2540 B & E
WetChem	HS-WC014	Percent Solids, Percent Moisture, Soils for RCRA Testing
WetChem	HS-WC015	Total Phosphorus by SM 4500P B & E
WetChem	HS-WC017	Silica (SiO2), SM 4500 Si D
WetChem	HS-WC018	Sulfide, SM 4500-S-2F (21st)
WetChem	HS-WC019	Sulfite - Iodometric Method, SM4500SO3 -2 / EPA 377.1
WetChem	HS-WC020	Cyanide, Total SW9010B / SW9014 / 4500-CN C& E
WetChem	HS-WC021	Total Organic Carbon, Aqueous SM5310 B&C / 9060A / E415.1
WetChem	HS-WC022	Total Organic Carbon, Soils
WetChem	HS-WC023	Color, SM 2120 B
WetChem	HS-WC025	COD, Hach 8000, Colorimetric
WetChem	HS-WC026	Ammonia as N, Colorimetric, SM 4500-NH3 B / F
WetChem	HS-WC027	Ammonia as N, by ISE, SM 4500-NH3 B / D
WetChem	HS-WC028	Residual Chlorine - SM 4500 Cl F
WetChem	HS-WC029	Total Recoverable Phenols, EPA 420.1 / SW9065

Department	SOP ID	SOP Title
WetChem	HS-WC030	Turbidity by E180.1 / SM2130B
WetChem	HS-WC032	Cyanide, Weak acid dissociable, SM 4500 CN - I
WetChem	HS-WC033	Total Kjeldahl Nitrogen, EPA 351.3, Rev. 2.0 (1993)
WetChem	HS-WC035	Sulfide by Methylene Blue, SM4500 S-2 D
WetChem	HS-WC036	Oil and Grease, SPE - EPA 1664
WetChem	HS-WC037	Flash Point by D93-02a / SW1010 Ignitability
WetChem	HS-WC039	Methylene Blue Active Substances (MBAS) by SM5540C/E425.1
WetChem	HS-WC040	TOC on Solids, by Walkley-Black titration
WetChem	HS-WC041	Ignitability of Solids - SW1030
WetChem	HS-WC042	Paint Filter Liquids Test - SW9095B
WetChem	HS-WC043	Dissolved Oxygen SM 4500-O G & EPA 360.1
WetChem	HS-WC044	Acidity by SM2310B / EPA 305.1
WetChem	HS-WC045	Total Phosphorus by EPA 365.3
WetChem	HS-WC053	Total Recoverable Phenols Distillation - Automated Colormetric
WetChem	HS-WC055	Specific Gravity by SM2710 F
WetChem	HS-WC057	Chloride 4500CL E/9250/325.1 & Sulfate 4500 SO4 E/9038/375.4 - Automated Colorimetric

APPENDIX H – Data Qualifiers

Qualifier	Description
*	Value exceeds Regulatory Limit
a	Not accredited
B	Analyte detected in the associated Method Blank above the Reporting Limit
E	Value above quantitation range
H	Analyzed outside of Holding Time
J	Analyte detected below quantitation limit
M	Manually integrated, see raw data for justification
n	Not offered for accreditation
ND	Not Detected at the Reporting Limit
O	Sample amount is > 4 times amount spiked
P	Dual Column results percent difference > 40%
R	RPD above laboratory control limit
S	Spike Recovery outside laboratory control limits
U	Analyzed but not detected above the MDL

Acronym	Description
DCS	Detectability Check Study
DUP	Method Duplicate
LCS	Laboratory Control Sample
LCSD	Laboratory Control Sample Duplicate
MBLK	Method Blank
MDL	Method Detection Limit
MQL	Method Quantitation Limit
MS	Matrix Spike
MSD	Matrix Spike Duplicate
PDS	Post Digestion Spike
PQL	Practical Quantitation Limit
SD	Serial Dilution
SDL	Sample Detection Limit
TRRP	Texas Risk Reduction Program

APPENDIX I – External Documents*

*External Documents current as of the effective date. Contact the laboratory for the most recent list.

ID	Vendor	Title	Version	Date	Part Number	Media	Department	Date Retired
1	CETAC Technologies	CETAC M-7600 Mercury Analyzer	1a	May 2012	480195 Rev 1a	Print	Metals	
2	CETAC Technologies	QuickTrace Mercury Analyzer Software Manual	1.0	June 2002	480114	Print	Metals	
3	CETAC Technologies	QuickTrace Mercury Analyzer Software	1.7.5		670093	CD	Metals	
4	CETAC Technologies	ASX520 Operator's Manual and Supplies Catalog			670034	CD	Metals	
5	Binder	Operating Manual APT line BD (E2), APT line ED (E2), APT line FD (E2)	BD/ED/FD (E2) 04/2012	4/2012	7001-0026	Print	WetChem	
7	Shimadzu	UV-2415/2550 User Guide	1997	1997	206-64649A	Print	WetChem	
8	Shimadzu	The Shimadzu User Authentication Tool			223-10284	Print	WetChem	
9	Thermo Fisher Scientific	Gallery Operation Manual	4.0A	February 2012	N10482	PDF	WetChem	
10	Thermo Fisher Scientific	Gallery Reference Manual	4.0A	February 2012	N11481	PDF	WetChem	
11	Thermo Fisher Scientific	Gallery LIS Interface	4.0A	February 2012	N12027	PDF	WetChem	
12	Misonix	Sonicator Ultrasonic Processor Operation Manual			S-4000	Print	Extractions	
13	Misonix	Sonicator Ultrasonic Liquid Processor Operation Manual				PDF	Extractions	
14	Mantech	PC-BOD Version 3.0 - Operator's Manual Version, Revision 1	1	04-20-2011		PDF	WetChem	
15	YSI	ProOBOD User Manual	B	Sept 2010	626471	PDF	WetChem	
16	LaMotte	TC-3000 Tri-Meters	1.5	11-27-2007	1964-MN	PDF	WetChem	
17	Caliper Life Sciences	TurboVap II User Manual	8	2010	46342	PDF	Extractions	
18	Omega	HH309A Data Logger Thermometer		05/2008	M4147A	PDF	WetChem	
19	Environmental Express	MicroBlock Instruction Manual	4.02			PDF	WetChem	
20	Thermo Scientific	User Guide Ammonium Ion Selective Electrode	B	12-2008	254803-001	PDF	WetChem	
21	OI Analytical/OI Analytical	4410 Flame-Ionization-Detector	3.2	12-1999	192229	Print	GCVOA	
22	Varian	Archon PT Autosampler System Operator Manual		05/24/200	03-914451-00:3	Print	MSVOA	
23	Teledyne Instruments Tekmar	Velocity XPT PT Concentrator		2003	14-8900-074_v9	Print	MSVOA	
24	Teledyne Instruments Tekmar	Stratum PT Concentrator		2011		Print	MSVOA	
25	Tekmar Dohrmann	SOLATeK 72 Multi-Matrix Vial Autosampler		2001	14-7200-074	Print	MSVOA	
26	Tekmar Dohrmann	SOLATeK 72 Multi-Matrix Vial Autosampler		2001	14-7200-074	Print	MSVOA	
27	Tekmar	3000 Purge and Trap Concentrator	12.07.94	1994		Print	MSVOA	
28	Tekmar	3000 Purge and Trap Concentrator	12.07.94	1994		Print	MSVOA	
29	Varian	Archon PT Autosampler System Operator Manual		05/24/2000	03-914642-00:7	Print	MSVOA	
30	Hewlett Packard	HP5890 Series II and Series II Plus Operating Manual		1994	05890-90261	Print	MSVOA	
31	Hewlett Packard	HP5890 Series II and Series II Plus Reference Manual		1994	05890-90271	Print	MSVOA	
32	Tekmar Dohrmann	3100 Purge and Trap Concentrator User Manual	12.20.98	1999		Print	MSVOA	
33	Tekmar Dohrmann	3100 Purge and Trap Concentrator User Manual	12.20.98	1999		Print	MSVOA	
34	Varian	Archon PT Autosampler System Operator Manual		05/24/2000	03-914451-00:3	Print	MSVOA	
35	Agilent	Agilent 6890 Series Gas Chromatograph Site Prep and Installation		1/2004	G1530-90307	Print	MSVOA	
36	Agilent	Agilent 6890 Series Gas Chromatograph Operator Manual Vol 3 - Detectors		1/2004	G1530-90467	Print	MSVOA	
37	Agilent	Agilent G1701EA GC/MSD ChemStation		3/2011	G1701-90069	Print	MSVOA	
38	Varian	Archon PT Autosampler System Operator Manual		05/24/2000	03-914642-00:7	Print	MSVOA	
39	Agilent	Agilent Technologies GC and GC/MS Hardware User Information & Utilities	B.01.03.SP3	1/2010	G4600-60127	CD	MSVOA	
40	Agilent	Agilent Technologies 5975 Accessory Kits G3393A, G3397A		8/2005	G3170-90097	CD	MSVOA	
41	OI Analytical	Model 4560 Sample Concentrator Operator's Manual	1.0	7/1992		Print	MSVOA	12/10/2013
42	OI Analytical	Model 4560 Sample Concentrator Operator's Manual	2.0	3/1994	227959	Print	MSVOA	12/10/2013
43	Hewlett Packard	HP7695 Purge and Trap		6/1994	G1900-90320	Print	MSVOA	
44	Agilent	Agilent 5975 Series MSD Operation Manual	1	1/2008	G3170-90023	Print	MSVOA	
45	Agilent	Agilent 5975 Series MSD Hydrogen Safety	1	6/2005	G3170-90010	Print	MSVOA	
46	Agilent	Agilent 7890A Gas Chromatograph Quick Reference	2	1/2010	G3430-90009	Print	MSVOA	
47	OI Analytical/OI Analytical	4410 Flame-Ionization-Detector		1/1992		Print	GCVOA	
48	OI Analytical/OI Analytical	4410 Flame-Ionization-Detector		1/1992		Print	GCVOA	
49	OI Analytical/OI Analytical	4430 Photoionization Detector		5/1988	186678	Print	GCVOA	
50	Barnstead/Thermolyne	Type FB1300 & FB1400 Furnaces		8/27/01	LT1256X1	Print	WetChem	
51	AWWA, APHA & WEF	Standard Methods for the Examination of Water and Wastewater	19th	1995	ISBN 0-87553-223-3	Print	QA	
52	AWWA, APHA & WEF	Standard Methods for the Examination of Water and Wastewater	21st	2005	ISBN 0-87553-047-8	Print	QA	
53	TNI Organization	2009 TNI Standard, Volume 1	2009	2009	EL-V1-2011	PDF	QA	
54	ISO/IEC	Internal Standard ISO/IEC 17025	2nd	05/15/2005	ISO/IEC 17025:2005	PDF	QA	
55	Department of Defense	Quality System Manual (QSM) for Environmental Testing	5.0	7/2013		PDF	QA	
56	YSI	Pro ODO User Manual	C	3/2009	626279	Print	WetChem	
57	Lutz	Drum Pump	IP24			PDF	Waste	
58	Mettler Toledo	Operating Instructions Five Easy Plus pH meter FEP20			51710598	Print	Extractions	

59	Ohaus	Scout Pro Balance Instruction Manual	D	2006	71160417	Print	Extractions	
60	Foss	2055 Soxtec Avanti Manual System User Manual 1000 7415	1.1	1999		Print	Extractions	
61	Zymark	TurboVap II Concentration Workstation Operator's Manual	7		46342	Print	Extractions	
62	CEM	Microwave Reaction System Operation Manual	4	2013	600284	PDF	Extractions	
63	Omega	HH309 Data Logger Thermometer			M4147	PDF	WetChem	
64	HACH	Oxygen Demand, Chemical	6	2010	Doc316.53.01100	PDF	WetChem	
65	Thermo Scientific	Gallery Operation Manual	4.0A	3/2012	N10482	PDF	WetChem	
67	VWR	VWR sympHony Meter User Guide	248589-001 Rev B	2/2005	87000-056	PDF	WetChem	
68	Fluke	Infrared Thermometer 58X		12/2010	3833028	Print	SA	
69	Fluke	Infrared Thermometer 58X		12/2010	3833028	Print	SA	
70	Fluke	Infrared Thermometer 58X		12/2010	3833027	CD	SA	
71	Fluke	Infrared Thermometer 58X		12/2010	3833027	CD	SA	
72	LaMotte	TC-3000 Tri-Meters	1.5	9-8-2005	1984-MN	Print	WetChem	
73	Thermo Scientific Orion	Thermo Scientific Orion AQUAfact AQ4500 Turbidimeter	A	06/2009	256473-001	Print	WetChem	
74	Philips	HeartStart OnSite Defibrillator	7	1/2007	M5066A	Print	QA	
75	CEM	Mars 6 Microwave Reaction System Manual	4	7/2013	600284	PDF	Extractions	
76	CEM	Mars 6 Microwave Reaction System Software	4		910960	Software	Extractions	
77	Thermo Scientific	High Performance Ammonia Ion Selective Electrode	A		266787-001	Print	WetChem	
78	Thermo Scientific	Dissolved Oxygen Probes	A		254778-001	Print	WetChem	
79	Fisher Scientific	AR50 Manual				Print	WetChem	
80	Orion	Laboratory Products Group Bench Top pH/ISE Meter Instruction Manual	B	1990	213357-001	Print	WetChem	
81	Thermo Scientific	Orion Versa Star Advanced Electrochemistry Meter	A	12-2011	68X592003	PDF	QA	
82	YSI	Pro ODO User Manual	C	3/2009	626279	Print	WetChem	
83	EST Analytical	EST Analytical Manuals	4.0			CD	MSVOA	
84	Teledyne Tekmar	Atomis VOC TecLink Ver1.0 & User Manual	D		15-0000-075 Rev D	CD	MSVOA	
85	OI Analytical	Model 4410 FID	4.1			CD	MSVOA	
86	OI Analytical	Model 4430 PID Operator's Manual	3.2	4/2008		CD	MSVOA	
87	Ohaus	Adventurer Pro Balances Instruction Manual		2012	80251161C	Print	WC	
88	FOSS	Soxtec 2055 Manual System User Manual	4	9/23/09	1000 7415	Print	Extractions	
89	FOSS	2500 Soxtec Manual System User Manual	2.0	2002	1000 7415	Print	Extractions	
91	FOSS	2500 Soxtec Manual System User Manual	2.0	2002	1000 7415	Print	Extractions	
119	Hewlett Packard	HP G1034C MS ChemStation Software User's Guide	1	2/1993	G1034-90043	Print	GCSemi	
122	Hewlett Packard	HP 5890 Series II and Series II Plus Tutorial	3	7/1994	05890-90291	Print	GCSemi	
124	Hewlett Packard	HP 1100 Series Fluorescence Detector Reference Manual	1	7/1998	G1321-90000	Print	GCSemi	
125	Hewlett Packard	HP 1100 Series Autosampler Reference Manual	3	7/99	G1313-90002	Print	GCSemi	
126	Hewlett Packard	HP 1100 Series Quaternary Pump Reference Manual	3	7/99	G1311-90002	Print	GCSemi	
127	Hewlett Packard	HP 1100 Series Variable Wavelength Detector Reference Manual	2	10/1996	G1314-90001	Print	GCSemi	
128	Hewlett Packard	HP 1100 Series Vacuum Degasser Reference Guide	3	6/1997	G1322-90002	Print	GCSemi	
129	Agilent	Agilent 1100 Series Thermostatted Column Compartment Reference Manual	01/00	1/2000	G1316-90003	Print	GCSemi	
130	Hewlett Packard	HP5890 Series II and Series II Plus Reference Manual	6	7/1994	05890-90271	Print	MSVOA	
131	Fisher Scientific	XL Series Meters XL15,20,25,360,40,50,60	4	11/2006	68X0674204	Print	WC	
132	Brand	Dispensette	9975.11		501213/18	Print	Extractions	
133	BeckmanCoulter	Avanti J-JC High Capacity Centrifuge		11/2013	PN.J3HC-IM-5AC	PDF	Extractions	
134	BeckmanCoulter	Rotors and Tubes for Beckman Coulter J2, J6 and Avanti J Series Centrifuge		3/2014	PN.JR-IM-10AF	PDF	Extractions	
135	Fisher Scientific	XL Series Meters XL15,20,25,360,40,50,60	5	01/2008	68X0674204	Print	WC	
136	Koehler	Operation and Instruction Manual K16200 Pensky Martens Closed Cup	A		2719	Print	WetChem	
137	Koehler	Operation and Instruction Manual K16200 Pensky Martens Closed Cup	A		2719	Print	WetChem	
138	Agilent	ECD Documentation		07/2008	G1533-91005	CD	GCSemi	
139	Agilent	ECD Documentation		07/2008	G1533-91005	CD	GCSemi	
140	Extech Instruments	Dual Laser InfraRed IR) Thermometer Model 42512	7.2	9/2010	42512-EV-V7.2-90/10	Print	SA	
141	Extech Instruments	Dual Laser InfraRed IR) Thermometer Model 42512	7.2	9/2010	42512-EV-V7.2-90/10	Print	SA	
142	Extech Instruments	Dual Laser InfraRed IR) Thermometer Model 42512	7.2	9/2010	42512-EV-V7.2-90/10	CD	SA	
143	Extech Instruments	Dual Laser InfraRed IR) Thermometer Model 42512	7.2	9/2010	42512-EV-V7.2-90/10	CD	SA	
144	EcoSense	pH10A pH/Temperature Pen Operation Manual	C	1/2011	0605112	Print	SA	
152	ThermoScientific	Thermo Scientific Thermolyne Furnace Benchtop Muffle Type 47900 & 4800	D	2013	LT1284X1	Print	Extractions	

153	Shimadzu	Shimadzu Analytical Balance Instruction Manual		3/2013	321-56861-21D	Print	WetChem	
154	Benchmark	Operator Manual Item BV1010 & BV1010-E				Print	Extractions	
155	Fluke	Infrared Thermometer 56X		12/2010	3833028	Print	SA	
156	Fluke	Infrared Thermometer 56X		12/2010	3833027	CD	SA	
157	Extech Instruments	Dual Laser InfraRed IR) Thermometer Model 42512	7.2	9/2010	42512-EV-V7.2-90/10	Print	SA	
158	Extech Instruments	Dual Laser InfraRed IR) Thermometer Model 42512	7.2	9/2010	42512-EV-V7.2-90/10	Print	SA	
159	Extech Instruments	Dual Laser InfraRed IR) Thermometer Model 42512	7.2	9/2010	42512-EV-V7.2-90/10	CD	SA	
160	Extech Instruments	Dual Laser InfraRed IR) Thermometer Model 42512	7.2	9/2010	42512-EV-V7.2-90/10	CD	SA	
161	Thermo Scientific	Orion Aquafast AQ4500 Turbidimeter	Rev A	8/2009	256473-001	PDF	WC	
162	Ohaus	Scout Pro Balance Instruction Manual		2011	71160417 F	Print	Extractions	
163	VWR	symphony Benchtop Meter B10P User Manual	Edition 1	06/2012	DOC022.98.80315	Print	WetChem	
164	VWR	symphony pH Probes	Edition 1	07/2012	DOC022.53.80316	Print	WetChem	
165	Entech	IR User Manual Model 42510A	3	4/13	42510A-EN-V3	Print	SA	
166	Entech	IR User Manual Model 42510A	3	4/13	42510A-EN-V3	Print	SA	
167	Entech	Model 42510A Product Manual	3.4	2013		CD	SA	
168	Entech	Model 42510A Product Manual	3.4	2013		CD	SA	
169	Ohaus	Scout SPX Balances Quick Guide Manual			30269069C	Print	Extractions	
170	Organomation	ROT-X-TRACT	v15.1	6/1/15		PDF	Extractions	
171	Ohaus	SPX Manual		2016	30268911	PDF	Extractions	
172	AEAdam	Highland Disc	2009	2009		CD	Extractions	
173	AEAdam	Highland Disc	2009	2009		CD	Extractions	
174	AEAdam	Highland Series	Revision F	6/2014	9520	Print	Extractions	
175	AEAdam	Highland Series	Revision F	6/2014	9520	Print	Extractions	
176	Unico	Power Spin Centrifuge (LX & FX) Operator Manual				Print	Extractions	
177	LAUDA	LAUDA Water Circulation Coolers Operating Instructions	YAWE0019/18.12.01	2001		PDF	QA	
178	LAUDA	LAUDA Water Circulation Coolers Operating Instructions	YAWE0019/18.12.01	2001		Print	Extractions	
179	Socorex	Socorex Calibra 832 Operating Instructions (Pipette ICP 12)				pdf	QA	
180	TNI Organization	2016 TNI Standard	2016	2016	EL-V1-2016	PDF	QA	
181	Department of Defense	Quality System Manual (QSM) for Environmental Testing	5.1.1	2018	DoD/DOE QSM 5.1.1	PDF	QA	
182	Department of Defense	Quality System Manual (QSM) for Environmental Testing	5.2	2018	DoD/DOE QSM 5.2	PDF	QA	
183	Department of Defense	Quality System Manual (QSM) for Environmental Testing	5.3	2019	DoD/DOE QSM 5.3	PDF	QA	
184	ISO/IEC	Internal Standard ISO/IEC 17025	3	2017	ISO/IEC 17025:2017	PDF	QA	
185	XL250 Software disc	Reference Guides and communication Software for accumet bench top meter				CD	WC	
186	Sigma-Aldrich Co.	AL-180 Diazald and Diazomethane Generators	2007	2007		PDF	QA	
187	VWR	VWR Signature Ergonomic High-Performance Pipettor Manual	None	7/12/2019	89079-974	PDF	QA	
188	VWR	VWR Signature Ergonomic High-Performance Pipettor Manual	None	7/12/2019	89079-974	Print	Metals	
189	VWR	VWR Start up Guide A-Series Balance Series (NAHST BALD11)	None	9/26/2019	VWR-224AC	Print	MSSemi	
190	VWR	VWR Start up Guide A-Series Balance Series (HRMS BALD4)	None	10/1/2019	VWR-164AC	Print	Dioxins	
191	VWR	VWR Signature Ergonomic High Performance Pipettor Manual	None	12/16/2019	VWR VE1000	Print	WetChem	
192	Shimadzu	High Performance Liquid Chromatograph Mass Specrrometer Instruction Manual	Rev. 1	Jun-13	SC038	Print	Dioxins	
193	Shimadzu	Autosampler for Shimadzu Ultra HPLC Instruction Manual	NEXERA X2	Mar-18	SIL-30ACMP	Print	Dioxins	
194	Traceable Products	Traceable Total-Range Thermometer Instructions	92-4015-00 Rev 4	3/19/2018	NIST Thermocouple 191961292	PDF	QA	
195	CETAC Technologies	Quick Trace	QT 1.5.1		670045	CD	Metals	
196	CETAC Technologies	ASX520 Operator's Manual	from CD 670034		670034	Print	Metals	
197	Thermo Scientific	Thermo Scientific User Guide Dissolved Oxygen Probes	254778-001 Rev. A	2007	091010MD	Print	WetChem	
198	YSI	ProOBOD IDS ProOBOD User Manual	626471 Rev. C	Apr-13		Print	WetChem	
199	YSI	ProOBOD Sensor Cap Instruction Sheet	626483 Rev. C	Mar-13	Probe SN 20A101085	Print	WetChem	
200	Thermo Scientific	Thermo Scientific User Guide Automatic Temperature Compensation (ATC) Probes	254793-001 Rev. A	2007	Probe SN XZ1-16329	Print	WetChem	
201	Ward's Scientific +	Bottle Top Dispenser Operation Manual			BTD-10 (1-10ml)	Print	Extractions	
202	Thermo Scientific	Thermo Scientific User Guide High Performance Ammonia Ion Selective Electrode	266787-001 RevA	2010	9512HPBNWP	Print	WetChem	

207	Pfeiffer Vacuum	HiPACE 300 Turbopump Operating Instructions	PT 0200 BN/J (1708)			Print	Dioxins	
208	Pfeiffer Vacuum	SPLITFLOW 310 Supplementary Information	PT0305BN_F	4/9/2018	PM P04 291 C	Print	Dioxins	
209	Pfeiffer Vacuum	TC 400 Electronic Drive Unit Operating Instructions	PT 0203 BN/S (1708)			Print	Dioxins	
210	Shimadzu	FCV-12AH Instruction Manual		1991	FCV-12AH	Print	Dioxins	
211	Shimadzu	HPLC Nexera X2 (for SIL-30ACMP) System Guide	228-91011D	Jun 2013 Rev D		Print	Dioxins	
212	Shimadzu	Autosampler Nexera X2 (for SIL-30ACMP) Instruction Manual	228-91008C	June 2013 Rev C		Print	Dioxins	
213	Shimadzu	Solvent Delivery Module Nexera X2 LC-30AD Instruction Manual	228-90791K	Apr-16		Print	Dioxins	
214	Shimadzu	System Controller CBM-20A/20Alite Instruction Manual	228-30947W	Jul-17		Print	Dioxins	
215	Shimadzu	HPLC Nexera X2 (for SIL-30ACMP) System Guide	228-91011F	Mar-18		Print	Dioxins	
216	Shimadzu	High Performance LCMS-8060 Instruction Manual	225-27752C	Mar-17		Print	Dioxins	
217	Shimadzu	Spectrophotometer UV-2450 Instruction Manual User's Guide	206-94649D	Sep-06		Print	WetChem	
218	Perry Johnson Laboratory Accreditation (PJLA)	Accreditation Symbol Procedure SOP-3	1.7	Oct-19	N/A	.pdf	QA	

APPENDIX J – Laboratory Accreditations and Scopes

Accrediting Body	Certificate Number*
Arkansas	20-030-0
California	2919
DoD (PJLA) ***	L2231
Florida	E87611
Illinois	2000322020-4
Kansas	E-10352
Kentucky	123043
Louisiana**	03087
North Carolina	624
North Dakota	R-193
Oklahoma	2020-123
Texas**	T1014704231-20-26
USDA Soil Permit	P330-19-00299

All certificates and scopes can be found on the laboratory's secure network.

*Certificate number at time of QAM generation, Certificate Number or list may have changed, please contact lab most recent listing.
**Primary TNI Accreditation Body
***The scope for DoD is attached per current QSM requirement.

Primary Scope of *Accreditation for DoD*

PERRY JOHNSON LABORATORY ACCREDITATION, INC.

Certificate of Accreditation

Perry Johnson Laboratory Accreditation, Inc. has assessed the Laboratory of:

ALS Group USA Corp
10450 Stancliff Road, Suite 210, Houston, TX 77099

(Hereinafter called the Organization) and hereby declares that Organization has met the requirements of ISO/IEC 17025:2017 General Requirements for the competence of Testing and Calibration Laboratories and the United States Department of Defense Environmental Laboratory Accreditation Program (DoD-ELAP) requirements identified within the DoD/DOE Quality Systems Manual (DoD/DOE QSM) Version 5.3 May 2019 and is accredited is accordance with the:

United States Department of Defense
Environmental Laboratory Accreditation Program
(DoD-ELAP)

This accreditation demonstrates technical competence for a defined scope and the operation of a laboratory quality management system (as outlined by the joint ISO-ILAC-IAF Communiqué dated April 2017):

Environmental Testing
(As detailed in the supplement)

Accreditation claims for such testing and/or calibration services shall only be made from addresses referenced within this certificate. This Accreditation is granted subject to the system rules governing the Accreditation referred to above, and the Organization hereby covenants with the Accreditation body's duty to observe and comply with the said rules.

For PJLA:

Tracy Szerszen
President

Perry Johnson Laboratory Accreditation, Inc. (PJLA)
755 W. Big Beaver, Suite 1325
Troy, Michigan 48084

Initial Accreditation Date:	*Issue Date:*	*Expiration Date:*
August 21, 2020	August 21, 2020	December 22, 2021

Accreditation No.:	*Certificate No.:*
111808	L20-507

The validity of this certificate is maintained through ongoing assessments based on a continuous accreditation cycle. The validity of this certificate should be confirmed through the PJLA website: www.pjlabs.com

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Certificate of Accreditation: Supplement

ISO/IEC 17025:2017 and DoD-ELAP

PJLA

ALS Global Houston

10450 Stancliff Road, Suite 210, Houston TX 77099
Contact Name: Erica Marinez Phone: 281-530-5656

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Aqueous	EPA 1010A	Pensky-Martens Closed Cup	Ignitability
Aqueous	EPA 1664A	Gravimetry	n-Hexane Extractable Material
Aqueous	EPA 300.0	Ion Chromatography	Bromide
Aqueous	EPA 300.0	Ion Chromatography	Chloride
Aqueous	EPA 300.0	Ion Chromatography	Fluoride
Aqueous	EPA 300.0	Ion Chromatography	Nitrate/Nitrite (as N)
Aqueous	EPA 300.0	Ion Chromatography	Nitrogen, Nitrate (As N)
Aqueous	EPA 300.0	Ion Chromatography	Nitrogen, Nitrite (As N)
Aqueous	EPA 300.0	Ion Chromatography	Phosphorus, Dissolved Orthophosphate (As P)
Aqueous	EPA 300.0	Ion Chromatography	Sulfate
Aqueous	EPA 335.2	UV-VIS	Cyanide
Aqueous	EPA 6020A	ICP-MS	Aluminum
Aqueous	EPA 6020A	ICP-MS	Antimony
Aqueous	EPA 6020A	ICP-MS	Arsenic
Aqueous	EPA 6020A	ICP-MS	Barium
Aqueous	EPA 6020A	ICP-MS	Beryllium
Aqueous	EPA 6020A	ICP-MS	Boron
Aqueous	EPA 6020A	ICP-MS	Cadmium
Aqueous	EPA 6020A	ICP-MS	Calcium
Aqueous	EPA 6020A	ICP-MS	Chromium
Aqueous	EPA 6020A	ICP-MS	Cobalt
Aqueous	EPA 6020A	ICP-MS	Copper
Aqueous	EPA 6020A	ICP-MS	Iron
Aqueous	EPA 6020A	ICP-MS	Lead
Aqueous	EPA 6020A	ICP-MS	Magnesium
Aqueous	EPA 6020A	ICP-MS	Manganese
Aqueous	EPA 6020A	ICP-MS	Molybdenum
Aqueous	EPA 6020A	ICP-MS	Nickel

Certificate of Accreditation: Supplement

ISO/IEC 17025:2017 and DoD-ELAP

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ALS Global Houston

10450 Stancliff Road, Suite 210, Houston TX 77099
Contact Name: Erica Marinez Phone: 281-530-5656

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Aqueous	EPA 6020A	ICP-MS	Potassium
Aqueous	EPA 6020A	ICP-MS	Selenium
Aqueous	EPA 6020A	ICP-MS	Silver
Aqueous	EPA 6020A	ICP-MS	Sodium
Aqueous	EPA 6020A	ICP-MS	Strontium
Aqueous	EPA 6020A	ICP-MS	Thallium
Aqueous	EPA 6020A	ICP-MS	Tin
Aqueous	EPA 6020A	ICP-MS	Titanium
Aqueous	EPA 6020A	ICP-MS	Vanadium
Aqueous	EPA 6020A	ICP-MS	Zinc
Aqueous	EPA 7196A	UV-VIS	Chromium, Hexavalent
Aqueous	EPA 7470A	CV-FAA	Mercury
Aqueous	EPA 8011	GC-ECD	1,2,3-Trichloropropane
Aqueous	EPA 8011	GC-ECD	1,2-Dibromo-3-chloropropane
Aqueous	EPA 8011	GC-ECD	1,2-Dibromoethane
Aqueous	EPA 8015C	GC-FID	TPH/Diesel Range Organics (C10-C28)
Aqueous	EPA 8015C	GC-FID	Ethanol
Aqueous	EPA 8015C	GC-FID	Ethylene Glycol
Aqueous	EPA 8015C	GC-FID	Isobutyl alcohol
Aqueous	EPA 8015C	GC-FID	Isopropyl alcohol
Aqueous	EPA 8015C	GC-FID	Methanol
Aqueous	EPA 8015C	GC-FID	Propylene Glycol
Aqueous	EPA 8015C	GC-FID	tert-Butyl alcohol
Aqueous	EPA 8015C	GC-FID	Gasoline Range Organics
Aqueous	EPA 8015C	GC-FID	TPH/Motor Range Organics (>C28-C35)
Aqueous	EPA 8081B	GC-ECD	4,4´-DDD
Aqueous	EPA 8081B	GC-ECD	4,4´-DDE
Aqueous	EPA 8081B	GC-ECD	4,4´-DDT
Aqueous	EPA 8081B	GC-ECD	Aldrin
Aqueous	EPA 8081B	GC-ECD	alpha-BHC
Aqueous	EPA 8081B	GC-ECD	alpha-Chlordane
Aqueous	EPA 8081B	GC-ECD	beta-BHC
Aqueous	EPA 8081B	GC-ECD	Chlordane
Aqueous	EPA 8081B	GC-ECD	delta-BHC
Aqueous	EPA 8081B	GC-ECD	Dieldrin
Aqueous	EPA 8081B	GC-ECD	Endosulfan I

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ALS Global Houston

10450 Stancliff Road, Suite 210, Houston TX 77099
Contact Name: Erica Marinez Phone: 281-530-5656

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Aqueous	EPA 8081B	GC-ECD	Endosulfan II
Aqueous	EPA 8081B	GC-ECD	Endosulfan sulfate
Aqueous	EPA 8081B	GC-ECD	Endrin
Aqueous	EPA 8081B	GC-ECD	Endrin aldehyde
Aqueous	EPA 8081B	GC-ECD	Endrin ketone
Aqueous	EPA 8081B	GC-ECD	gamma-BHC
Aqueous	EPA 8081B	GC-ECD	gamma-Chlordane
Aqueous	EPA 8081B	GC-ECD	Heptachlor
Aqueous	EPA 8081B	GC-ECD	Heptachlor epoxide
Aqueous	EPA 8081B	GC-ECD	Methoxychlor
Aqueous	EPA 8081B	GC-ECD	Toxaphene
Aqueous	EPA 8082A	GC-ECD	Aroclor 1016
Aqueous	EPA 8082A	GC-ECD	Aroclor 1221
Aqueous	EPA 8082A	GC-ECD	Aroclor 1232
Aqueous	EPA 8082A	GC-ECD	Aroclor 1242
Aqueous	EPA 8082A	GC-ECD	Aroclor 1248
Aqueous	EPA 8082A	GC-ECD	Aroclor 1254
Aqueous	EPA 8082A	GC-ECD	Aroclor 1260
Aqueous	EPA 8260C	GC/MS	1,1,1,2-Tetrachloroethane
Aqueous	EPA 8260C	GC/MS	1,1,1-Trichloroethane
Aqueous	EPA 8260C	GC/MS	1,1,2,2-Tetrachloroethane
Aqueous	EPA 8260C	GC/MS	1,1,2-Trichloro-1,2,2-trifluoroethane
Aqueous	EPA 8260C	GC/MS	1,1,2-Trichloroethane
Aqueous	EPA 8260C	GC/MS	1,1-Dichloroethane
Aqueous	EPA 8260C	GC/MS	1,1-Dichloroethene
Aqueous	EPA 8260C	GC/MS	1,1-Dichloropropene
Aqueous	EPA 8260C	GC/MS	1,2,3-Trichlorobenzene
Aqueous	EPA 8260C	GC/MS	1,2,3-Trichloropropane
Aqueous	EPA 8260C	GC/MS	1,2,4-Trichlorobenzene
Aqueous	EPA 8260C	GC/MS	1,2,4-Trimethylbenzene
Aqueous	EPA 8260C	GC/MS	1,2-Dibromo-3-chloropropane
Aqueous	EPA 8260C	GC/MS	1,2-Dibromoethane
Aqueous	EPA 8260C	GC/MS	1,2-Dichlorobenzene
Aqueous	EPA 8260C	GC/MS	1,2-Dichloroethane
Aqueous	EPA 8260C	GC/MS	1,2-Dichloroethene, Total
Aqueous	EPA 8260C	GC/MS	1,2-Dichloropropane
Aqueous	EPA 8260C	GC/MS	1,3,5-Trimethylbenzene

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ISO/IEC 17025:2017 and DoD-ELAP

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ALS Global Houston

10450 Stancliff Road, Suite 210, Houston TX 77099
Contact Name: Erica Marinez Phone: 281-530-5656

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Aqueous	EPA 8260C	GC/MS	1,3-Dichlorobenzene
Aqueous	EPA 8260C	GC/MS	1,3-Dichloropropane
Aqueous	EPA 8260C	GC/MS	1,4-Dichlorobenzene
Aqueous	EPA 8260C	GC/MS	1,4-Dioxane
Aqueous	EPA 8260C	GC/MS	1-Chlorohexane
Aqueous	EPA 8260C	GC/MS	2,2-Dichloropropane
Aqueous	EPA 8260C	GC/MS	2-Butanone
Aqueous	EPA 8260C	GC/MS	2-Chloro-1,3-butadiene
Aqueous	EPA 8260C	GC/MS	2-Chloroethyl vinyl ether
Aqueous	EPA 8260C	GC/MS	2-Chlorotoluene
Aqueous	EPA 8260C	GC/MS	2-Hexanone
Aqueous	EPA 8260C	GC/MS	4-Chlorotoluene
Aqueous	EPA 8260C	GC/MS	4-Isopropyltoluene
Aqueous	EPA 8260C	GC/MS	4-Methyl-2-pentanone
Aqueous	EPA 8260C	GC/MS	Acetone
Aqueous	EPA 8260C	GC/MS	Acetonitrile
Aqueous	EPA 8260C	GC/MS	Acrolein
Aqueous	EPA 8260C	GC/MS	Acrylonitrile
Aqueous	EPA 8260C	GC/MS	Allyl Chloride
Aqueous	EPA 8260C	GC/MS	Benzene
Aqueous	EPA 8260C	GC/MS	Benzyl Chloride
Aqueous	EPA 8260C	GC/MS	Bromobenzene
Aqueous	EPA 8260C	GC/MS	Bromochloromethane
Aqueous	EPA 8260C	GC/MS	Bromodichloromethane
Aqueous	EPA 8260C	GC/MS	Bromoform
Aqueous	EPA 8260C	GC/MS	Bromomethane
Aqueous	EPA 8260C	GC/MS	Carbon disulfide
Aqueous	EPA 8260C	GC/MS	Carbon tetrachloride
Aqueous	EPA 8260C	GC/MS	Chlorobenzene
Aqueous	EPA 8260C	GC/MS	Chloroethane
Aqueous	EPA 8260C	GC/MS	Chloroform
Aqueous	EPA 8260C	GC/MS	Chloromethane
Aqueous	EPA 8260C	GC/MS	cis-1,2-Dichloroethene
Aqueous	EPA 8260C	GC/MS	cis-1,3-Dichloropropene
Aqueous	EPA 8260C	GC/MS	Dibromochloromethane

Certificate of Accreditation: Supplement

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ALS Global Houston

10450 Stancliff Road, Suite 210, Houston TX 77099
Contact Name: Erica Marinez Phone: 281-530-5656

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Aqueous	EPA 8260C	GC/MS	Dibromomethane
Aqueous	EPA 8260C	GC/MS	Dichlorodifluoromethane
Aqueous	EPA 8260C	GC/MS	Diethyl Ether
Aqueous	EPA 8260C	GC/MS	Ethanol
Aqueous	EPA 8260C	GC/MS	Ethyl acetate
Aqueous	EPA 8260C	GC/MS	Ethyl methacrylate
Aqueous	EPA 8260C	GC/MS	Ethylbenzene
Aqueous	EPA 8260C	GC/MS	Hexachlorobutadiene
Aqueous	EPA 8260C	GC/MS	Isobutyl alcohol
Aqueous	EPA 8260C	GC/MS	Isopropyl alcohol
Aqueous	EPA 8260C	GC/MS	Isopropylbenzene
Aqueous	EPA 8260C	GC/MS	m,p-Xylene
Aqueous	EPA 8260C	GC/MS	Methacrylonitrile
Aqueous	EPA 8260C	GC/MS	Methyl acetate
Aqueous	EPA 8260C	GC/MS	Methyl methacrylate
Aqueous	EPA 8260C	GC/MS	Methyl tert-butyl ether
Aqueous	EPA 8260C	GC/MS	Methylcyclohexane
Aqueous	EPA 8260C	GC/MS	Methylene chloride
Aqueous	EPA 8260C	GC/MS	Naphthalene
Aqueous	EPA 8260C	GC/MS	n-Butyl alcohol
Aqueous	EPA 8260C	GC/MS	n-Butylbenzene
Aqueous	EPA 8260C	GC/MS	n-Propylbenzene
Aqueous	EPA 8260C	GC/MS	o-Xylene
Aqueous	EPA 8260C	GC/MS	Propionitrile
Aqueous	EPA 8260C	GC/MS	sec-Butylbenzene
Aqueous	EPA 8260C	GC/MS	Styrene
Aqueous	EPA 8260C	GC/MS	Tert-amylmethylether (TAME)
Aqueous	EPA 8260C	GC/MS	Tert-butyl alcohol
Aqueous	EPA 8260C	GC/MS	tert-Butyl ethyl ether
Aqueous	EPA 8260C	GC/MS	tert-Butylbenzene
Aqueous	EPA 8260C	GC/MS	Tetrachloroethene
Aqueous	EPA 8260C	GC/MS	Toluene
Aqueous	EPA 8260C	GC/MS	trans-1,2-Dichloroethene
Aqueous	EPA 8260C	GC/MS	trans-1,3-Dichloropropene
Aqueous	EPA 8260C	GC/MS	trans-1,4-Dichloro-2-butene

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ALS Global Houston

10450 Stancliff Road, Suite 210, Houston TX 77099
Contact Name: Erica Marinez Phone: 281-530-5656

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Aqueous	EPA 8260C	GC/MS	Trichloroethene
Aqueous	EPA 8260C	GC/MS	Trichlorofluoromethane
Aqueous	EPA 8260C	GC/MS	Vinyl acetate
Aqueous	EPA 8260C	GC/MS	Vinyl chloride
Aqueous	EPA 8260C	GC/MS	Xylenes, Total
Aqueous	EPA 8270D	GC/MS	1,1´-Biphenyl
Aqueous	EPA 8270D	GC/MS	1,2,4-Trichlorobenzene
Aqueous	EPA 8270D	GC/MS	1,2-Dichlorobenzene
Aqueous	EPA 8270D	GC/MS	1,2-Diphenylhydrazine
Aqueous	EPA 8270D	GC/MS	1,3-Dichlorobenzene
Aqueous	EPA 8270D	GC/MS	1,3-Dinitrobenzene
Aqueous	EPA 8270D	GC/MS	1,4-Dichlorobenzene
Aqueous	EPA 8270D	GC/MS	2,3,4,6-Tetrachlorophenol
Aqueous	EPA 8270D	GC/MS	2,4,6-Trichlorophenol
Aqueous	EPA 8270D	GC/MS	2,4-Dichlorophenol
Aqueous	EPA 8270D	GC/MS	2,4-Dimethylphenol
Aqueous	EPA 8270D	GC/MS	2,4-Dinitrophenol
Aqueous	EPA 8270D	GC/MS	2,4-Dinitrotoluene
Aqueous	EPA 8270D	GC/MS	2,6-Dinitrotoluene

PJLA

Certificate of Accreditation: Supplement

ISO/IEC 17025:2017 and DoD-ELAP

ALS Global Houston

10450 Stancliff Road, Suite 210, Houston TX 77099
Contact Name: Erica Marinez Phone: 281-530-5656

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Aqueous	EPA 8270D	GC/MS	2-Chloronaphthalene
Aqueous	EPA 8270D	GC/MS	2-Chlorophenol
Aqueous	EPA 8270D	GC/MS	2-Methylnaphthalene
Aqueous	EPA 8270D	GC/MS	2-Methylphenol
Aqueous	EPA 8270D	GC/MS	2-Nitroaniline
Aqueous	EPA 8270D	GC/MS	2-Nitrophenol
Aqueous	EPA 8270D	GC/MS	3,3´-Dichlorobenzidine
Aqueous	EPA 8270D	GC/MS	3-Nitroaniline
Aqueous	EPA 8270D	GC/MS	3&4-Methylphenol
Aqueous	EPA 8270D	GC/MS	4,6-Dinitro-2-methylphenol
Aqueous	EPA 8270D	GC/MS	4-Bromophenyl phenyl ether
Aqueous	EPA 8270D	GC/MS	4-Chloro-3-methylphenol
Aqueous	EPA 8270D	GC/MS	4-Chloroaniline
Aqueous	EPA 8270D	GC/MS	4-Chlorophenyl phenyl ether
Aqueous	EPA 8270D	GC/MS	4-Nitroaniline
Aqueous	EPA 8270D	GC/MS	4-Nitrophenol
Aqueous	EPA 8270D	GC/MS	7,12-Dimethylbenz(a)anthracene
Aqueous	EPA 8270D	GC/MS	Acenaphthene
Aqueous	EPA 8270D	GC/MS	Acenaphthylene
Aqueous	EPA 8270D	GC/MS	Acetophenone
Aqueous	EPA 8270D	GC/MS	Aniline
Aqueous	EPA 8270D	GC/MS	Anthracene

PJLA

Certificate of Accreditation: Supplement

ISO/IEC 17025:2017 and DoD-ELAP

ALS Global Houston

10450 Stancliff Road, Suite 210, Houston TX 77099
Contact Name: Erica Marinez Phone: 281-530-5656

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Aqueous	EPA 8270D	GC/MS	Atrazine
Aqueous	EPA 8270D	GC/MS	Benzidine
Aqueous	EPA 8270D	GC/MS	Benzo(a)anthracene
Aqueous	EPA 8270D	GC/MS	Benzo(a)pyrene
Aqueous	EPA 8270D	GC/MS	Benzo(b)fluoranthene
Aqueous	EPA 8270D	GC/MS	Benzo(g,h,i)perylene
Aqueous	EPA 8270D	GC/MS	Benzo(k)fluoranthene
Aqueous	EPA 8270D	GC/MS	Benzoic acid
Aqueous	EPA 8270D	GC/MS	Benzyl alcohol
Aqueous	EPA 8270D	GC/MS	Bis(2-chloroethoxy)methane
Aqueous	EPA 8270D	GC/MS	Bis(2-chloroethyl)ether
Aqueous	EPA 8270D	GC/MS	Bis(2-chloroisopropyl)ether
Aqueous	EPA 8270D	GC/MS	Bis(2-ethylhexyl)phthalate
Aqueous	EPA 8270D	GC/MS	Butyl benzyl phthalate
Aqueous	EPA 8270D	GC/MS	Caprolactam
Aqueous	EPA 8270D	GC/MS	Carbazole
Aqueous	EPA 8270D	GC/MS	Chrysene
Aqueous	EPA 8270D	GC/MS	Cresols, Total
Aqueous	EPA 8270D	GC/MS	Dibenz(a,h)anthracene
Aqueous	EPA 8270D	GC/MS	Dibenz(a,j)acridine
Aqueous	EPA 8270D	GC/MS	Dibenzofuran
Aqueous	EPA 8270D	GC/MS	Diethyl phthalate
Aqueous	EPA 8270D	GC/MS	Dimethyl phthalate
Aqueous	EPA 8270D	GC/MS	Di-n-butyl phthalate
Aqueous	EPA 8270D	GC/MS	Di-n-octyl phthalate
Aqueous	EPA 8270D	GC/MS	Diphenylamine
Aqueous	EPA 8270D	GC/MS	Fluoranthene
Aqueous	EPA 8270D	GC/MS	Fluorene
Aqueous	EPA 8270D	GC/MS	Hexachlorobenzene
Aqueous	EPA 8270D	GC/MS	Hexachlorobutadiene
Aqueous	EPA 8270D	GC/MS	Hexachlorocyclopentadiene
Aqueous	EPA 8270D	GC/MS	Hexachloroethane
Aqueous	EPA 8270D	GC/MS	Indeno(1,2,3-cd)pyrene
Aqueous	EPA 8270D	GC/MS	Isophorone
Aqueous	EPA 8270D	GC/MS	Naphthalene
Aqueous	EPA 8270D	GC/MS	Nitrobenzene
Aqueous	EPA 8270D	GC/MS	N-Nitrosodiethylamine

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ALS Global Houston

10450 Stancliff Road, Suite 210, Houston TX 77099
Contact Name: Erica Marinez Phone: 281-530-5656

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Aqueous	EPA 8270D	GC/MS	N-Nirosodi-n-propylamine
Aqueous	EPA 8270D	GC/MS	N-Nitrosodiphenylamine
Aqueous	EPA 8270D	GC/MS	Pentachlorophenol
Aqueous	EPA 8270D	GC/MS	Phenanthrene
Aqueous	EPA 8270D	GC/MS	Phenol
Aqueous	EPA 8270D	GC/MS	Pyrene
Aqueous	EPA 8270D	GC/MS	Pyridine
Aqueous	EPA 8270D	GC/MS	Quinoline
Aqueous	EPA 8316	HPLC-UV	Acrylamide
Aqueous	EPA 8330A	HPLC-UV	1,3,5-Trinitrobenzene
Aqueous	EPA 8330A	HPLC-UV	1,3-Dinitrobenzene
Aqueous	EPA 8330A	HPLC-UV	2,4,6-Trinitrotoluene
Aqueous	EPA 8330A	HPLC-UV	2,4-Dinitrotoluene
Aqueous	EPA 8330A	HPLC-UV	2,6-Dinitrotoluene
Aqueous	EPA 8330A	HPLC-UV	2-Amino-4,6-dinitrotoluene
Aqueous	EPA 8330A	HPLC-UV	2-Nitrotoluene
Aqueous	EPA 8330A	HPLC-UV	3-Nitrotoluene
Aqueous	EPA 8330A	HPLC-UV	4-Amino-2,6-dinitrotoluene
Aqueous	EPA 8330A	HPLC-UV	4-Nitrotoluene
Aqueous	EPA 8330A	HPLC-UV	HMX
Aqueous	EPA 8330A	HPLC-UV	Nitrobenzene
Aqueous	EPA 8330A	HPLC-UV	RDX
Aqueous	EPA 8330A	HPLC-UV	Tetryl
Aqueous	EPA 9014	UV-VIS	Cyanide
Aqueous	EPA 9040B	Electrode	pH
Aqueous	EPA 9050	Electrode	Specific Conductivity
Aqueous	EPA 9056A	Ion Chromatography	Nitrate/Nitrite (as N)
Aqueous	EPA 9056A	Ion Chromatography	Nitrogen, Nitrate (As N)
Aqueous	EPA 9056A	Ion Chromatography	Nitrogen, Nitrite (As N)
Aqueous	EPA 9056A	Ion Chromatography	Phosphorus, Dissolved Orthophosphate as P
Aqueous	EPA 9056A	Ion Chromatography	Sulfate
Aqueous	EPA 9056A	Ion Chromatography	Fluoride
Aqueous	EPA 9056A	Ion Chromatography	Bromide

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ALS Global Houston

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Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Aqueous	EPA 9056A	Ion Chromatography	Chloride
Aqueous	EPA 9065	UV-VIS	Phenolics, Total Recoverable
Aqueous	EPA 9066	UV-VIS	Phenolics, Total Recoverable
Aqueous	MA-EPH	GC-FID	C19-C36 Aliphatics
Aqueous	MA-EPH	GC-FID	C9-C18 Aliphatics
Aqueous	MA-EPH	GC-FID	C11-C22 Aromatics (unadjusted)
Aqueous	MA-VPH	GC-FID	C5-C8 Aliphatics (unadjusted)
Aqueous	MA-VPH	GC-FID	C9-C10 Aromatics (unadjusted)
Aqueous	MA-VPH	GC-FID	C9-C12 Aliphatics (unadjusted)
Aqueous	RSK-175	GC-FID	Ethane
Aqueous	RSK-175	GC-FID	Ethene
Aqueous	RSK-175	GC-FID	Methane
Aqueous	RSK-175	GC-FID	Propane
Aqueous	TX1005	GC-FID	Total Petroleum Hydrocarbons
Aqueous	EPA 3510C	Separatory Funnel	Organic Extraction
Aqueous	EPA 3511	Microextraction	Organic Microextraction
Aqueous	EPA 3010A	Hotblock Digestion	Metals Digestion
Aqueous	EPA 9010C	Distillation	Cyanide Distillation
Solid	ASTM D2216	Gravimetry	Percent Moisture
Solid	EPA 1010A	Pensky-Martens Closed Cup	Ignitability
Solid	EPA 300.0	Ion Chromatography	Bromide
Solid	EPA 300.0	Ion Chromatography	Chloride
Solid	EPA 300.0	Ion Chromatography	Fluoride
Solid	EPA 300.0	Ion Chromatography	Nitrate/Nitrite (as N)
Solid	EPA 300.0	Ion Chromatography	Nitrogen, Nitrate (As N)
Solid	EPA 300.0	Ion Chromatography	Nitrogen, Nitrite (As N)
Solid	EPA 300.0	Ion Chromatography	Phosphorus, Dissolved Orthophosphate (As P)
Solid	EPA 300.0	Ion Chromatography	Sulfate

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ALS Global Houston

10450 Stancliff Road, Suite 210, Houston TX 77099
Contact Name: Erica Marinez Phone: 281-530-5656

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Solid	EPA 365.3	UV-VIS	Phosphorus, Dissolved Orthophosphate (As P)
Solid	EPA 365.3	UV-VIS	Phosphorus, Total Orthophosphate (as P)
Solid	EPA 6020A	ICP-MS	Aluminum
Solid	EPA 6020A	ICP-MS	Antimony
Solid	EPA 6020A	ICP-MS	Arsenic
Solid	EPA 6020A	ICP-MS	Barium
Solid	EPA 6020A	ICP-MS	Beryllium
Solid	EPA 6020A	ICP-MS	Boron
Solid	EPA 6020A	ICP-MS	Cadmium
Solid	EPA 6020A	ICP-MS	Calcium
Solid	EPA 6020A	ICP-MS	Chromium
Solid	EPA 6020A	ICP-MS	Cobalt
Solid	EPA 6020A	ICP-MS	Copper
Solid	EPA 6020A	ICP-MS	Iron
Solid	EPA 6020A	ICP-MS	Lead
Solid	EPA 6020A	ICP-MS	Magnesium
Solid	EPA 6020A	ICP-MS	Manganese
Solid	EPA 6020A	ICP-MS	Molybdenum
Solid	EPA 6020A	ICP-MS	Nickel
Solid	EPA 6020A	ICP-MS	Potassium
Solid	EPA 6020A	ICP-MS	Selenium
Solid	EPA 6020A	ICP-MS	Sodium
Solid	EPA 6020A	ICP-MS	Strontium
Solid	EPA 6020A	ICP-MS	Thallium
Solid	EPA 6020A	ICP-MS	Tin
Solid	EPA 6020A	ICP-MS	Titanium
Solid	EPA 6020A	ICP-MS	Vanadium
Solid	EPA 6020A	ICP-MS	Zinc
Solid	EPA 7196A	UV-VIS	Chromium, Hexavalent
Solid	EPA 8015C	GC-FID	TPH/Diesel Range Organics (C10-C28)
Solid	EPA 8015C	GC-FID	Ethanol

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Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Solid	EPA 8015C	GC-FID	Ethylene Glycol
Solid	EPA 8015C	GC-FID	Isobutyl alcohol
Solid	EPA 8015C	GC-FID	Isopropyl alcohol
Solid	EPA 8015C	GC-FID	Methanol
Solid	EPA 8015C	GC-FID	Propylene Glycol
Solid	EPA 8015C	GC-FID	tert-Butyl alcohol
Solid	EPA 8015C	GC-FID	Gasoline Range Organics
Solid	EPA 8015C	GC-FID	TPH/Motor Range Organics (>C28-C35)
Solid	EPA 8081B	GC-ECD	4,4´-DDD
Solid	EPA 8081B	GC-ECD	4,4´-DDE
Solid	EPA 8081B	GC-ECD	4,4´-DDT
Solid	EPA 8081B	GC-ECD	Aldrin
Solid	EPA 8081B	GC-ECD	alpha-BHC
Solid	EPA 8081B	GC-ECD	alpha-Chlordane
Solid	EPA 8081B	GC-ECD	beta-BHC
Solid	EPA 8081B	GC-ECD	Chlordane
Solid	EPA 8081B	GC-ECD	delta-BHC
Solid	EPA 8081B	GC-ECD	Dieldrin
Solid	EPA 8081B	GC-ECD	Endosulfan I
Solid	EPA 8081B	GC-ECD	Endosulfan II
Solid	EPA 8081B	GC-ECD	Endosulfan sulfate
Solid	EPA 8081B	GC-ECD	Endrin
Solid	EPA 8081B	GC-ECD	Endrin aldehyde
Solid	EPA 8081B	GC-ECD	Endrin ketone
Solid	EPA 8081B	GC-ECD	gamma-BHC
Solid	EPA 8081B	GC-ECD	gamma-Chlordane
Solid	EPA 8081B	GC-ECD	Heptachlor
Solid	EPA 8081B	GC-ECD	Heptachlor epoxide
Solid	EPA 8081B	GC-ECD	Methoxychlor
Solid	EPA 8081B	GC-ECD	Toxaphene
Solid	EPA 8082A	GC-ECD	Aroclor 1016
Solid	EPA 8082A	GC-ECD	Aroclor 1221
Solid	EPA 8082A	GC-ECD	Aroclor 1232
Solid	EPA 8082A	GC-ECD	Aroclor 1242
Solid	EPA 8082A	GC-ECD	Aroclor 1248

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ALS Global Houston

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Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Solid	EPA 8082A	GC-ECD	Aroclor 1254
Solid	EPA 8082A	GC-ECD	Aroclor 1260
Solid	EPA 8260C	GC/MS	1,1,1,2-Tetrachloroethane
Solid	EPA 8260C	GC/MS	1,1,1-Trichloroethane
Solid	EPA 8260C	GC/MS	1,1,2,2-Tetrachloroethane
Solid	EPA 8260C	GC/MS	1,1,2-Trichloro-1,2,2-trifluoroethane
Solid	EPA 8260C	GC/MS	1,1,2-Trichloroethane
Solid	EPA 8260C	GC/MS	1,1-Dichloroethane
Solid	EPA 8260C	GC/MS	1,1-Dichloroethene
Solid	EPA 8260C	GC/MS	1,1-Dichloropropene
Solid	EPA 8260C	GC/MS	1,2,3-Trichloropropane
Solid	EPA 8260C	GC/MS	1,2,4-Trimethylbenzene
Solid	EPA 8260C	GC/MS	1,2-Dibromo-3-chloropropane
Solid	EPA 8260C	GC/MS	1,2-Dibromoethane
Solid	EPA 8260C	GC/MS	1,2-Dichlorobenzene
Solid	EPA 8260C	GC/MS	1,2-Dichloroethane
Solid	EPA 8260C	GC/MS	1,2-Dichloroethene, Total
Solid	EPA 8260C	GC/MS	1,2-Dichloropropane
Solid	EPA 8260C	GC/MS	1,3-Dichlorobenzene
Solid	EPA 8260C	GC/MS	1,3-Dichloropropane
Solid	EPA 8260C	GC/MS	1,4-Dichlorobenzene
Solid	EPA 8260C	GC/MS	1,4-Dioxane
Solid	EPA 8260C	GC/MS	1-Chlorohexane
Solid	EPA 8260C	GC/MS	2,2-Dichloropropane
Solid	EPA 8260C	GC/MS	2-Butanone
Solid	EPA 8260C	GC/MS	2-Chloro-1,3-butadiene
Solid	EPA 8260C	GC/MS	2-Chlorotoluene
Solid	EPA 8260C	GC/MS	2-Hexanone
Solid	EPA 8260C	GC/MS	4-Chlorotoluene
Solid	EPA 8260C	GC/MS	4-Isopropyltoluene
Solid	EPA 8260C	GC/MS	4-Methyl-2-pentanone
Solid	EPA 8260C	GC/MS	Acetone
Solid	EPA 8260C	GC/MS	Acetonitrile
Solid	EPA 8260C	GC/MS	Acrolein
Solid	EPA 8260C	GC/MS	Acrylonitrile

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ALS Global Houston

10450 Stancliff Road, Suite 210, Houston TX 77099
Contact Name: Erica Marinez Phone: 281-530-5656

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Solid	EPA 8260C	GC/MS	Allyl Chloride
Solid	EPA 8260C	GC/MS	Benzene
Solid	EPA 8260C	GC/MS	Bromobenzene
Solid	EPA 8260C	GC/MS	Bromochloromethane
Solid	EPA 8260C	GC/MS	Bromodichloromethane
Solid	EPA 8260C	GC/MS	Bromoform
Solid	EPA 8260C	GC/MS	Bromomethane
Solid	EPA 8260C	GC/MS	Carbon disulfide
Solid	EPA 8260C	GC/MS	Carbon tetrachloride
Solid	EPA 8260C	GC/MS	Chlorobenzene
Solid	EPA 8260C	GC/MS	Chloroethane
Solid	EPA 8260C	GC/MS	Chloroform
Solid	EPA 8260C	GC/MS	Chloromethane
Solid	EPA 8260C	GC/MS	cis-1,2-Dichloroethene
Solid	EPA 8260C	GC/MS	cis-1,3-Dichloropropene
Solid	EPA 8260C	GC/MS	Dibromochloromethane
Solid	EPA 8260C	GC/MS	Dibromomethane
Solid	EPA 8260C	GC/MS	Dichlorodifluoromethane
Solid	EPA 8260C	GC/MS	Ethyl methacrylate
Solid	EPA 8260C	GC/MS	Ethylbenzene
Solid	EPA 8260C	GC/MS	Hexachlorobutadiene
Solid	EPA 8260C	GC/MS	Isobutyl alcohol
Solid	EPA 8260C	GC/MS	Isopropyl alcohol
Solid	EPA 8260C	GC/MS	Isopropylbenzene
Solid	EPA 8260C	GC/MS	m,p-Xylene
Solid	EPA 8260C	GC/MS	Methacrylonitrile
Solid	EPA 8260C	GC/MS	Methyl acetate
Solid	EPA 8260C	GC/MS	Methyl tert-butyl ether
Solid	EPA 8260C	GC/MS	Methylcyclohexane
Solid	EPA 8260C	GC/MS	Methylene chloride
Solid	EPA 8260C	GC/MS	Naphthalene
Solid	EPA 8260C	GC/MS	n-Butyl alcohol
Solid	EPA 8260C	GC/MS	n-Butylbenzene
Solid	EPA 8260C	GC/MS	o-Xylene
Solid	EPA 8260C	GC/MS	Propionitrile
Solid	EPA 8260C	GC/MS	sec-Butylbenzene

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ALS Global Houston

10450 Stancliff Road, Suite 210, Houston TX 77099
Contact Name: Erica Marinez Phone: 281-530-5656

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Solid	EPA 8260C	GC/MS	Styrene
Solid	EPA 8260C	GC/MS	Tert-butyl alcohol
Solid	EPA 8260C	GC/MS	tert-Butylbenzene
Solid	EPA 8260C	GC/MS	Tetrachloroethene
Solid	EPA 8260C	GC/MS	Toluene
Solid	EPA 8260C	GC/MS	trans-1,2-Dichloroethene
Solid	EPA 8260C	GC/MS	trans-1,3-Dichloropropene
Solid	EPA 8260C	GC/MS	trans-1,4-Dichloro-2-butene
Solid	EPA 8260C	GC/MS	Trichloroethene
Solid	EPA 8260C	GC/MS	Trichlorofluoromethane
Solid	EPA 8260C	GC/MS	Vinyl acetate
Solid	EPA 8260C	GC/MS	Vinyl chloride
Solid	EPA 8260C	GC/MS	Xylenes, Total
Solid	EPA 8270D	GC/MS	1,1´-Biphenyl
Solid	EPA 8270D	GC/MS	1,2,4-Trichlorobenzene
Solid	EPA 8270D	GC/MS	1,2-Dichlorobenzene
Solid	EPA 8270D	GC/MS	1,2-Diphenylhydrazine
Solid	EPA 8270D	GC/MS	1,3-Dichlorobenzene
Solid	EPA 8270D	GC/MS	1,3-Dinitrobenzene
Solid	EPA 8270D	GC/MS	1,4-Dichlorobenzene
Solid	EPA 8270D	GC/MS	1,4-Dinitrobenzene
Solid	EPA 8270D	GC/MS	2,3,4,6-Tetrachlorophenol
Solid	EPA 8270D	GC/MS	2,4,6-Trichlorophenol
Solid	EPA 8270D	GC/MS	2,4-Dichlorophenol
Solid	EPA 8270D	GC/MS	2,4-Dimethylphenol
Solid	EPA 8270D	GC/MS	2,4-Dinitrotoluene
Solid	EPA 8270D	GC/MS	2-Chloronaphthalene
Solid	EPA 8270D	GC/MS	2-Chlorophenol
Solid	EPA 8270D	GC/MS	2-Methylnaphthalene
Solid	EPA 8270D	GC/MS	2-Methylphenol
Solid	EPA 8270D	GC/MS	2-Nitroaniline
Solid	EPA 8270D	GC/MS	2-Nitrophenol
Solid	EPA 8270D	GC/MS	3&4-Methylphenol
Solid	EPA 8270D	GC/MS	3,3´-Dichlorobenzidine
Solid	EPA 8270D	GC/MS	4-Bromophenyl phenyl ether
Solid	EPA 8270D	GC/MS	4-Chloro-3-methylphenol

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ALS Global Houston

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Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Solid	EPA 8270D	GC/MS	4-Chloroaniline
Solid	EPA 8270D	GC/MS	4-Chlorophenyl phenyl ether
Solid	EPA 8270D	GC/MS	4-Nitrophenol
Solid	EPA 8270D	GC/MS	7,12-Dimethylbenz(a)anthracene
Solid	EPA 8270D	GC/MS	Acenaphthene
Solid	EPA 8270D	GC/MS	Acenaphthylene
Solid	EPA 8270D	GC/MS	Acetophenone
Solid	EPA 8270D	GC/MS	Aniline
Solid	EPA 8270D	GC/MS	Anthracene
Solid	EPA 8270D	GC/MS	Atrazine
Solid	EPA 8270D	GC/MS	Benzidine
Solid	EPA 8270D	GC/MS	Benzo(a)anthracene
Solid	EPA 8270D	GC/MS	Benzo(a)pyrene
Solid	EPA 8270D	GC/MS	Benzo(b)fluoranthene
Solid	EPA 8270D	GC/MS	Benzo(g,h,i)perylene
Solid	EPA 8270D	GC/MS	Benzo(k)fluoranthene
Solid	EPA 8270D	GC/MS	Benzoic acid
Solid	EPA 8270D	GC/MS	Benzyl alcohol
Solid	EPA 8270D	GC/MS	Bis(2-chloroethoxy)methane
Solid	EPA 8270D	GC/MS	Bis(2-chloroethyl)ether
Solid	EPA 8270D	GC/MS	Bis(2-chloroisopropyl)ether
Solid	EPA 8270D	GC/MS	Bis(2-ethylhexyl)phthalate
Solid	EPA 8270D	GC/MS	Butyl benzyl phthalate
Solid	EPA 8270D	GC/MS	Caprolactam
Solid	EPA 8270D	GC/MS	Carbazole
Solid	EPA 8270D	GC/MS	Chrysene
Solid	EPA 8270D	GC/MS	Dibenz(a,h)anthracene
Solid	EPA 8270D	GC/MS	Dibenzofuran
Solid	EPA 8270D	GC/MS	Diethyl phthalate
Solid	EPA 8270D	GC/MS	Dimethyl phthalate
Solid	EPA 8270D	GC/MS	Di-n-butyl phthalate
Solid	EPA 8270D	GC/MS	Di-n-octyl phthalate
Solid	EPA 8270D	GC/MS	Diphenylamine
Solid	EPA 8270D	GC/MS	Fluoranthene
Solid	EPA 8270D	GC/MS	Fluorene
Solid	EPA 8270D	GC/MS	Hexachlorobenzene

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Contact Name: Erica Marinez Phone: 281-530-5656

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Solid	EPA 8270D	GC/MS	Hexachlorobutadiene
Solid	EPA 8270D	GC/MS	Hexachloroethane
Solid	EPA 8270D	GC/MS	Indeno(1,2,3-cd)pyrene
Solid	EPA 8270D	GC/MS	Isophorone
Solid	EPA 8270D	GC/MS	Naphthalene
Solid	EPA 8270D	GC/MS	Nitrobenzene
Solid	EPA 8270D	GC/MS	N-Nitrosodimethylamine
Solid	EPA 8270D	GC/MS	N-Nitrosodi-n-propylamine
Solid	EPA 8270D	GC/MS	N-Nitrosodiphenylamine
Solid	EPA 8270D	GC/MS	Pentachlorophenol
Solid	EPA 8270D	GC/MS	Phenanthrene
Solid	EPA 8270D	GC/MS	Phenol
Solid	EPA 8270D	GC/MS	Pyrene
Solid	EPA 8270D	GC/MS	Pyridine
Solid	EPA 8270D	GC/MS	Quinoline
Solid	EPA 8316	HPLC-UV	Acrylamide
Solid	EPA 8330A	HPLC-UV	1,3,5-Trinitrobenzene
Solid	EPA 8330A	HPLC-UV	1,3-Dinitrobenzene
Solid	EPA 8330A	HPLC-UV	2,4,6-Trinitrotoluene
Solid	EPA 8330A	HPLC-UV	2,4-Dinitrotoluene
Solid	EPA 8330A	HPLC-UV	2,6-Dinitrotoluene
Solid	EPA 8330A	HPLC-UV	2-Amino-4,6-dinitrotoluene
Solid	EPA 8330A	HPLC-UV	2-Nitrotoluene
Solid	EPA 8330A	HPLC-UV	3-Nitrotoluene
Solid	EPA 8330A	HPLC-UV	4-Amino-2,6-dinitrotoluene
Solid	EPA 8330A	HPLC-UV	HMX
Solid	EPA 8330A	HPLC-UV	Nitrobenzene
Solid	EPA 8330A	HPLC-UV	RDX
Solid	EPA 8330A	HPLC-UV	Tetryl
Solid	EPA 9014	UV-VIS	Cyanide
Solid	EPA 9040C	Electrode	Corrosivity
Solid	EPA 9040C	Electrode	pH
Solid	EPA 9045D	Electrode	Corrosivity
Solid	EPA 9045D	Electrode	pH
Solid	EPA 9050	Electrode	Conductivity
Solid	EPA 9056A	Ion Chromatography	Fluoride
Solid	EPA 9056A	Ion Chromatography	Bromide

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Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Solid	EPA 9056A	Ion Chromatography	Chloride
Solid	EPA 9056A	Ion Chromatography	Nitrate/Nitrite (as N)
Solid	EPA 9056A	Ion Chromatography	Nitrogen, Nitrate (As N)
Solid	EPA 9056A	Ion Chromatography	Nitrogen, Nitrite (As N)
Solid	EPA 9056A	Ion Chromatography	Phosphorus, Dissolved Orthophosphate as P
Solid	EPA 9056A	Ion Chromatography	Sulfate
Solid	EPA 9071	Gravimetry	Oil & Grease, Total Recoverable
Solid	EPA 9095A	Gravimetry	Free Liquid (Paint Filter)
Solid	MA-EPH	GC-FID	C19-C36 Aliphatics
Solid	MA-EPH	GC-FID	C9-C18 Aliphatics
Solid	MA-EPH	GC-FID	C11-C22 Aromatics (unadjusted)
Solid	MA-VPH	GC-FID	C5-C8 Aliphatics (unadjusted)
Solid	MA-VPH	GC-FID	C9-C10 Aromatics (unadjusted)
Solid	MA-VPH	GC-FID	C9-C12 Aliphatics (unadjusted)
Solid	TX1005	GC-FID	Total Petroleum Hydrocarbons

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PJLA

Certificate of Accreditation: Supplement

ISO/IEC 17025:2017 and DoD-ELAP

ALS Global Houston

10450 Stancliff Road, Suite 210, Houston TX 77099
Contact Name: Erica Marinez Phone: 281-530-5656

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Solid	EPA 1311	Leaching Procedure	TCLP
Solid	EPA 1312	Leaching Procedure	SPLP
Solid	EPA 3050B	Hotblock Digestion	Metals Digestion
Solid	EPA 3060A	Alkaline Digestion	Hexavalent Chrome Digestion
Solid	EPA 3541	Auto-Soxhlet	Organic Extraction
Solid	EPA 3546	Microwave	Microwave Extraction
Solid	EPA 3580A	Waste Dilution	Waste Dilution
Solid	EPA 3640A	GPC Clean-up	Gel Permeation Cleanup
Solid	EPA 3665A	Sulfuric Acid - Permanganate	Cleanup
Solid	EPA 3620C	Florisil	Cleanup
Solid	EPA 9010C	Distillation	Cyanide Distillation

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APPENDIX K – Calibration Criteria and DQOs

Table K.1 Calibration And Maintenance Schedule – Houston Facility

Instrument	Activity	Frequency	Documentation
pH electrometers	Calibration: pH buffer aliquot are used only once Buffers used for calibration will bracket the pH of the media, reagent, or sample tested.	Before use	Worksheet/log book
pH probe / ISE probes	Maintenance: Use manufacturer's specifications	As needed	Worksheet/log book
Spectrophotometer	1. Keep cells clean 2. Service contract. Check wavelength settings with color standards	Annually	Post service date on Unit
Refrigerators, Freezers, and BOD incubators	1. Thermometers are immersed in liquid to the appropriate immersion line 2. The thermometers are graduated in increments of 0.5 °C or less	Temperatures are recorded each day in use	Worksheet/log book
DO electrometer	Calibrate as specified in SOP	Before use	Worksheet/log book
DO probe	Maintenance as specify by manufacturer	As needed	Worksheet/log book
CETAC Mercury Analyzer	Check tubing for wear Fill rinse tank with 10% HCl Insert clean drying tube filled with Magnesium Perchlorate Fill reductant bottle with 10% Stannous Chloride Clean/ Align/ Lubricate Autosampler Linear Range Study	Daily Daily Daily Daily As Needed Semi-annually	Worksheet/log book
UV-Vis Spectrophotometer	Clean ambient flow cell Precision check/alignment of flow cell Wavelength verification check Empty Waste and/or Fill Rinse Containers (Gallery)	As required As required Semi-annually As Needed	Worksheet/log book
ICP/MS	Check pump tubing Check liquid argon supply Check fluid level in waste container Check filters Clean or replace filters Check torch Check sample spray chamber for debris	Daily Daily Daily Weekly As required Daily Monthly	Worksheet/log book

Table K.1 Calibration And Maintenance Schedule – Houston Facility

Instrument	Activity	Frequency	Documentation
	Clean and align nebulizer Check entrance slit for debris Change printer ribbon Replace pump tubing Install cleaned/new skimmer cones Linear Range Study	Monthly Monthly As required As required As needed Semi-annually	
GC/MS Systems	Ion gauge tube degassing Pump oil-level check Diffusion Pump oil changing Analyzer bake-out Analyzer cleaning Resolution adjustment – Tune MSD Auto sampler maintenance Purge and Trap maintenance	As required Monthly Annually As required As required As required As required As required	Worksheet/log book
Electron Capture Detector (ECD)	Detector wipe test (Ni-63) Detector cleaning Detector refoiled	Semi-annually As required As needed	Worksheet/log book
Gas Chromatograph	Compare standard response to previous day or since last initial calibration Check carrier gas flow rate in column Check temp. of detector, inlet, column oven Septum replacement Glass wool replacement Check system for gas leaks with SNOOP Check for loose/fray wires and insulation Bake injector/column Change/remove sections of guard column Replace connectors/liners Change/replace column(s) Autosampler Maintenance	Daily Daily via use of known RT Daily As required As required W/cylinder change as required Monthly As required As required As required As required As required	Worksheet/log book
Flame Ionization Detector (FID)	Detector cleaning	As required	Worksheet/log book
Photoionization Detector (PID)	Change O-rings Clean lamp window Replace PID Lamp	As required As required As needed	Worksheet/log book
HPLC / IC units	Change guard columns Change lamps Change pump seals Replace tubing Change fuses in power supply Filter all samples and solvents	As required As required Semi-annually or as required As required As required Daily	Worksheet/log book

Table K.1 Calibration And Maintenance Schedule – Houston Facility

Instrument	Activity	Frequency	Documentation
	Change autosampler rotor/stator	As required	
TOC Analyzer	Check Sample Delivery Tubing Check Gas and Reagent supplies Replace Catalyst IR Detector cleaning	Daily Daily As required As required	Maintenance Log
Balances	Class "S" traceable weight check Clean pan and check if level Field service	Daily, when used Daily At least annually	Calibration Log
Conductivity Meter	0.01 M KCl calibration Conductivity cell cleaning	Daily, when used As required	
Turbidimeter	Check light bulb Calibrate using three points, use fresh standards daily Linear Range Study	Daily, when used Daily Semi-annually	
Deionized/ Water	Check resistance Check deionizer light Monitor for VOA's Replace cartridge & large mixed bed resins	Daily Daily Daily As required	DI Water Log
Drying Ovens	Temperature monitoring Temperature adjustments	Daily As required	
Refrigerators/ Freezers	Temperature monitoring Temperature adjustment Defrosting/cleaning	Daily As required As required	
pH/Specific Ion Meter	Calibration/check slope Clean electrode	Daily As required	
BOD Incubator	Temperature monitoring Coil and incubator cleaning	Daily Monthly	
Auto analyzer (Gallery)	Clean surfaces and waste container Clean cuvette waste bin, racks, probes, mixer paddle, wash wells and wipe off moisture. Clean incubator and water containers	Daily Weekly Monthly	Maintenance Log
Auto analyzer (Mantech)	Empty waste, check pH, keep rinse solution clean Replace seed lines Replace dilution, inhibitor line Replace all tubes, electrodes Clean Carboys	Daily Quarterly Semi-annually As Needed Weekly	Maintenance Log
Microwave Oven	Clean Cavity Replace Door Shield	Daily As Needed	
Water Chiller	Clean Coils Add coolant	Monthly As Needed	

PROCUREMENT AND CONTROL OF LABORATORY SERVICES AND SUPPLIES

DOCUMENT ID: CE-GEN0007, REV 2.1

Approved By: Hoai. Van
Technical and Laboratory Director, Hoai Van

Date: 2/22/19

Prepared By: Erica M Howard
Quality Assurance Manager, Erica Howard

Date: 2/22/2019

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1) Scope & Applicability

1.1 The purpose of this Standard Operating Procedure (SOP) is to describe procedures for requesting laboratory products and materials from vendors, purchasing those products, and approving the vendors.

1.2 Procedures used to evaluate suppliers and critical consumables are also described.

1.3 Procedures described in this SOP apply to all laboratory purchases of supplies and materials made by ALS Houston through the purchasing department. This includes reagents, standards, consumables, metrology calibration services, and reference materials.

1.4 Maintenance and use of a vendor list is also discussed.

1.5 This SOP does not address the additional requisition considerations required for capital expenditure purchases (CAPEX; please consult with the Laboratory Director regarding CAPEX purchases).

1.6 This SOP does not address the evaluation and qualification of subcontract laboratories, which is addressed in SOP CE-QA004.

2) Summary of Procedure

2.1 All supplies and materials ordered must meet all applicable technical requirements as defined by the appropriate Department Manager, as applicable. An ALS Houston Purchase Order Requisition is used to document the purchase request. Packing slips are used to document receipt. All received materials are inspected for damage. Some materials require verification by the laboratory before use. Material certifications, as applicable, are maintained by the primary Department that utilizes the material. All materials are stored in an appropriate area, under suitable environmental conditions per manufacturer requirements. Some supplies (e.g., standards, reagents, solvents), are subject to additional cataloging and labeling requirements. Evaluation of services provided is the responsibility of the Managers/Supervisors that procured the service rendered, who in-turn let the quality department know who the quality of service received at least once per year for documentation purpose.

3) Definitions

3.1 Vendor: Supplier of laboratory supplies, materials, consumables, and services. This includes subcontract laboratories

3.2 Purchaser: the Purchasing Supervisor or designated purchasing staff.

4) Responsibilities

4.1 Laboratory management (Laboratory Director and Supervisors)

It is the responsibility of the laboratory management to perform required vendor evaluations, use vendors and select materials that are suitable for the intended purpose, and to properly complete the purchase order requisition. It is also the laboratory management responsibility to manage the verification of materials, as

applicable; to retain material certifications, as applicable; and to ensure that storage and ancillary cataloguing and labeling requirements are met.

4.2 Laboratory Quality Assurance Manager (QAM)

The QAM is responsible for performing or facilitating required vendor evaluations and for monitoring ongoing compliance with this SOP.

4.3 Procurement Manager (PM)

The PM will be responsible for directing and coordinating activities of personnel engaged in buying materials and supplies. The PM will be responsible for maintaining an approved vendor list.

5) Procedure

5.1 Vendor selection

5.1.1 Vendors and suppliers must be established businesses or entities which are capable of providing the materials, goods, or services meeting the requirements of ALS Houston and its customers.

5.1.2 Vendors of supplies and services which affect the quality of test results, including critical consumables, must be evaluated following the procedure described below. Records on the evaluation are maintained by the laboratory. After successful evaluation, these vendors may be selected for these types of supplies and services.

5.1.3 Vendors of supplies, materials, consumables, and services not expected to affect the quality of test results do not need an evaluation, unless required by contract between ALS and its customer.

5.1.4 In the event that problems arise with quality, availability, or possible financial concerns, vendors on the approved list will be removed.

5.2 Identification of items requiring vendor evaluation

5.2.1 The following list defines laboratory supplies and services which potentially affect the quality of test results and require vendor evaluation.

- Analytical calibration and QC standards, including neat chemicals
- QC reference materials
- Acids and solvents
- Reagents used in test procedures
- Laboratory gases
- Consumables potentially impacting test performance or accuracy of test results. Examples include:
    - Extraction disks, cartridges, and extract cleanup materials
    - Filters (used in sample analysis)
    - Pipets, syringes, and volumetric ware
    - Digestion vessels
    - Centrifuge tubes
    - Autosampler vials
- Critical consumables – as defined in Section 5.5 and Appendix B
- Equipment consumables (syringes, tubing, chromatography columns,

injection parts, etc.)
- Proficiency testing provider products
- Support equipment (balances, thermometers, weights)
- Sample containers
- Laboratory deionized water systems, components, and service
- Calibration and calibration verification services
- Analytical equipment (instruments and manually used lab equipment used to produce sample results)

5.2.2 Suppliers of other items may be evaluated using the appropriate supervisor's professional judgement.

5.3 Vendor evaluation - If a required product or service is not available from an approved vendor and a new vendor is being evaluated, the following steps are taken:

NOTE: this section applies only to supplies and services identified in Section 5.2.

5.3.1 Business evaluation and approval

5.3.1.1 The corporate purchasing department completes a Business Certification Sheet (Appendix A). This information establishes that the vendor is a viable business entity and is required before the vendor is set up in the requisition and payment systems.

5.3.1.2 A Purchasing approved vendor list will be maintained by the Procurement Manager or designee. This is a list of vendors for which the business evaluation is complete.

5.3.2 Laboratory evaluation and approval

5.3.2.1 The person needing a supply, material, or service from a vendor not already evaluated will notify the QAM. This is usually the supervisor of the lab work area.

5.3.2.2 The QAM, or designee, will complete a Laboratory Vendor Evaluation Form (example form in Appendix B).

- All fields should be completed or marked otherwise
- Accompanying documents should be identified
- Requirements for Certificates of Analysis (or similar product documentation) must be identified
- Vendors of laboratory gases must be capable of providing traceability to certificates of analysis for gases.
- Vendors of de-ionized water systems and maintenance will also be evaluated by the vendor's ability to provide systems which generate water meeting the specifications for the laboratory.
- Vendors of calibration services of metrology equipment (balances, weights, thermometers, etc) must be pre-approved by the laboratory QAM. Approval is performed by obtaining the required certifications or accreditations required by ALS Houston laboratory quality programs. The vendor (and documentation) must meet the requirements of

NELAP, DoD QSM, DOE, Navy LAP and (for ALS ISO accredited labs) ISO 17025.

5.3.2.3 Evaluation is based on relevant evaluation items, such as those listed on the example Laboratory Vendor Evaluation Form in Appendix B. For established vendors who have the business approval and whose product has been in use, approval may be based on evaluation of historical product or service acceptability and performance by the appropriate laboratory supervisor and QAM.

5.3.2.4 Once the form is completed and accompanying information is obtained, and it is acceptable, it is approved by the QAM and kept on file. A copy is sent to the department supervisor requesting the evaluation.

5.3.2.5 A Laboratory approved vendor list will be maintained by the QAM. This is a list of vendors for which the laboratory evaluation is complete.

5.4 Purchasing from approved vendors

5.4.1 ALS-Houston laboratory use the ALS Requisition System. The person filling out the purchase requisition will ensure that the product or service meets the requirements or specifications in the SOP or method. An adequate description of the quality or specification should be provided on the purchase requisition or attachment (e.g. grade, class, specification, purity, etc.). This may be incorporated by reference with the vendor's product or catalogue number. Refer to SOP CE-QA012, Quality of Reagents and Standards, for additional information on determining reagents and standards quality.

5.4.2 Purchase requisitions may be processed for vendors where the business evaluation is complete the laboratory evaluation is underway and expected to be completed. The lack of a final completed laboratory evaluation, including critical consumable testing, should not prevent purchasing as long as the evaluation and/or testing is completed prior to product use.

5.4.3 If a new critical consumable product or service is required from an approved vendor, the products or services must be evaluated prior to use as described in Section 5.5.

5.5 Critical consumables, supplies, and services

5.5.1 Critical products and services are listed in Appendix C. These products and services must be evaluated prior to use. Vendors must be listed as an approved vendor in order to purchase these items.

5.5.2 Sample bottles will be approved by acquiring and reviewing the Certificate of Analysis for the particular bottle type against test specifications.

5.5.3 SPE extraction disks and cartridges will be pre-tested by conducting routine extraction procedures.

5.5.4 Lot pretesting – see Table 1

- Refer to SOP CE-QA012, Quality of Reagents and Standards, for details on critical consumable testing procedures.

- A sample of the product will be requested and will be analyzed to determine it meets the laboratory requirement, as applicable to the specific use.
- If it is determined it meets the lab's criteria the vendor and lot number will be forwarded to corporate purchasing. Subsequent orders must specify or sequester the defined lot number.

5.6 Receiving Incoming Materials

5.6.1 A general inspection of the materials is performed and the appropriate supervisor or manager is notified that the materials have arrived. The supervisor will release for use based on receipt inspection results.

5.6.1.1 The products are inspected for damage by the ordering department for evaluation.

5.6.1.2 The packing list and/or products are verified as being what was requested in the associated requisition.

5.6.1.3 The packing list is compared to the physical product, label, or identification to verify the correct product was received.

5.6.2 For items not affecting the quality of test results the receipt of undamaged materials is the extent of the acceptability evaluation that needs to be conducted. Hence, in these cases, relocation of these items to the appropriate lab department or general supply area constitutes release for use.

5.6.3 Receipt of products or materials not meeting inspection requirements will be held and either returned or further evaluated for use by the appropriate supervisor prior to release for use. Documentation of in-house evaluations shall be retained by the quality department.

5.6.4 Incoming materials may be kept in the Receiving area until the department who ordered them, relocates the items. This may be done to avoid misplacement, loss, or potential contamination, as well as to keep the items segregated should further evaluative testing need to be conducted before the items are put into use.

NOTE: All materials, but with particular note of reference materials, shall be handled and stored safely, and in a manner that preserves the material's integrity. Where additional evaluation practices exist, staff is not permitted to use the materials until the evaluation has been completed successfully.

5.7 Storage of Purchased Materials and Consumables

5.7.1 Reagent containers must be labeled with the date received and the certificate of analysis must be kept by the laboratory, as appropriate.

5.7.2 Materials received should be stored as recommended by the manufacturer to avoid degradation.

5.7.3 Temperature dependent materials are stored in designated temperature monitored refrigerators or freezers.

5.7.4 Standards and mixtures must be segregated from sample material to prevent the possibility of cross-contamination.

5.7.5 Solvents are segregated based on flammability and stored in the appropriate cabinets under the hoods in the extraction laboratory, wet chemistry, or chromatography. Reference standard/material integrity is protected by separation from incompatible materials and/or minimizing exposure to degrading environments or materials (using manufacturer's recommendations).

5.7.6 Flammable solvents must be stored away from potential sources of ignition and heat.

5.7.7 Acids and bases must be stored separately as required by the laboratory safety policy.

5.7.8 Bottles and VOA vials must be stored appropriately and the Certificate for Cleanliness must be kept for all types of sample bottles.

6) Quality Assurance

6.1 Contaminants traced back to a consumable material will result in the removal of the material from the laboratory use.

6.2 Each ALS Houston laboratory will ensure that applicable laboratory employees are trained on the requirements of this SOP.

7) Documentation and Records

7.1 As part of the requirements of this SOP for checking new lots of chemicals, the laboratories retain the testing records for the chemical pre-tested.

7.2 The "Certificate of Analysis" or "Certificate of Cleanliness" must be filed by the laboratory as appropriate.

7.3 The completed Business Certification Sheet used for business approval of vendors will be kept on file by corporate accounting.

7.4 Purchase requisitions will be used to document that the proper products were obtained to ensure the quality of subsequent testing results.

7.5 Receiving documents will be used to document that the purchased products are those requested and received, and meet the requirements of the requesting department, the lot number will also documented on the receiving documents prior to being submitted to the QA department.

8) Summary of Changes

Table 8.1 Summary of Revision Changes

Revision Number	Effective Date	Document Editor	Description of Changes
00.0	09/01/2012	I. Williams	New SOP
1.00	06/30/2014	I. Williams	Cover page and footer
1.00	06/30/2014	I. Williams	Added to 5.1.1.2 Traceability for gases
1.00	06/30/2014	I. Williams	Clarify Section 6.2 and use of

			Acknowledgement Form
1.00	06/30/2014	I. Williams	Added snapshot of ALS purchasing tracking system
2.00	11/15/15	L. Wolf	1.2 – Added suppliers 3.1 – revised definition 4.2 – revised to include vendor evaluations Section 5 – this revision represents a major reorganization of topics in this section. Revisions focused on ISO 17025 requirements for vendor evaluation. Topics were simplified for better understanding and clarity of procedures. Moved critical consumables table to appendix. Added Appendix A and vendor form. Added references to CE-QA012. Section 5.6 added inspection and verification details (ISO). Section 7.4 and 7.5 – New Appendix A and B – New
2.1	02/22/2019	G. Moulton	Updated to new ALS Cover and new quality manager.
2.1	02/22/2019	G. Moulton	Modified sec 1.3, 1.5, 2.1, 7.5
2.1	02/22/2019	G. Moulton	Modified sec 9.1 and 9.2

9) References and Related Documents

9.1 Current TNI Standard.

9.2 Current Department of Defense Quality System Manual.

9.3 ISO/IEC 17025:2005.

10) Appendices

APPENDIX A - VENDOR BUSINESS CERTIFICATION SHEET

BUSINESS CERTIFICATIONS

Subcontractor/Vendor/Bidder hereby represents that it (Check applicable boxes):

Business Type: ☐ Corporation ☐ Partnership ☐ Joint Venture ☐ Sole Proprietorship ☐ Other _____

Number of Employees (all affiliates): ☐ 500 or less ☐ More than 500

☐ Large business ☐ Small business

☐ Certified as a Small Disadvantaged Business with the Small Business Administration*

☐ Certified as an 8(a) Business Concern with the Small Business Administration*

☐ Certified as a HUBZone Business Concern with the Small Business Administration*

☐ A historically black college or university / minority institution

☐ An other education institution

☐ A business concern owned / controlled (51% or more) by the following classification (Please check correct classification):
- ☐ Black Americans
- ☐ Hispanic Americans
- ☐ Asian-Pacific Americans (Origins in Japan, China, Philippines, Vietnam, Korea, Somoa, Guam, US Trust Territory of Pacific Is., N. Mariana Is., Laos, Cambodia or Taiwan)
- ☐ Native Americans (American Indian, Eskimos, Aleuts, and Native Hawaiians)
- ☐ Asian-Indian Americans (Origins in India, Pakistan, and Bangladesh)
- ☐ Other _____

☐ A business concern owned or controlled (51% or more) which is (more than one category may apply—check all that apply):
☐ Woman-owned ☐ Disabled veteran ☐ Vietnam veteran ☐ Non-profit organization

☐ A business concern in any of the categories listed above that also operates in a:
☐ Labor surplus area ☐ Rural Area ☐Labor surplus area and rural area

☐ A business concern certified as a HUBZone Enterprise/MBE/WBE by federal, state, or local government (specify which federal agency, state or local government): _____

☐ Is ☐ Is not Subject to "Cost Accounting Standards"
☐ Is ☐ Is not As of the time of award of this subcontract, debarred or suspended by the Federal government from government contracting or subcontracting.

*For additional information, visit the Small Business Administrations website at http://www.sba.gov or call (800) 827-5722.

NOTICE: Under 15 U.S.C. § 646(d), any person who misrepresents a firm's status as a small business concern in order to obtain a contract to be awarded under the preference programs established pursuant to section 8 (a), or (b), 9 or 15 of the Small Business Act or any other provision of Federal law that specifically references section 8 (d) for a definition of program eligibility, shall (1) Be punished by imposition of fine, imprisonment, or both; (2) Be subject to administrative remedies, including suspension and debarment; and (3) Be ineligible for participation in programs conducted under the authority of the Act.

Legal Name: _____
Use person's legal name if sole proprietor; otherwise use company name

Phone: _____

Remit to address: _____

Fax: _____

_____

e-mail: _____

_____

Federal TIN: _____
(Federal Tax Identification Number or Social Security Number associated with the legal name)

Signature: _____

Date: _____

Print or Type Name: _____

Title: _____

Return completed form to:

Attn: Accounts Payable
10450 Stancliff Road Suite 210
Houston, TX 77099
FAX: 281-561-6125

[] WBE [] MBE [] SB [] HUB [] 1099

[] Resale [] Tax Exempt

To our Valued Suppliers:

We are in the process of update our records and would appreciate it you would take the time to complete the attached W-9 form, Business Certifications, and Tax Resale Certificate, please return it by December 15th 2012.

We value you as a supplier, and would like to thank you for your cooperation in this matter.

Please note the special instructions listed below:

- Make sure you check the appropriate box indicating your type of business entity.
- If your tax id number is a Social Security number enter the individual's name on the "Name line", the business name (if applicable) on the "Business Name" line, and the individual's social security number in section 1 of the form.
- If your company is a corporation or tax-exempt organization, please compete the attached form even though you may be exempt from 1099 reporting and backup withholding.

Please mail the competed forms to:

ALS Group
10450 Stancliff Road, Suite 210
Houston, TX 77099

Or Fax to:
Attn: Phillip Zagotti
Fax# 281-561-6125
Phillip.Zagolli@ALSGlobal.com

If you have any questions or comments, please contact me at the phone number or email address listed.

Regards,

APPENDIX B - VENDOR LABORATORY EVALUATION FORM EXAMPLE

Laboratory Vendor Evaluation Form

ALS Environmental

Requested by: Date:

Vendor Information	
Vendor Name:	
Product or Service Provided:	
Contact:	
E-mail:	
Address:	
Telephone:	
Fax:	
Website:	

Evaluation

Evaluation Item	Result	Comment
1. Does the vendor have a formal Quality Assurance Program in place?		
• If so, what is the basis of the Quality System (i.e. ISO)?		
• Formal certification or accreditation of the Quality System (i.e. ISO)?		
2. Do products or services meet applicable standards?		
3. Vendor makes available products of suitable grades, quality, or purity meeting test requirements?		
4. For services, is the service readily available?		
5. Specific product certifications available (e.g. C of A) where applicable?		
6. Laboratory evaluation of historical product or service and acceptable performance?		
• Department Supervisor		
• QA Manager		
7. Alternative evaluation (explain)		

Approval	
QA Manager:	
Date:	
Comments:	

APPENDIX C – CRITICAL CONSUMABLES LIST

Critical consumables, supplies, and services	
Product	Evaluation
Consumables and Supplies	
Sample bottles	Acceptable Certificate of Analysis
SPE Extraction disks	Acceptable negative and positive control
SPE Extraction cartridges	Acceptable negative and positive control
Calibration standards	Acceptable Certificate of Analysis
Sodium sulfate (extraction)	Acceptable negative and positive control
Extraction Solvents	Required lot pre-test
Methylene chloride	Acceptable negative control
Hexane	Acceptable negative control
Acetone	Acceptable negative control
Purge&trap methanol	Acceptable negative control
Extraction Cleanup	Required lot pre-test
Florisil	Acceptable negative and positive control
Silica gel	Acceptable negative and positive control
Acids	Required lot pre-test
Nitric acid (metals digestion)	Acceptable negative control
Sulfuric acid (metals digestion)	Acceptable negative control
Hydrochloric acid (metals digestion)	Acceptable negative control
Radioactive materials	Radioactive survey within limits
Services	
Deionized water systems	QAM assessment of qualifications
Calibration services	QAM assessment of qualifications

QUALITY OF REAGENTS AND STANDARDS

DOCUMENT ID: CE-QA012, REV 1.1

Approved By: Hoai. Van
Laboratory/Technical Director, Hoai Van

Date: 2/22/19

Prepared By: Erica M Howard
Quality Assurance Manager, Erica Howard

Date: 2/22/2019

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1) Scope & Applicability

1.1 This Standard Operating Procedure (SOP) addresses policies and procedures for ensuring the quality of reagents, chemicals, and standards used in performing laboratory analyses.

1.2 This SOP includes procedures for checking chemical lots (new lots) for unacceptable levels of contaminants prior to their use in sample preservation and in sample preparation and analysis. The purpose of this check is to verify that chemicals do not introduce contamination into samples. This check procedure does not apply to standards and reference materials since the quality of standards is specified in the analytical SOP.

1.3 The SOP also includes default requirements for establishing the expiration periods for reagents and standards. These default expiration periods do not apply to materials used in radiochemical analysis.

1.4 It is a requirement of most laboratory accreditation or certification programs that the laboratory shall implement a quality system appropriate to the scope of its activities. As part of these requirements, including those written in the TNI/NELAP Standards, DOD, CLP, DOE, and ISO/IEC 17025:2005, reagents and standards shall be of adequate quality to facilitate the generation of accurate results. This procedure is also applicable to laboratories conducting analyses under the AIHA Laboratory Accreditation Program (AIHA-LAP, LLC) and the Naval Sea Systems Command Laboratory Accreditation Program (NAVSEA-LAP).

2) Summary of Procedure

2.1 When a new lot of a chemical is to be introduced into an analytical procedure, the new lot should be evaluated to ensure that it does not contain the analyte(s) being measured at unacceptable levels, or contains interfering non-target contaminants. This evaluation should be done before the new lot of chemical is used on samples.

2.2 Some chemicals are used in more than one different analysis procedure. Because a particular lot of a particular chemical may contain contamination that may not be acceptable in one application but be inconsequential in another, that chemical should be tested for acceptability in each application.

2.3 To minimize the time spent and the amount of solvent or acid expended on contamination testing, solvents and acids that are used in greater volume and by multiple laboratories may be tested by a single ALS laboratory and the results made available to all labs. Also, ALS may establish purchasing agreements with vendors of these chemicals to sequester individual lots for subsequent purchasing.

2.4 Specifications or certificates of analysis provided by the manufacturer are also used as a source of information about chemical suitability. To be useful, these manufacturer specifications must be for the actual lot received and include information about the analyte(s) being measured.

3) Definitions

3.1 Chemical - For the purpose of this SOP, chemical shall refer to any solvent, acid, base, or reagent used in sample preservation, sample preparation, or any step of sample analysis that comes in contact with the sample or sample handling apparatus.

Note: The SOP for Procurement and Control of Laboratory Services and Supplies (CE-GEN007) contains information on critical consumables. For the purposes of this SOP, procedures are described for critical chemicals (a subset of critical consumables).

3.2 Lot Number - The number assigned by the manufacturer or vendor to distinguish one manufactured or prepared batch of the chemical from another. The lot number is written on the container label.

3.3 Method Blank - The method blank is either analyte-free water or analyte-free solid matrix that is subjected to the entire analytical process and analyzed to demonstrate that the analytical system (including all the chemicals used in the procedure) is not contaminated with the analyte(s) being measured or with contaminants that will interfere with the analyte(s) being measured.

3.4 RL – Reporting Limit. Synonymous with Method Reporting Limit (MRL).

3.5 Certificate of Analysis (CoA) – The certificate or attestation supplied with a standard, reagent, or reference material that establishes the quality (concentration, purity, accuracy, etc.) of the material as provided by the vendor. The CoA provides traceability to a national metrology institute or other source (national or international standards, primary standards, basic physical constants or properties, or reference materials – TNI 2009).

3.6 Laboratory Reference Material – Materials accompanied by a certificate and having a stated value; and used in the laboratory for a defined intended use. These include, but are not limited to, the following:

3.6.1 NIST SARM – National Institute of Standards and Technology (NIST) Standard Analytical Reference Material (SARM).

3.6.2 Reference Materials produced by an accredited Reference Material Producer to ISO Guide 34: 2000 – General requirements for the competence of reference material producers.

3.6.3 EPA Certified Reference Standard Solutions or Vendor Certified Reference Standard Solutions

3.6.4 Certified Reference Material (CRM) – Reference material, accompanied by a certificate, having a value, measurement uncertainty, and stated metrological traceability chain to a national metrology institute. (TNI 2009).

3.6.5 Reference Material (RM) – Material or substance one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials. (TNI 2009).

3.6.6 Neat or primary standard materials. These are undissolved solids or undiluted liquids and are nearly 100 % pure.

4) Responsibilities

4.1 Management is responsible for the development of this procedure and distributing the procedure to the quality departments of the laboratories.

4.2 It is the responsibility of the laboratory Quality Assurance Manager (QAM) to implement this procedure at the laboratory facilities. The lab QAM is responsible for training laboratory staff on how to use this SOP and for ensuring testing is documented.

4.3 Laboratory supervisors are responsible for implementation of this SOP in their lab area. Supervisors must ensure that there is an effective mechanism for removing expired standards from use so that may not be used for calibration (or verification), or quality control.

5) Procedure

5.1 Before using a new bottle of solvent, acid, or reagent the analyst should check the lot number on the new bottle against the lot number on the empty bottle. If they are the same, it can be assumed that the new bottle of material is also acceptable for use. If they are different, the chemical from the new bottle should be tested following the procedure in this SOP. In either case, the analyst must list information on containers used in the lab which allows for tracing the chemical or reagent back to the lot number.

5.2 Although all chemicals used in a test procedure are essential, a determination of how a new lot of chemical will be checked should first be made based on the chemical.

5.2.1 For chemicals where pre-testing for contamination is not considered critical, an evaluation of the suppliers CoA or specifications is adequate to ensure chemical quality before use. The following are some examples:

- In tests where reagent grade chemicals are called for, and reagent grade is purchased and used.
- The chemical is not significantly concentrated to result in a solution or 'carrier' used in the final analysis.
- The chemical plays a distinct and specific role (e.g. chemical reaction) in the test procedure and where any potential contamination will not interfere with the analysis.
- The target analytes are unique to the sampling site or type of sample and the presence in the chemical/reagent is highly unlikely (e.g. EPA 1653).

For this evaluation the supplier's information and specifications are used to verify that a chemical may be used as received, as follows:

- The grade and/or purity of the chemical is that which was specified or ordered.
- Where a CoA is provided, the information is specific for the lot number received.

- When provided, the CoA (and/or associated documentation) includes information about the concentration of the target analyte(s) to be sure it is (they are) not present at a concentration interfering with the analysis; and includes information indicating that other contaminants which may interfere with the detection and reporting of the target analyte(s) are not present.
- For these chemicals, the evaluation of initial method blanks using the chemical will serve as verification of suitability for use. However, the chemical may also be pre-tested (as described below) if desired.

Note: The CoA is also used to establish traceability of the chemical or material.

5.3 Pre-testing of critical chemicals

5.3.1 Pre-testing for contamination is considered critical for chemicals that, as used in the test, may directly impact the quality of laboratory test results due to the amount used or concentration steps performed. This includes solvents that are concentrated as part of the test, acids used for metals digestion/analysis, purge and trap methanol, and extract clean-up materials.

5.3.2 The table below lists the materials that, at a minimum, require pre-testing of a new lot.

Critical Consumables Requiring Pre-Testing	
Product	Evaluation
Sodium sulfate (extraction)	Acceptable negative and positive control
Extraction Solvents	Required lot pre-test
Methylene chloride	Acceptable negative control
Hexane	Acceptable negative control
Acetone	Acceptable negative control
Extraction Cleanup	Required lot pre-test
Florisil	Acceptable negative and positive control
Silica gel	Acceptable negative and positive control
Methanol	Required lot pre-test
Purge&trap methanol	Acceptable negative control
Acids	Required lot pre-test
Nitric acid (metals digestion)	Acceptable negative control
Sulfuric acid (metals digestion)	Acceptable negative control
Hydrochloric acid (metals digestion)	Acceptable negative control

5.3.3 For extraction solvents the following procedure is used:

5.3.3.1 Concentrate a volume of solvent representing the most used in any routine extraction (e.g. 200-500 mL) to a volume representing that similarly used for the smallest routinely used final volume (e.g. 1-2 mL). Since this test is being done to test the solvent only, dedicated clean glassware should be used to isolate the solvent evaluation.

5.3.3.2 For GC/ECD tests it may be necessary to solvent exchange to hexane prior to analysis.

5.3.3.3 Split the concentrated solvent between three autosampler vials; one designated for GC/ECD analysis, one designated for GC/MS full scan analysis, and one designated for GC/MS-SIM PAH analysis, and label. For GC/ECD tests it may be necessary to solvent exchange to hexane prior to analysis.

Note: If the laboratory does not do SIM analysis and the solvent will not be used for SIM PAH analyses, the separate SIM vial is not needed.

5.3.3.4 Analyze the GC/ECD portion by the appropriate low-level analysis, typically the lowest level EPA 8081 analysis. Analyze the GC/MS full scan portion by the appropriate low-level GC/MS analysis, typically the lowest level full scan EPA 8270 analysis. Analyze the SIM PAH portion by the applicable low-level SIM PAH analysis.

5.3.3.5 Use normal sample analysis, quantitation, and qualitative evaluation procedures to evaluate the data (although these may be analyzed outside of sequence brackets or tune clocks). Compare the result to the applicable criteria in the attached tables, or as specific to the particular laboratory performing the testing.

5.3.4 For all other chemicals being pre-tested, the chemical is checked for unacceptable levels of contaminants by processing the quantity of that chemical that is typically used in an analytical procedure (including in sample preservation) through a method blank analysis. That is, the new lot of chemical is to be used as prescribed in the analytical procedure in the preparation and analysis of a method blank. At a minimum this includes all acids used in metals digestions, purge-and-trap grade methanol, sodium sulfate used in extractions, Florisil, and silica gel.

Note: Laboratories may establish their own more specific SOP for testing of certain chemical or materials (e.g. sodium sulfate).

5.3.5 For any of the above tests, compare the results to the established acceptability criteria. The default criteria are one half of the RL. That is, no contaminant or interference present at a level greater than one half of the RL of target analytes for the associated tests.

5.3.6 Document the evaluation using an appropriate form or summary of the pre-testing and results. Documentation should be maintained by the laboratory department or forwarded to the laboratory QA Manager for filing. This

documentation may be shared with other ALS laboratories or provided to purchasing staff for the purpose of sequestering lot numbers.

5.4 Sequestering Lots of Solvents and Acids

5.4.1 Individual lots of certain solvents and acids may be sequestered by the vendor at the request of ALS. Any ALS laboratory may request to purchase these solvents and acids from a sequestered lot through the purchasing representative.

5.5 Testing of Chemicals Used for Sample Preservation

5.5.1 Chemicals used for sample preservation (such as nitric acid, hydrochloric acid, sodium hydroxide, etc.) need to be tested for contamination prior to their use in preserving samples, if they are not purchased with an appropriate C of A. The chemicals (as prepared for use) are to be tested for the analytes that will be measured in the samples that are preserved with that chemical. For example, the nitric acid solution used to preserve samples for metals analyses needs to be tested for metals contamination prior to use.

5.5.2 The testing is to be done following the procedure described in Section 5.3. This testing is to be done by the individual laboratories on the chemical preservatives used in their laboratories.

5.6 Establishing Expiration Periods for Standards and Reagents

5.6.1 This section provides standard requirements for assigning expiration dates to standards and reagents used. It is a requirement of NELAP Quality System standards, the DoD Quality System Manual (QSM), and ISO 17025:2005 to have written protocols to ensure the use of standards and reagents of appropriate quality. Additionally, documentation of the expiration date of reagents and standards is required.

5.6.2 The requirements are applicable to all purchased and prepared standards and reagents used by the laboratory to generate reported data. This includes raw (neat) materials, stock, intermediate, working, and calibration standards and/or reagents. This does not include solvents and acids.

5.6.3 In general, the expiration date is the date after which a standard or reagent shall not be used. It is either the date assigned by the manufacturer, the date (duration) specified by the applicable reference method, or it is a date assigned by the laboratory under this SOP.

5.6.4 General requirements:

5.6.4.1 All standard and reagent expiration dates/periods are based on proper storage conditions and shall be listed in the applicable laboratory SOP.

5.6.4.2 When establishing an expiration date, the following hierarchy will be used:

- If the cited analytical method specifies the expiration date/period, that date shall be used.
- If the cited analytical method does not specify the expiration date/period, then the date assigned by the manufacturer will be used.
- If the cited analytical method does not specify the expiration date/period, and an expiration date is not assigned by the manufacturer, then the laboratory will assign the expiration date according to the ALS Standardized Expiration Dates (Table 1).

5.6.4.3 The expiration date of a prepared reagent or standard cannot exceed the expiration date of the starting (or parent) material, with the exception of standards prepared via in-lab derivatization to yield a different compound. The expiration date of a reagent or standard cannot be extended by preparing a dilution of it.

5.6.4.4 A multicomponent prepared reagent or standard will be assigned an expiration date not to exceed the expiration date of any of the starting (or parent) components' expiration date.

5.6.4.5 The stability and concentration of the reagent or standard are to be taken into account when assigning the expiration date. Certain solutions, depending on use and storage, may have shorter usable life time than defined by the method, manufacturer, or this SOP; and should be assigned expiration dates accordingly. Reagents and standards must be stored under conditions specified by the test method and outlined in the analytical SOP.

5.6.4.6 Expiration dates can be extended under the following conditions:

- A new, replacement reagent or standard is not readily available from vendors and,
- The cited analytical method does not specify the expiration date/period and,
- The material has been stored under conditions specified by the analysis method and outlined in the analytical SOP and,
- The material is not reactive, volatile, or prone to degradation under the specified storage conditions and,
- The suitability of the material is verified by the laboratory as follows, under the same valid analysis conditions used for sample analysis, and meet the following criteria:

  <u>For reagents</u>:
  - Perform a blank and LCS pair of analysis three times using three different subaliquots of the reagent.
  - Each LCS result must be within the specified control limits for the test.
  - The %RSD for the three LCS's must be <10%.
  - Each blank result must be < 1/2MRL for every compound to be reported from subsequent analysis.

For standards:

- Analyze three separate dilutions of the standard at a concentration near the midpoint of the calibration range. (Note that standards below this concentration cannot be re-verified).
- The average result must be within ± 5% of the original true value.
- The %RSD for the three results must be <10%.

If these conditions and criteria are met and documented, the material may be assigned a new expiration period the same as newly prepared material.

6) Quality Assurance and Quality Control

6.1 ALS Houston laboratory will ensure that all laboratory employees are trained on the requirements of this SOP. The training shall be documented using the SOP Concurrence Form included in this SOP or other similar form as appropriate.

6.2 For a chemical to have unrestricted application for all of the chemical's intended uses, the results of the analysis described in Section 5.0 must be less than half of the RL for the applicable test for each target analyte and for interfering contaminants. Chemicals with contaminant concentration(s) greater than this level may be used so long as the contaminant(s) does (do) not interfere with the detection of the target analytes to the customer-specified reporting limits.

6.3 The chemicals used as preservatives in sample bottles must be acceptable for all the intended uses. For example, the sulfuric acid used in ammonia, COD, TKN, oil and grease, etc. analyses must be free of contaminants that would interfere with all of these analyses.

6.4 If the contamination levels are such that the chemical is not useable, the chemical should be returned to the vendor for replacement with a new lot of the chemical. Returns and new samples to test are requested through ALS' purchasing representative.

6.5 If problems are encountered with any of the sequestered lots, the laboratory should cease use of that lot and promptly contact ALS' purchasing representative.

7) Documentation and Records

7.1 Records for standards, reagents, and reference materials shall include lot numbers. The lot number of each of the solvents, acids, reagents, etc. used in an analytical procedure is to be documented in the analysis raw data. To facilitate comparison of lot numbers of new and old lots of chemicals, the laboratory should maintain a record of the lots tested and the results. The reagents or standards logbook could be used for this purpose.

7.2 The laboratory should maintain records of critical chemical pre-testing.

7.3 When vendor documentation (i.e. CoA) is used to verify that the material's stated purity will meet the intended use, record of the verification shall be maintained.

8) Summary of Changes

Table 8.1 Summary of Revision Changes

Revision Number	Effective Date	Document Editor	Description of Changes
00.0	02/15/2013	L. Wolf	New SOP
1.00	10/31/2016	L. Wolf	Updated overall format & style
1.00	10/31/2016	L. Wolf	Section 1.4 – new section
1.00	10/31/2016	L. Wolf	Section 2.3 – minor revision
1.00	10/31/2016	L. Wolf	Section 3.3 – minor revision
1.00	10/31/2016	L. Wolf	Section 3.5 – revised to expand the definition
1.00	10/31/2016	L. Wolf	Section 3.6 – revised to clarify and add TNI definitions
1.00	10/31/2016	L. Wolf	Section 4.1 and 4.2 – minor revisions
1.00	10/31/2016	L. Wolf	Section 5.2.1 – added Note at end
1.00	10/31/2016	L. Wolf	Section 5.3.3 – revised to describe procedure applicable to all tested extraction solvents
1.00	10/31/2016	L. Wolf	Prior section 5.3.4 deleted
1.00	10/31/2016	L. Wolf	Section 5.3.6 and 5.5.1 – minor revisions
1.00	10/31/2016	L. Wolf	Section 7.3 – new section
1.00	10/31/2016	L. Wolf	Section 9 – updated references
1.00	10/31/2016	L. Wolf	Minor format and wording changes not affecting context.
1.1	02/22/2019	G. Moulton	Updated cover and new QA Manager.
1.1	02/22/2019	G. Moulton	Modified sec 4.1 and 6.1
1.1	02/22/2019	G. Moulton	Modified sec 9.1 and 9.2

9) References and Related Documents

9.1 Current TNI) Quality Systems Standard.

9.2 Current Department of Defense Quality Systems Manual for Environmental Laboratories.

9.3 ISO/IEC 17025:2005(E), "General Requirements for the Competence of Testing and Calibration Laboratories."

9.4 AIHA Laboratory Accreditation Program; AIHA-LAP, LLC

9.5 Naval Sea Systems Command Laboratory Accreditation Program (NAVSEA-LAP)

TABLE 1

ALS Expiration Dates for Reagents	
Chemical	Expiration Date
Purchased neat reagents	5 years after receipt
Inorganic reagent solutions	1 year from preparation or receipt
Organic reagent solutions	6 months from preparation or receipt
ALS Expiration Dates for Standards	
Chemical	Expiration Date
Purchased neat standards	5 years from receipt
Metals*	
Metals stock standard solutions	10 years from preparation or receipt
Metals secondary, intermediate, or working standard solutions	1 year from preparation or receipt
Mercury stock standard solutions	1 year from preparation or receipt
Mercury secondary, intermediate, or working standard solutions	1 month from preparation Calibration standards are prepared daily
Inorganics (non-metals)*	
Inorganic stock standard solutions	1 year from preparation or receipt
Inorganic secondary, intermediate, or working standard solutions	6 months from preparation or receipt
Organics*	
Volatile organics stock standards – lab prepared	1 year from preparation
Volatile organics stock standards – purchased **unopened** ampules	1 year from receipt
Volatile organics stock standards – purchased **opened** ampules	3 months after opening
All volatile organics secondary, intermediate, or working standards	Common 'gases' 7 days ≤200 mg/L 1 month >200 mg/L 3 months Note: standards used for calibration should not be older than 7 days
Purchased semivolatile organic stock standard solutions	1 year from receipt
Prepared semivolatile organics stock standards	1 year from preparation
Semivolatile organic secondary, intermediate, or working standard solutions	6 months from preparation or receipt
Dioxin/Furan and PCB stock standards	5 years from receipt
Dioxin/Furan and PCB working standards	1 year from preparation or receipt
Derivatized (prepared) semivolatile organics standard solutions	1 year from date of derivatization
High Explosives stock standards	1 year from receipt; 6 months for method 8332
High Explosives intermediate standards	1 month if < 1000 mg/L

* Expiration periods are defaults. Standards shall be replaced sooner if analyte degradation or stability problems are known or encountered, or if the standard becomes contaminated.

USE AND MAINTENANCE OF BALANCES

DOCUMENT ID: HS-EQ001, REV 9.2

Approved By: Hoai. Van
Technical and Laboratory Director, Hoai Van

Date: 11/9/18

Prepared By: Erica M Howard
Quality Assurance Manager, Erica Howard

Date: 11/9/2018

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1) Scope and Applicability

1.1 The purpose of this standard operating procedure (SOP) is to describe the procedures to be followed by ALS Laboratory staff for the proper use and care of analytical and top loading balances. The balance is one of the most critical pieces of support equipment in an analytical laboratory. Primarily, balances are used to weigh chemicals for the preparation of standards and to weigh samples for analysis. Improper use, or abuse, of the analytical balances will cause erroneous results. The SOP address documentation requirements for the calibration, calibration verification, and recording and reporting of weighed materials for all applicable laboratory procedures were weight measurements are part of a calibration, preparation or analytical procedure.

2) Summary of Procedure

2.1 Balances shall have calibration checks performed each day of use laboratory staff to verify the accuracy of the unit over its expected working use range. Balance calibration checks are to be performed using Class 1 or equivalent (such as Class S) reference materials.

2.2 On an annual basis, balances will be serviced and re-certified for use by a qualified vender.

2.3 The reference materials must be re-certified every five years by a qualified vender.

2.4 Weight measurement recording and reporting requirements are discussed for both the Analytical Balance and the Top Loading Balance.

2.5 Balance must be check daily prior to use.

3) Definitions

3.1 Demonstration of Capability: The analysis of QC samples in series to verify the ability to produce data of acceptable precision and bias.

3.2 Exception Report: Appropriate comments reported with the associated sample batch that addresses sample anomalies such as demonstrated sample matrix effects.

3.3 Laboratory Control Sample (LCS): A sample matrix, free from the analytes of interest, spiked with known amounts of analytes or a material containing known and verified amounts of analytes.

3.4 Limit of Detection (LOD): an estimate of the minimum amount of a substance that an analytical process can reliably detect. The LOD is determined annually through the execution of a Method Detection Limit Study, and verified quarterly through the analysis of a Detectability Check Sample (DCS).

3.5 Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of

confidence. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met.

3.6 Matrix Spike (MS): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available.

3.7 Matrix Spike Duplicate (MSD): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of recovery for each analyte.

3.8 Matrix: The substrate (e.g., water, soil, etc.) which may contain the analyte of interest.

3.9 Method Blank (MBLK): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analysis.

3.10 Method Detection Limit (MDL) study: a procedure described in 40CFR Part 136, Appendix B, that describes how to produce an MDL, a reporting element of certain EPA methods. The MDL study is one approach to determine the LOD.

3.11 NCAR: Nonconformance Corrective Action Report (refer to SOP HSQS003, current revision).

3.12 Reagent Water: Deionized (DI) reagent purified by filtration thru mix resin and carbon beds. For additional purification, the DI water is passed through an activated carbon filter.

3.13 Preparation Batch: A defined set of one to 20 client samples of the same matrix, meeting the batch definition criteria, and prepared for analysis within 24 hours. The preparation batch must also contain the required determinative method defined batch QC samples (e.g. method blank, laboratory control samples, matrix spikes, duplicates, etc.).

3.14 Surrogate: An analyte added to a sample, which is unlikely to be found in any sample at significant concentration, and which is added directly to a sample aliquot in known amounts before any sample processing procedures are conducted. It is measured with the same procedures used to measure other sample components. The purpose of the surrogate analyte is to monitor method performance with each sample.

3.15 Surrogate Spike: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environmental samples and is added to them for quality control purposes.

3.16 Batch: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** is composed of one (1) to twenty (20) environmental sample of the same quality systems matrix, meeting the above mentioned criteria and with a maximum time between the

start of processing of the first and last sample in the batch to be twenty-four (24) hours. An **analytical batch** is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.

4) Health and Safety Warnings

4.1 Lab Safety: Due to various hazards in the laboratory, safety glasses and laboratory coats or aprons must be worn at all times while in the laboratory. In addition, gloves and a face shield should be worn when dealing with toxic, caustic, and/or flammable chemicals.

4.2 Chemical Hygiene: The toxicity or carcinogenicity of each reagent used has not been precisely defined; however, each chemical used should be treated as a potential health hazard. Exposure to laboratory reagents should be reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets (MSDS) is available to all personnel involved in these analyses.

4.3 Waste Management: The principal wastes generated by this procedure are the method-required chemicals and standards. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required. Laboratory procedures in SOP HS-SAF-001, Waste Disposal Procedures, must be followed.

4.4 Pollution Prevention: The materials used in this method pose little threat to the environment when recycled and managed properly. The quantities of chemicals purchased should be based on the expected usage during its shelf life. Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards or reagents to be disposed.

4.5 Job Safety Assessment

HAZARD ASSESSMENT		
Job Task #1:	**Hazards**	**Preventative Measures**
Sample handling.	Injury due to lifting heavy coolers and placing/removing samples to/from storage locations. .	Use proper lift technique and cart to move coolers and stool/stepladder when working reaching above shoulder height in sample storage cooler.
Job Task #2:	**Hazards**	**Preventative Measures**
Sample container handling and sample analysis	Exposure to possible hazardous chemicals.	Use of proper PPE, i.e. Lab coats, safety glasses, gloves, etc. Work in fume hood and avoid skin contact with solvents/acids/reagents. Know location of safety shower, first aid kits, spill kits and fire extinguisher when handling

		flammable material.

5) Cautions

5.1 Routine preventative maintenance must be performed and documented to assure optimum instrument performance. Refer to the current revision of SOP HS-EQ004 for preventative maintenance schedules.

5.2 Balances areas must be kept clean to ensure continued proper balance operation.

5.3 Analytical Balance Doors must be closed for all measurements.

5.4 Always check balance "Level" condition before use, and re-level as necessary.

5.5 When handling heavier certified weights, the use of a cotton glove may be preferable over the use of plastic forceps to avoid dropping and damaging the weight.

5.6 **Never** handle weights with a bare hand. One's finger prints may alter the accurate weight of the certified mass.

6) Interferences

6.1 Vibrations from activities on the bench top where a balance is located will cause errors. Use of heavy balance tables (such as marble) will minimize these effects.

6.2 Wind currents in a lab caused by use of fans, etc. can cause errors. Placing balances away from all possible drafts is recommended.

6.3 Doors on analytical balances must always be closed while weighing to eliminate errors from even small drafts.

6.4 Drift is a progressive (continuously upward or continuously downward) change in the number displayed on the digital readout. The weight reading does not stabilize, or an unstable reading with no weight applied. All analytical balances show some uncertainty. Some do so more than others. Two environmental factors affect the instrument's stability dramatically—temperature and static electricity. Temperature control is imperative. This includes both control of the room temperature and maintaining the internal temperature of the instrument. For best stability, maintain the room temperature within two degrees constantly (day and night). Leave the instrument plugged in and turned ON. Static discharge can also be accomplished by putting some ionizing devices around the weighing pan.

6.5 Static electricity will cause erratic readings. Instruments should be operated on a static dissipating surface (anti-static mat). Operators should stand on anti-static floor covering. Avoid the use of plastic containers for items being weighed. Never replace broken glass doors on instruments with plastic ones. Maintain humidity at 65% or more. Eliminate sources of floor vibration and air currents.

7) Personnel Qualifications and Responsibilities

7.1 General Responsibilities - This method is restricted to use by or under the supervision of analysts experienced in the method.

7.2 Analyst - It is the responsibility of the analyst(s) to:

- 7.2.1 Each must read and understand this SOP and follow it as written. Any deviations or non-conformances must be documented and submitted to the QA Manager for approval.
- 7.2.2 Produce method compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP (HS-QS-009).
- 7.2.3 Complete the required initial demonstration of proficiency before performing this procedure without supervision.
- 7.2.4 Complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 7.2.5 The analysts must submit data for peer or supervisor review.

7.3 Section Supervisor - It is the responsibility of the section supervisor to:

- 7.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.
- 7.3.2 Ensure analysts have completed the required initial demonstration of proficiency before performing this procedure without supervision.
- 7.3.3 Ensure analysts complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 7.3.4 Ensure analysts produce method compliant data that meet all quality requirements using this procedure and the Data Reduction, Review and Validation SOP.

7.4 Project Manager - It is the responsibility of the Project Manager to ensure that all method requirements for a client requesting this procedure are understood by the laboratory prior to initiating this procedure for a given set of samples.

7.5 QA Manager: The QA Manager is responsible for

- 7.5.1 Approving deviations and non-conformances
- 7.5.2 Ensuring that this procedure is compliant with method and regulatory requirements,
- 7.5.3 Ensuring that the analytical method and SOP are followed as written through internal method and system audits.

8) Sample Collection, Handling, and Preservation

8.1 Not Applicable

9) Equipment and Supplies

9.1 Tongs or plastic forceps

9.2 Cotton glove

9.3 Weigh dishes, assorted sizes

9.4 Top Loading Balances, capable of weighing to nearest 0.01 g.
- 9.4.1 Mettler PC 4400
- 9.4.2 Highland HBC302
- 9.4.3 Ohaus ScoutPro 200g

9.5 Analytical Balances, capable of weighing to nearest 0.1 mg.
- 9.5.1 Mettler AE 163
- 9.5.2 Mettler AE 200
- 9.5.3 Shimadzu Electronic Balance, Model AUX220
- 9.5.4 Mettler Toledo, Model XS 105

10) Standards and Reagents

10.1 Note: Store purchased standards according to manufacturer specifications. Store standard solutions (remaining stock, composite, calibration and surrogate) below 6 °o. in glass containers having Teflon™ lined lids or in accord with the manufacturer's recommended conditions. All purchased stock standard solutions must be replaced after reaching the manufacturer's expiration date assigned to the standard. All laboratory prepared standard solutions must be replaced after six months or sooner if routine QC indicates a problem or if required by reference method. An assigned expiration date of a lab prepared standard cannot exceed the manufacturer's expiration date for any component used in the standard formulation. When analyzing or preparing samples, all standards, lot numbers must be associated with the run batch or prep batch.

10.2 Standard masses: Certified ASTM Class 1 for all balances.

11) Method Calibration

11.1 Re-calibration of Mettler AE 163 and AE 200 Balances.
- 11.1.1 With balance doors closed, check balance bubble level and level as necessary.
- 11.1.2 Set the "Cal" lever on the right side of the balance to its most forward position (toward the front of the balance) and depress the "On/Off/Mode" lever on the front of the balance and hold down until "Cal ----" appears on the balance display. Release pressure from the lever and wait until the display reads " CAL 100".
- 11.1.3 As "100" flashes on and off, move the "Cal" lever on the side to its most rear position and wait until the display reads "Cal 0" (a flashing "0").
- 11.1.4 To complete the re-calibration steps, move the "Cal" lever on the right side back to its most forward position.
- 11.1.5 With balance is now re-calibrated, verify the re-calibration using the Class S or Class 1 weights.

11.2 Calibration of Mettler PC 4400
- 11.2.1 Only an approved service contractor can perform this procedure.

11.3 Calibration of the Shimadzu Electronic Balance, Model AUX220
- 11.3.1 Refer to balance instruction manual for weight calibration.

11.4 Calibration of the Mettler Toledo Balance, Model XS 105
- 11.4.1 Refer to balance instruction manual for weight calibration.

11.5 Calibration Verification of Balances – a balance calibration must be verified each day prior to use. The accuracy of the verifications must meet the applicable acceptance criteria stated in Table 12.5 (Analytical Balance) or 12.6 (Top loading Balance). Verification must cover the possible range of possible sample weights.

12) Sample Preparation/Analysis

12.1 Basics of Balance Use: Location and preparation of the balance

12.1.1 The balance must rest on a stable, vibration-free platform. Specially manufactured balance tables provide the best balance platforms. A securely placed laboratory bench is also satisfactory if the bench is used only as a balance platform.

12.1.2 The room in which the balance is located must not experience wide and rapid temperature variations. Furthermore, the atmosphere around the balance must be free of drafts and excessive humidity.

12.1.3 The balance must not be located in an area where it is likely to be exposed to corrosive fumes.

12.1.4 The balance must have a current external calibration certification issued by a qualified vender. A dated calibration sticker is affixed to the balance indicates the date of the most current calibration performed by an external, qualified vendor. External calibration and balance cleaning must be performed annually.

12.1.5 The electronic and physical components of the balance must be in thermal equilibrium. Ensure that the balance has had sufficient time to warm up properly. Five minutes is adequate.

12.1.6 The balance pan must be clean and dry. Examine the pan carefully to ensure that it is free of particles, fibers, and any liquid.

12.1.7 The balance must be level. Examine the balance level bubble for the balance level status and adjust the balance feet as necessary to assure level positioning. The balance is acceptably level when the bubble is centered in the balance level indicator circle.

12.1.8 The balance must be zeroed. Ensure that the balance doors are closed. The balance display should indicate zero mass. If it indicates a stable non-zero mass, tare the balance.

12.1.9 The balance must be operated at all times according to the procedures specified in this SOP.

12.2 Preparation of the Object to be weighed

12.2.1 Check balance logbook or electronic log to ensure balance has been calibrated. If balance has not been calibrated, calibrate the balance prior to use, see Section 12.5.

12.2.2 An object placed on the balance pan must not leave any residue when removed from the pan. The exterior surface of a weighed object must be free of loose particles, liquid, grease, etc. Powdered or granular solid chemicals and liquids must be placed in a container for weighing.

12.2.3 The object to be weighed must be at the same temperature as the air within the balance case (room temperature). A warm object generates rising air currents that lift the object, decreasing its apparent mass. Cold objects show erroneously large masses.

12.2.4 The object to be weighed must have a stable mass. Many chemicals are

efflorescent or deliquescent, releasing or absorbing moisture to the atmosphere depending on the local temperature and humidity. Strong bases absorb carbon dioxide from the air. Liquids evaporate. Substances having these properties must be weighed in airtight weighing bottles.

12.2.5 The object being weighed must not support a static electrical charge. Dry plastic weighing boats and glass containers readily obtain and retain large static charges. These objects may be attracted or repelled by a static charge on the glass balance case, resulting in an erroneously large or small indicated mass. If possible, weigh chemicals in a metal dish, such as an aluminum pan. If this is not possible, use the smallest practicable glass or plastic container.

12.2.6 The object being weighed must not chemically attack (corrode) the balance. NEVER PLACE CHEMICALS DIRECTLY ON THE BALANCE PAN. Do not weigh open containers of concentrated acids that produce corrosive vapors. Seal such compounds in an airtight container before weighing.

12.2.7 The object being weighed must have a mass less than the capacity of the balance. NOTE: An excessively heavy object may damage the balance.

12.2.8 When weighing out a required mass of a chemical, pour the estimated required quantity of the chemical from its original container into a second clean container, and transfer the chemical from the second container to the container on the balance pan with a spatula. Always remove a chemical from its original container; avoid putting anything into the original container. Inserting a spatula into an original chemical container virtually guarantees that the chemical will eventually become contaminated.

12.3 WEIGHING AN OBJECT

12.3.1 Carry an object to be weighed with clean tongs or forceps. Do not hold the object with the ungloved hand. Oil or dirt could be transferred from the fingers to the object, giving an erroneously high mass indication. Touching the object with clean fingers raises the temperature of the object, resulting in an erroneously low mass indication.

12.3.2 Center the object to be weighed on the balance pan. An off-center object may give an erroneous mass indication.

12.3.3 Close the balance case.

12.3.4 Allow the mass indication to reach a stable value. In general, the indicated mass value should be constant for at least 30 seconds. If a constant mass value cannot be obtained, the object or chemical being weighed may be reacting with the atmosphere, or the container may be leaking an electrostatic charge.

12.3.5 If a required mass of a chemical is being weighed into a container on the balance pan, the container mass may be tarred to zero, or the mass of the container may be recorded and later subtracted from the total mass of the container and chemical. The latter method is preferable since it obviates the possibility that someone else may re-tare the balance while the original user is temporarily away from the balance.

12.3.6 When transferring a chemical or sample into a container on the balance pan, be extremely careful not to spill any of the material on the balance pan or in the balance case.

12.3.7 To minimize erroneous notebook entries, record the object mass directly by electronic entry into a spreadsheet.

12.4 AFTER WEIGHING

12.4.1 Immediately remove the weighed object from the balance pan. This prevents

permanent flexure of the balance beam and is a courtesy to other laboratory personnel who may need to use the balance.

12.4.2 Carefully inspect the balance pan and balance case. If necessary, immediately clean up any spilled material and close the balance case doors.

12.5 RECORDING DATA FROM BALANCE MEASUREMENTS

12.5.1 Analytical Balance Measurement: The analytical balances in use at ALS measure weights to the nearest 0.0001-gram. All weight measurements must be recorded directly by electronic entry into a spreadsheet to the nearest 0.0001-g.

12.5.2 The one exception to this requirement is when an approved SOP allows the weight measurement to a lesser degree of accuracy (e.g. the SOP instructs to measure to the nearest 0.01-g). Whenever an analyst is unsure whether a lesser degree of accuracy is required by an SOP, the analyst must then record to the nearest 0.0001-g.

12.5.3 Top Loading Balance: The Top Loading Balances in use at ALS measure weights to the nearest 0.01-gram. All weight measurements must be recorded in a logbook or directly by electronic entry into a spreadsheet if balance is linked to a computer.

12.6 Balance Calibration and Electronic Logbook

12.6.1 Calibration must bracket the entire range of possible weights measured on the balance. Example for metals since 0.5 gram of sample is being measured the first weight should be less than 0.5 such as 0.1 grams. The upper limit check should be better than the entire weight of the sample plus the digestion cup. If the digestion cup weigh 15 grams that the upper weight check must be greater than 15 plus the sample weight, therefore a weight of 25 or 50 would be appropriate.

12.6.2 Calibration must be performed before sample weight weighing. DO NOT weigh sample at beginning of the day and do calibration at the close of the day.

12.6.3 Manual logbook,

12.6.3.1 Enter weight serial number and weights used in logbook.

12.6.3.2 Record sample weights and complete check for all weights need to cover possible range of sample weights.

12.6.3.3 Check acceptance range light of the weights. IF a weight does not meet acceptance criteria, perform corrective action such as cleaning balance, leveling balance, etc. and repeated until acceptance is achieved.

12.6.4 Electronic Logbook

12.6.4.1 If balance is connected to network weights may be captured to the database and daily reports generated by the database.

12.6.4.2 Open Electronic Logbook using LIMS portal.

12.6.4.3 Enter user ID and password.

12.6.4.4 Click Calibration Log sand select Balance and click the submit button.

12.6.4.5 Click ADD NEW Bach at bottom of the page.

12.6.4.6 Next select Balance ID from drop down list, System will automatically record user ID from module entry and time. Click Save icon. Click the Calibrate box for the newly created batch.

12.6.4.7 Select weight from the drop down list, only current unexpired weights can be selected. System will enter the corresponding serial

number for the wright. Place weight on balance and click the weight box and press print/read on the balance and click submit. Repeat until all weigh have been completed.

12.6.4.8 Click Report by Batch box to view results. If all weights are acceptable click the Review button to finalize report. IF a weight does not achieve criteria Batch Report will indicate weight is out. Repeat weight(s) after corrective action until all weights achieve acceptance limits. Finalize report by clicking the Review button.

12.6.4.9 Once all weight achieve acceptance limits the balance is ready for use.

13) Troubleshooting

13.1 Not Applicable to this SOP.

14) Data Acquisition

14.1 When performing a weighing, record the identity of the object or material being weighed and the indicated mass of the object or material in the appropriate gravimetric logbook. All hard copy data and electronic data must be maintained for ten (10) years minimally.

14.2 Balance Calibration Checks: Each balance must have its own controlled logbook for recording daily balance calibration checks. Record the information listed below as a minimum in the bound logbook for each balance calibration:

14.2.1 Weight ID
14.2.2 Date of Calibration Check
14.2.3 Analyst Initials
14.2.4 Theoretical Weight
14.2.5 Actual Weight
14.2.6 Corrective Action (if applicable)

14.3 General Balance Use - REPORTING DATA FROM BALANCE MEASUREMENTS

14.3.1 Analytical Balance Weight Reporting: Since analytical balances in use at ALS measure weights to the nearest 0.0001-gram, reporting all weight measurements must be reported (e.g. in LIMS) to the nearest 0.0001-gram.

14.3.1.1 The one exception to this requirement is when an approved SOP allows the weight measurement to be reported to a lesser degree of accuracy (e.g. a method SOP instructs the measurement to be to the nearest 0.01-g). Whenever an analyst is unsure whether a lesser degree of accuracy is required by an SOP, the analyst must then record to the nearest 0.0001-g. This exception often occurs when the approved SOP only requires the use of a Top Loading Balance, but the Analytical balance is used for the measurement.

14.3.2 Top Loading Balance Reporting: The Top Loading Balances in use at ALS measure weights to the nearest 0.01-gram. All weight measurements must be reported (e.g. in LIMS) to the nearest 0.01-gram.

14.4 Effective Date – Assures the reader that the information contained in the SOP is current as of this date. This date is defined as the date in the header of the SOP or the last signature date, whichever is most recent.

15) Calculation, and Data Reduction Requirements

15.1 QC Calculations: LIMS calculates the percent recovery for various QC samples (LCS) according to the following equations:

15.1.1 % Recovery, %R (for MS and MSD Samples)

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SR = Sample Result (unspiked).
SA = Spike Amount Added (mg/L or mg/kg).

15.1.2 % Recovery, %R (for standards and LCS)

$$\%R = \frac{SSR}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SA = Spike Amount Added (mg/L or mg/kg).

15.1.3 RPD (for precision or duplicate evaluation)

$$RPD = \frac{|SR_1 - SR_2|}{½(SR_1 + SR_2)} \times 100$$

Where:
SR_1 = Sample result for duplicate 1.
SR_2 = Sample result for duplicate 2.

15.2 Sample Concentration Calculation

16) Quality Control, Acceptance Criteria and Corrective Action

16.1 Balances must be cleaned and calibrated once a year by a qualified, external vendor using NIST-traceable masses.

16.2 For balances with re-calibration features (Mettler AE163 and AE200 Analytical Balances), re-calibration by ALS Laboratory personnel is to be performed whenever calibration criteria in 12.5 are not met. See Section 9.1.

16.3 Balance calibration must be monitored before use or daily using masses that cover the working range of items measured.

16.4 The NIST Class "S" or ASTM Class 1 weights must be calibrated every five years by an external qualified source and certificates must be maintained in Quality Assurance Files.

16.5 Analytical Balance Acceptance Range for Class 1 Weights: ± 0.1% of certified value

Table 14.5 – Analytical Balance Calibration Verification Acceptance Criteria			
Analytical Balance (0.0001g)	Acceptance Range for mass used (± 0.1%)	Analytical Balance (0.0001g)	Acceptance Range for mass used (± 0.1%)
200.0000g	199.8000 – 200.2000	2.0000 g	1.9980 - 2.0020 g
100.0000 g	99.9000 – 100.1000 g	1.0000 g	0.9990 - 1.0010 g
50.0000 g	49.9500 – 50.0500g	0.5000 g	0.4995 – 0.5005 g
20.0000 g	19.9800 – 20.0200g	0.2000 g	0.1998 - 0.2002 g
10.0000 g	9.9900 - 10.0100g	0.1000 g	0.0999 - 0.1001 g
5.0000 g	4.9950 - 5.0050 g	0.0020g	0.0018 – 0.0022 g

16.6 Top-Loading Balance acceptance range for Class 1 Weights: ± 1.0% of certified value. Note: Class 1 weights are used, but a Top Loading Balance cannot measure to the known mass accuracy of the Class 1 weight.

Table 14.6 – Top Loading Balance Calibration Verification Acceptance Criteria			
Top Loading Balance (0.01 g)	Acceptance range for mass used (±1%)	Top Loading Balance (0.01 g)	Acceptance range for mass used (±1%)
200.00 g	198.00 – 202.00g	10.00 g	9.90 - 10.10 g
100.00 g	99.00 – 101.00 g	5.00 g	4.95 - 5.05 g
50.00 g	49.50 – 50.50 g	2.00 g	1.98 - 2.02 g
20.00 g	19.80 – 20.20 g	1.00 g	0.99 - 1.01 g

16.7 If a solid is spilled onto the bottom of the balance case or onto the balance pan, immediately sweep it off the pan and out of the case with a soft paper towel or "camel's hair" brush.

16.8 If a liquid is spilled onto the bottom of the balance case or onto the balance pan, immediately absorb as much as possible of the liquid with a paper towel. If the liquid is volatile, leave the balance case open until the liquid has completely evaporated and the vapors have dissipated. If the liquid is not volatile (such as an oil), use a paper towel soaked in a suitable non-corrosive solvent to remove the last traces of the liquid. Leave the balance case open to evaporate and dissipate the solvent.

16.9 Corrective Action for acceptance criteria (Tables 14.5 and 14.6) failure:

- 16.9.1 Document the failure in the logbook;
- 16.9.2 Recheck the balance zero, re-zero as necessary;
- 16.9.3 Check balance for any excessive dirt or dust that will bias a result, clean area as necessary;
- 16.9.4 Evaluate room conditions for excessive drafts or extreme temperature changes (if A/C is working poorly, the balance accuracy could be affected);
- 16.9.5 Check the balance with another set of standard weights (ASTM Class 1) and evaluate reproducibility;
- 16.9.6 Re-calibrate the balance according to manufacturer's instructions (see §10).

16.9.7 If any of the above fail to correct the problem;

16.9.7.1 Notify the area supervisor and QA so that the balance service can be scheduled by a qualified vender for repairs;

16.9.7.2 Place a visible note on the balance that to indicate the balance is "Out of Service" and do not use until service is performed to bring the balance back into the operating acceptance range.

16.9.7.3 Document MAINTENANCE activities in the appropriate logbook designated for the balance.

17) Data Records Management

17.1 All data is stored electronically and/or hard copy for five (5) years or ten (10) years for data to be submitted to the state of Louisiana. Operational software is maintained for the same duration.

17.2 All analytical sequence IDs and standard preparation information must be recorded in the Run logbook. Hardcopy computer printouts of analytical sequences and raw data must be retained and initialed by the analyst (electronic initials are acceptable). To simplify standard and reagent tracking, analyst must attempt to use single lots of reagents and standards.

17.3 Complete all pertinent sections in the respective logbooks. If not-applicable then line out the section and “Z” out or “X” out all large sections of the worksheet that are not used. Make all corrections with single line through, date and initial. Make NO obliterations when manually recording data.

17.4 Logbooks are controlled. Never remove a page from a logbook. Completed logbooks are returned to the QA department when filled and no longer needed in the work area.

17.5 SOP effective date is the date noted in the header or last signature date, whichever is most recent.

18) Contingencies for Handling Out of Control Data

18.1 When method required QC exceedances occur, in every case where sample data quality are affected, the source of the QC exceedance must be determined, corrected and sample reanalysis carried out when possible.

18.2 When affected sample analysis can not be repeated due to limitations (i.e. sample availability, or if reanalysis can only be performed after expiration of a sample hold time), the reporting of data associated with exceeded QC data must be appropriately flagged and narrated. This documentation is necessary to define for the data user the effect of the error has upon the data quality of the results reported (e.g. E flag data indicate the result to be only an estimate).

18.3 All analysts must report sufficient comments in laboratory data review checklist for exceeded QC associated with sample results so that project management can further narrate and ensure data qualifiers (flags) are properly assigned to the reported data.

18.4 NCARs must be issued for QC system exceedances. Matrix interferences are reported

using the analyte reporting comment section in LIMS or using the Laboratory Data review checklist.

19) Method Performance

19.1 Refer to Section 16.

20) Summary of Changes

Table 20.1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
9.2	11/09/2018	G. Moulton	Updated to new ALS Cover and new quality manager.
9.2	11/09/2018	G. Moulton	Modified sec 21.2 and 21.2
9.2	11/09/2018	G. Moulton	Modified sec 17.1
09.1	08/15/2015	T. Yen	Lab Director.
09.1- Section 4.5	08/15/2015	T. Yen	Jos Safety Assessment
09.1- Sections 12.2.1 & 12.5	08/15/2015	T. Yen	Daily calibration, acceptance checks and electronic logbook procedures.
09.0	09/15/2014	T. Yen	New SOP Format and New Lab Director.
09.0	09/15/2014	T. Yen	Weights certified every 5 years.
09.0 – Section 9.4	09/15/2014	T. Yen	Equipment list updated
09.00 – Section 22.	09/15/2014	T. Yen	References update
08.2	05/15/2013	T. Yen	Signature Page – New Department Supervisor, QA Manager and Lab Director.
08.2	05/15/2013	T. Yen	Document Footer – "A Campbell Brothers Limited Company" changed to "An ALS Limited Company" to reflect parent company name change.
08.2 – Section 9.4	05/15/2013	T. Yen	Balance list update.
08.2 – Section 9.4	05/15/2013	T. Yen	Weights recorded in logbook or spreadsheet depending on balance.
08.2 – Section 10.1	05/15/2013	T. Yen	Only Class 1 weight are to be used.
08.2 – Section 13.8	05/15/2013	T. Yen	SOP effective date defined.
08.2 – Section 14.2	05/15/2013	T. Yen	ASTM Class 1 weight certified every two years.
08.2 – Section 14.3	05/15/2013	T. Yen	Daily calibration must cover working range of items weighed.
08.1	04/15/2012	J. Cady	Minor document revision.
08.0	07/15/2011	J. Cady	Major document revision.

21) References and Related Documents

21.1 Current TNI Standards.

21.2 Current Department of Defense Quality Systems Manual.

21.3 ASTM E898-00, "Standard Method for Testing Top-Loading, Direct-Reading Laboratory Scales and Balances"

21.4 U.S. Environmental Protection Agency. Handbook for Analytical Quality Control in Water and Wastewater Laboratories. EPA-600/4-79-019.

22) Appendix

Table 22.0 Calibration and Maintenance of Balances

Instrument	Activity	Frequency	Documentation
Balance	1. Clean 2. Check alignment 3. Service Contract	1. Before use 2. Before use 3. Annually	Manual or electronic logbook. Post annual service date on balance
ASTM Class 1 Weights	1. Only use for the intended purpose. 2. Use plastic forceps to handle or for larger weight clean cotton gloved hand. 3. Keep weights in case when not in use.	Certify weights every 2 years	Keep certificate on file. Record calibration and expiration date in weight list of electronic logbook

CALIBRATION OF LAB VOLUMETRIC APPARATUS

DOCUMENT ID: HS-EQ003, REV 8.2

Approved By: Hoai. Van
Technical and Laboratory Director, Hoai Van

Date: 11/09/18

Prepared By: Erica M Howard
Quality Assurance Manager, Erica Howard

Date: 11/09/2018

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1) Scope and Applicability

1.1 This standard operating procedure (SOP) describes the procedures for verification of laboratory volumetric apparatus calibrations. It is based on the gravimetric determination of the quantity of water either contained or delivered. Typical products falling within this SOP are graduated burettes, graduated cylinders, volumetric flasks, measuring and dilution pipettes, micropipettes, transfer and capacity pipettes, syringes used for standard preparations or sample spiking and for bottle top reagent dispensers. These procedures are not required for Class A volumetric ware. Syringe with certificate of compliance such as Class A certificate, will not require calibration.

1.2 The following procedures are required for calibration for mechanical volumetric pipettes and glass microsyringes.

1.2.1 Accuracy for all checks performed for mechanical volumetric pipettes must be verified quarterly to be within the requirements in Table 22.1. If the check reveals error greater than those listed in Table 22.1, then steps must be taken to improve the accuracy of these measurements (e.g. cleaning and maintenance) or replacement of the defective equipment.

1.2.2 For accuracy of glass microsyringes used for organic standard preparations and sample spiking, all syringes greater than 10uL must be check semi-annually and before initial use

2) Summary of Procedure

2.1 The method is based upon a determination of the volume of water either contained in or delivered by the vessel.

2.2 The labware calibration checks shall consist of at least five measurements, and the precision, bias and individual % Recovery calculated and recorded in the E-Logbook.

2.3 All volumetric labware shall be initially and thereafter annually inspected for possible defects. All cracked or damaged items are to be removed from use.

2.4 The calibration of mechanical type pipettes shall be verified at the lowest volume setting and at the largest volume setting. The verifications MUST be performed quarterly. If pipette is used a fixed point, then only the level used is checked. For DOD projects all mechanical pipets must be check daily using three point at the nominal volume.

2.5 All glass microliter syringes are to be considered in the same manner as Class A glassware, but however, analysts must still check syringes before initial used and semi-annually afterwards.

2.6 If Class A volumetric labware are received with accuracy certificates, initial accuracy verification is not required before using in production, and annual accuracy verification is not required. Certificates are to be retained for verification.

2.7 Lab should always attempt to use Class A labware, but in situation where such ware is not available like disposable pipette, disposable test tubes and autosampler vials must be calibrated if the item is used for critical volumetric measurement.

3) Definitions

3.1 Demonstration of Capability (DOC): procedure to establish the ability of the laboratory to generate acceptable accuracy and precision which is included in many of the EPA's analytical test methods. In general, an initial DOC procedure involves the analysis of four separate Laboratory Control Samples (LCS) as prescribed by the analytical method Each LCS must meet the specified LCS acceptance limits for percent recovery, and standard deviation. Ongoing DOC requirements are met by acceptable analysis of annual NELAC accepted proficiency test (PT) samples, or by the analysis of four LCS if PT samples are not available

3.2 Exception Report: Appropriate comments reported with the associated sample batch that addresses sample anomalies such as demonstrated sample matrix effects.

3.3 Laboratory Control Sample (LCS): A sample matrix, free from the analytes of interest, spiked with known amounts of analytes or a material containing known and verified amounts of analytes.

3.4 Limit of Detection (LOD): an estimate of the minimum amount of a substance that an analytical process can reliably detect. The LOD is determined annually through the execution of a Method Detection Limit Study, and verified quarterly through the analysis of a Detectability Check Sample (DCS).

3.5 Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met.

3.6 Matrix Spike (MS): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available.

3.7 Matrix Spike Duplicate (MSD): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of recovery for each analyte.

3.8 Matrix: The substrate (e.g., water, soil, etc.) which may contain the analyte of interest.

3.9 Method Blank (MBLK): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analysis.

3.10 Method Detection Limit (MDL) study: a procedure described in 40CFR Part 136, Appendix B, that describes how to produce an MDL, a reporting element of certain EPA methods. The MDL study is one approach to determine the LOD.

3.11 NCAR: Nonconformance Corrective Action Report (refer to SOP HSQS003, current revision).

3.12 Reagent Water: Deionized (DI) reagent purified by filtration thru mix resin and carbon beds. For additional purification, the DI water is passed through an activated carbon filter.

3.13 Preparation Batch: A defined set of one to 20 client samples of the same matrix, meeting the batch definition criteria, and prepared for analysis within 24 hours. The preparation batch must also contain the required determinative method defined batch QC samples (e.g. method blank, laboratory control samples, matrix spikes, duplicates, etc.).

3.14 Surrogate: An analyte added to a sample, which is unlikely to be found in any sample at significant concentration, and which is added directly to a sample aliquot in known amounts before any sample processing procedures are conducted. It is measured with the same procedures used to measure other sample components. The purpose of the surrogate analyte is to monitor method performance with each sample.

3.15 Surrogate Spike: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environmental samples and is added to them for quality control purposes.

3.16 Batch: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** is composed of one (1) to twenty (20) environmental sample of the same quality systems matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be twenty-four (24) hours. An **analytical batch** is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.

3.17 Retention Time Window: The length of time between sample injection and the appearance of a peak at the detector. The window of time is established for each analyte or group of analytes and is set for complete elution of analyte peaks. It is based upon a series of analyses and statistical calculations that establish the measured band on the chromatogram that can be associated with a specific analyte or group of analytes.

3.18 Second Source Calibration Verification (ICV): A standard obtained or prepared from a source independent of the source of standards for the ICAL. Its concentration should be at or near the middle of the calibration range. It is performed after the ICAL.

3.19 Calibration Standard (CAL): A solution prepared from the primary dilution standard solution or stock standard solutions and the surrogate analyte. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.20 Linear Calibration Range (LCR): The concentration range over which the instrument response is linear

3.21 Instrument Performance Check Sample (IPC): A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.22 Continuing Calibration Verification (CCV): A known interference free matrix spiked with a known concentration of the target analyte. The CCV is prepared from the same source that was used to prepare the calibration standards, and is used to verify that the instrument calibration is in control before and after sample analysis.

3.23 Quality Control Sample (QCS): A solution of method analytes of known concentrations that is used as the spiking solution for the LCS. The QCS is obtained from a source external to the laboratory and different from the source of calibrations standards. It is used to check laboratory performances with externally prepared test materials.

3.24 Detectability Check Sample (DCS): a sample spiked at 2 to 3 times the calculated LOD (refer to SOP HS-QS006, LOD and LOQ), or alternatively spiked near the LOQ.

3.25 Organic Free Water: Deionized (DI) reagent water meeting purity characteristics of Type I laboratory distilled water (daily resistance ≥17 megohms-cm). For additional purification, the DI water is passed through an activated carbon filter.

3.26 Calibration: Set of operations that establish the relationship between values of quantities indicated by a measuring instrument and the corresponding values realized by standards.

3.27 To Contain or TC: Volumetric ware designed to contain a specified volume of liquid at a specified temperature. To Deliver or TD: Volumetric ware designed to deliver a specified volume of liquid at a specified temperature.

3.28 Class B labware: Glass volumetric ware manufactured to contain or deliver accurately to ±2 % calibrated volume, may not be used.

3.29 Class A labware: Glass volumetric ware manufactured to contain or deliver accurately to typically less than 1% calibrated volume. The actual specification may vary with the volume and glassware type.

3.30 Class A microsyringe: For the purpose of this SOP, this is defined as a glass microsyringe with a volume of 1000 uL or less.

3.31 Verification: Confirmation by examination and provision of evidence that specified requirements have been met.

3.32 Volumetric glassware is used to measure liquids with accuracy ranging from moderate to very high. Many standard beakers and flasks have graduations accurate to + or - 5%. Although this level of accuracy is sufficient for many routine tasks in the lab, you will often need to measure liquids much more precisely. Volumetric glassware allows you to measure liquids ranging from + or - 1% to + or - 0.1% or less, depending on its type, design, and quality.

Class A volumetric glassware provides the highest accuracy, but it may be expensive. Class A volumetric glassware complies with the Class A tolerances defined in ASTM E694, must be permanently labeled as Class A, and is supplied with a serialized certificate of precision. (Most manufacturers have begun supplying "generic" Class A vessels which meet Class A tolerances but are not technically Class A because they are not serialized or certified.) All Class A volumetric glassware is actually glass; volumetric plasticware is not eligible for Class A status.

Class B volumetric glassware has tolerances twice those of Class A (except graduated cylinders, which have rules of their own.) Class B volumetric glassware must comply with the Class B tolerances defined in ASTM E694 and must be permanently labeled as Class B. Class B glassware must never be used in the lab.

Depending on its type and design, volumetric glassware may be rated To Contain (TC) or To Deliver (TD). A vessel marked TC contains the amount specified when it is filled to the graduation line. A vessel marked TD delivers the amount when it is filled to the graduation line and emptied using the proper procedure. The difference arises because of drainage holdback error. For example, volumetric flasks are rated TC. If you fill a 500 ml volumetric flask to the graduation line, it contains exactly 500 ml of solution (within its tolerance). If you empty that flask into another container, a bit less than 500 ml will transfer. That's because some of the solution remains in the flask, wetting its inner surface.

4) Health and Safety Warnings

4.1 Lab Safety: Due to various hazards in the laboratory, safety glasses and laboratory coats or aprons must be worn at all times while in the laboratory. In addition, gloves and a face shield should be worn when dealing with toxic, caustic, and/or flammable chemicals.

4.2 Chemical Hygiene: The toxicity or carcinogenicity of each reagent used has not been precisely defined; however, each chemical used should be treated as a potential health hazard. Exposure to laboratory reagents should be reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets (MSDS) is available to all personnel involved in these analyses.

4.3 Waste Management: The principal wastes generated by this procedure are the method-required chemicals and standards. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required. Laboratory procedures in SOP HS-SAF-001, Waste Disposal Procedures, must be followed.

4.4 Pollution Prevention: The materials used in this method pose little threat to the environment when recycled and managed properly. The quantities of chemicals purchased should be based on the expected usage during its shelf life. Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards or reagents to be disposed.

4.5 Job Safety Assessment

HAZARD ASSESSMENT		
Job Task #1:	**Hazards**	**Preventative Measures**
Cleaning pipette	I Exposure to possible hazardous chemicals.	Use of proper PPE, i.e. Lab coats, safety glasses, gloves, etc.

	.	
Job Task #2:	**Hazards**	**Preventative Measures**
Syringe needle	Exposure to possible hazardous chemicals and puncture wound.	Use of proper PPE, i.e. Lab coats, safety glasses, gloves, etc. and handle syringe with care. Broken syringes MUST be disposed in proper containers.

5) Cautions

5.1 Routine preventative maintenance must be performed and documented to assure optimum instrument performance. Refer to the current revision of SOP HS-EQ004 for preventative maintenance schedules.

5.2 Different pipet systems may operate differently. Performing calibration checks evaluates both the device accuracy and the operator's skill and knowledge of handling each device.

6) Interferences

6.1 Eppendorf-type pipette operation can deteriorate over time due to several factors including improper operator technique and use of solvents, acids or alkali that cause corrosion and damage to the pipette mechanical parts (pipette o-rings, etc.). Examination of the pipette prior to use to detect the obvious signs of pipette deterioration and routine cleaning and pipette verification are effective ways to eliminate the use of a pipette that no longer meets a manufacturer's operating performance specification.

6.2 Borosilicate volumetric glassware will hold its calibration indefinitely provided that it is not exposed to corrosive acids (hydrofluoric acid, hot phosphoric acid) or strong, hot alkalis, and that it is not heated above 150˚C when dry. A frosted glass surface (viewed when dry) indicates that chemical attack has occurred, and calibration check must be performed

7) Personnel Qualifications and Responsibilities

7.1 General Responsibilities - This method is restricted to use by or under the supervision of analysts experienced in the method.

7.2 Analyst - It is the responsibility of the analyst(s) to:

- 7.2.1 Each must read and understand this SOP and follow it as written. Any deviations or non-conformances must be documented and submitted to the QA Manager for approval.
- 7.2.2 Produce method compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP (HS-QS-009).
- 7.2.3 Complete the required initial demonstration of proficiency before performing this procedure without supervision.
- 7.2.4 Complete an ongoing demonstration of proficiency annually when continuing

to perform the procedure.

7.2.5 The analysts must submit data for peer or supervisor review.

7.3 Section Supervisor - It is the responsibility of the section supervisor to:

7.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.

7.3.2 Ensure analysts have completed the required initial demonstration of proficiency before performing this procedure without supervision.

7.3.3 Ensure analysts complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.

7.3.4 Ensure analysts produce method compliant data that meet all quality requirements using this procedure and the Data Reduction, Review and Validation SOP.

7.4 Project Manager - It is the responsibility of the Project Manager to ensure that all method requirements for a client requesting this procedure are understood by the laboratory prior to initiating this procedure for a given set of samples.

7.5 QA Manager: The QA Manager is responsible for

7.5.1 Approving deviations and non-conformances

7.5.2 Ensuring that this procedure is compliant with method and regulatory requirements,

7.5.3 Ensuring that the analytical method and SOP are followed as written through internal method and system audits.

8) Sample Collection, Handling, and Preservation

8.1 Not Applicable to this SOP.

9) Equipment and Supplies

9.1 Analytical balance and certified weights – accuracy to four (4) decimal places (nearest 0.0001-g). Balance must be check daily or prior to use, see SOP HS-EQ001.

9.2 Small weight boat.

9.3 Plastic Pipette tips (appropriate manufacturer and volume).

9.4 Glass Scintillation vial, 20 mL or other suitable weighing container.

9.5 Pipette/Volumetric eLogbook.

9.6 “00” steel wool, or equivalent – required for pipette maintenance.

9.7 Kimwipes or equivalent – required for pipette maintenance.

9.8 Beakers of varying sizes.

10) Standards and Reagents

10.1 Note: All purchased standards according to manufacturer specifications. Store standard solutions (remaining stock, composite, calibration and surrogate) below 6 °C in glass containers having Teflon™ lined lids or in accord with the manufacturer's recommended conditions. All purchased stock standard solutions must be replaced after reaching the manufacturer's expiration date assigned to the standard. All laboratory prepared standard solutions must be replaced after six months or sooner if routine QC indicates a problem or if required by reference method. An assigned expiration date of a lab prepared standard cannot exceed the manufacturer's expiration date for any component used in the standard formulation. When analyzing or preparing samples, all standards, lot numbers must be associated with the run batch or prep batch.

10.2 DI Water.

10.3 Silicone grease – required for pipette maintenance

10.4 Methanol – required for pipette maintenance

11) Method Calibration

11.1 Not Applicable to this SOP.

12) Sample Preparation/Analysis

12.1 Assignment of Unique Volumetric Ware Identification: Each volumetric labware (except Class A volumetric glassware with a certificate) must be assigned for tracking identification by department of use. Each department must perform the volumetric checks as required in Table 22.1. These identifications are to be recorded in the E-Logbook that documents the volumetric calibration checks. Only QA can add or delete/deactivate items in eLogbook.

12.2 Pipette/Bottle Top Dispenser Calibration -

- 12.2.1 LIMS Entry
  - 12.2.1.1 Upon receipt of new pipette contract QA to create pipette ID and calibration ranges in LIMS
  - 12.2.1.2 When pipette is to be removed be removed from service, contact QA to remove unit LIMS module.
- 12.2.2 Place approximately 100 ml of DI water in a beaker.
- 12.2.3 Place the scintillation vial or disposable cup on the analytical balance. Tare the balance to zero.
- 12.2.4 Select the manufacturer's recommended pipette tip or suitable substitute. Using the pipette at the highest user-select volume, deliver the fixed volume of DI water into the vial.
- 12.2.5 Record the weight in the pipette verification E-Logbook by send data from the

balance to e-Logbook and enter volume in eLogbook.

12.2.6 Repeat the steps 12.2.3 through 12.2.5 four (4) more times.

12.2.7 Verify acceptance criteria for %Recovery, Bias and Precision using Table 22.1.

12.2.8 If adjustable volume pipettes are used for more than one fixed volume, perform step 12.2.3 through 12.2.7 for the lowest user-select volume setting.

12.2.9 This procedure MUST to be repeated on a quarterly basis.

12.2.10 Upon calibration the pipette/dispenser must be labeled with ID, number, date calibrated, next calibration date and analyst initials.

12.2.10.1 Variable Volume Pipettes – such pipettes must be check at the lower and upper limits.

12.3 Fixed or Adjustable Volume Pipette Maintenance (typical)

12.3.1 On a quarterly basis, prior to calibration check, the following maintenance should be performed.

12.3.2 Disassemble each pipette, clean with methanol and Kimwipes, and dry thoroughly.

12.3.3 Remove any corrosion on the metal plunger with “00” steel wool.

12.3.4 Lubricate the rubber “o” rings with silicone grease

12.3.5 Reassemble each pipette.

12.4 Other Volumetric Ware Calibration Checks are performed in manner similar to the volumetric/gravimetric approach described for the pipette checks (§12.2.2 to 12.2.6). These checks include all laboratory volumetric dispensers where the volume is used in the calculation of the sample results.

12.5 Syringe Check

12.5.1 LIMS Entry

12.5.1.1 Prior to initial use contract QA to create syringe ID.

12.5.1.2 When syringe is to be removed be removed from service, contact QA to remove unit LIMS module.

12.5.2 Tare empty syringe.

12.5.3 Fill syringe with water and send final weight to eLogbook and enter volume in eLogbook.

12.5.4 Repeat 12.5.2-12.5.3 two (2) more times.

12.5.5 Verify acceptance criteria for %Recovery, Bias and Precision using Table 22.1.

12.5.6 Label syringe with ID number.

12.6 DOD mechanical pipette calibration

12.6.1 All pipettes used to prepare daily standards, spikes, reagents and samples must be check prior to use.

12.6.2 Use procedure in 12.2.1-12.2.4, by performing three replicates.

12.6.3 Complete the Pipette Cal spreadsheet to document prep and calculate acceptance limits.

12.7 All Labware not Class A require Bias and Precision Verification (disposable graduated pipets, digestion tubes and autosampler vials).

12.7.1 Procedure for – Bias (Accuracy) Check

12.7.1.1 Perform this check upon receipt of each new lot of class B volumetric labware. Entry items in inventory logbook for tracking.

12.7.1.2 Gravimetric testing is used to check calibration accuracy or bias. To perform a bias check the labware is measured 10 times and the average is calculated.

12.7.1.3 Place a clean, dry weighing vessel onto the analytical balance and

tare.

12.7.1.4 Dispense the total volume from the labware into the tared vessel and send to elogbook.

12.7.1.5 **Note:** If checking TD pipettes they should not be rinsed after they have delivered their contents. If checking a TD-EX pipet, the water is blown out to obtain the correct amount of material. For TC pipettes, the water should be blown out to obtain the correct amount of material.

12.7.1.6 The weight must be within acceptance criteria listed in Table 1. If not, repeat the test, ensuring that the balance is operating properly and pipetting technique is correct. If the 2nd set of 10 readings is not within acceptable criteria perform maintenance or take it out of service and consult with QA.

13) Troubleshooting

13.1 None are defined for this procedure.

14) Data Acquisition

14.1 Data are entered into the designated e-Logbook via the LAB LIMS or Spreadsheet (DOD) projects. The e-Logbook will calculate mean, deviation and uncertainty.

15) Calculation, and Data Reduction Requirements

15.1 QC Calculations: LIMS calculates the percent recovery for various QC samples (LCS) according to the following equations:

15.1.1 % Recovery, %R (for MS and MSD Samples)

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SR = Sample Result (unspiked).
SA = Spike Amount Added (mg/L or mg/kg).

15.1.2 % Recovery, %R (for standards and LCS)

$$\%R = \frac{SSR}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SA = Spike Amount Added (mg/L or mg/kg).

15.1.3 RPD (for precision or duplicate evaluation)

$$\mathrm{RPD} = \frac{|\mathrm{SR}_1 - \mathrm{SR}_2|}{½(\mathrm{SR}_1 + \mathrm{SR}_2)} \times 100$$

Where:
SR_1 = Sample result for duplicate 1.
SR_2 = Sample result for duplicate 2.

15.2 Sample Concentration Calculation

16) Quality Control, Acceptance Criteria and Corrective Action

16.1 Initial Demonstration of Capability - Not Applicable to this SOP.

16.2 Continuing Demonstration of Capability - Not Applicable to this SOP.

16.3 Initial Calibration:

16.3.1 Balance must be check daily and pass acceptance limit prior to use. If initial check does not pass, clean balance with compress air under the pan and near the pressure transducer to dislodge any foreign material. Repeat check, if balance stills fail check, contact supervisor or QA to place unit out of service and schedule repair if needed.

16.4 Initial Calibration Verification (second source) Not Applicable to this SOP.

16.5 Continuing Calibration Verification (CCV) - Not Applicable to this SOP.

16.6 Method Blank (MB) - Not Applicable to this SOP.

16.7 Laboratory Control Sample: The LCS is prepared from a calibration standard - Not Applicable to this SOP.

16.8 Matrix Spike (If field sample is not available to perform both an MS and MSD, then perform an LCS and LCSD - Not Applicable to this SOP.

16.9 Duplicate Samples - Not Applicable to this SOP.

16.10 Surrogate Spikes - Not Applicable to this SOP.

16.11 Limit of Detection Determination and Verification - Not Applicable to this SOP.

16.12 Limit of Quantitation Establishment and Verification: - Not Applicable to this SOP.

17) Data Records Management

17.1 All data is stored electronically and/or hard copy for five (5) years or ten (10) years for data to be submitted to the state of Louisiana. Operational software is maintained for the same duration

17.2 All analytical sequence IDs and standard preparation information must be recorded in the Run logbook. Hardcopy computer printouts of analytical sequences and raw data must be retained and initialed by the analyst (electronic initials are acceptable). To simplify standard and reagent tracking, analyst must attempt to use single lots of reagents and standards.

17.3 Complete all pertinent sections in the respective logbooks. If not-applicable then line out the section and "Z" out or "X" out all large sections of the worksheet that are not used. Make all corrections with single line through, date and initial. Make NO obliterations when manually recording data.

17.4 Logbooks are controlled. Never remove a page from a logbook. Completed logbooks are returned to the QA department when filled and no longer needed in the work area.

17.5 SOP effective date is the date noted in the header or last signature date, whichever is most recent.

18) Contingencies for Handling Out of Control Data

18.1 When method required QC exceedances occur, in every case where sample data quality are affected, the source of the QC exceedance must be determined, corrected and sample reanalysis carried out when possible.

18.2 When affected sample analysis can not be repeated due to limitations (i.e. sample availability, or if reanalysis can only be performed after expiration of a sample hold time), the reporting of data associated with exceeded QC data must be appropriately flagged and narrated. This documentation is necessary to define for the data user the effect of the error has upon the data quality of the results reported (e.g. E flag data indicate the result to be only an estimate).

18.3 All analysts must report sufficient comments in laboratory data review checklist for exceeded QC associated with sample results so that project management can further narrate and ensure data qualifiers (flags) are properly assigned to the reported data.

18.4 NCARs must be issued for QC system exceedances. Matrix interferences are reported using the analyte reporting comment section in LIMS or using the Laboratory Data review checklist.

19) Method Performance

19.1 None are defined for this procedure

20) Summary of Changes

Table 20.1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
8.2	11/09/2018	G. Moulton	Updated to new ALS Cover and new quality manager.
8.2	11/09/2018	G. Moulton	Modified sec 21.2 and 21.2 and 17.1
8.2	11/09/2018	G. Moulton	Modified sec 17.1
08.1 – Section 2.7	1/31/2018	T. Yen	Procedure for non-class A ware such as disposable pipettes.
08.1 – Section 12.7	1/31/2018	T. Yen	Procedure for checking non-class A volumetric ware.
08.1 – Section 21.0	1/38/2017	T. Yen	Reference update.
08.1 – Table 22.1	1/31/2018	T. Yen	Acceptance limits for non-class A volumetric labware.
08.0	11/30/2015	T. Yen	New SOP format and Lab Director.
08.0 – Section 2.4	11/30/2015	T. Yen	Pipette calibration language change to MUST and DOD frequency added to procedure.
08.0 – Section 4.6	11/30/2015	T. Yen	Job safety assessment added.
08.0 – Section 12.5	11/30/2015	T. Yen	Syringe check procedure added.
08.0 – Section 12.6	11/30/2015	T. Yen	DOD mechanical pipette procedure added.
08.0 – Section 22.0	11/30/2015	T. Yen	Calibration criteria, include DOD criteria.
07.2	05/15/2013	T. Yen	Signature Page – New Department Supervisor, QA Manager and Lab Director.
07.2	05/15/2013	T. Yen	Document Footer – "A Campbell Brothers Limited Company" changed to "An ALS Limited Company" to reflect parent company name change.
07.2 – Section 1.2.2	05/15/2013	T. Yen	Microsyringes must be check prior to use and semiannually afterwards.
07.2 – Section 2.4	05/15/2013	T. Yen	Mechanical pipettes check at two points if used as variable volume and one point if fix volume.
07.2 – Section 2.5	05/15/2013	T. Yen	Class A glassware does not need to be checked, except for microsyrignes.
07.2 – Sections 8.5 & 8.6	05/15/2013	T. Yen	Removed sections, no reference to Class B calibration. Class B labware may not be used in the lab.
07.2 –	05/15/2013	T. Yen	SOP effective date defined.

Revision Number	Effective Date	Document Editor	Description of Changes
Section 15.5			
07.1	04/15/2012	J. Cady	Calculations and procedural clarifications, including Class A labware.
07.0	06/30/2011	I. Williams	Format and requirements changes.
06.0	08/01/2008	R. Pierrot	Major document revision.

21) References and Related Documents

21.1 Current TNI Standards.

21.2 Current Department of Defense Quality Systems Manual.

22) Appendix

Table 22.1 Volumetric Equipment Calibration and Maintenance

Table 22.1 – Volumetric Equipment Calibration And Maintenance			
Instrument	Activity – Criteria	Frequency	Documentation
Mechanical volumetric pipettes including burettes(except Class A glassware) and Bottle Top Dispensers	%Recovery Each entry 98% - 102% Bias: Mean within 2% of nominal volume Precision: 1% (based on 5 replicates) **Note**: For Variable volume mechanical pipettes, the High Volume is the highest user-select volume and the Low Volume is the lowest user-select volume – both are required.	Before first use. Quarterly thereafter or upon evidence of deterioration	E-Logbook
Glass microliter syringes (excluding 10uL or smaller)	1000 uL or Less: All glass microliter syringes are to be considered in the same manner as Class A glassware. There are no longer any calibration requirements. The accuracy provided by the vendor as meeting Class A requirements are now enough. Therefore, no more verifications or certificates are needed. However, analysts are to check for signs of deterioration. %Recovery: Each Entry 98% - 102% Bias: Mean within 2% of nominal volume Precision: RSD $\leq$1% of nominal value	1000 uL or Less: Check for signs of deterioration >1000 uL: Before first use and quarterly verification thereafter or upon evidence of deterioration	E-Logbook

Table 22.1 – Volumetric Equipment Calibration And Maintenance			
Instrument	Activity – Criteria	Frequency	Documentation
	(based on 3 replicate measurements) .		
Non-volumetric labware (Applicable only when used for measuring initial sample volume or final extract / digestate volume) such as Digestion vials or extract vials. Calibration not needed if certificate of accuracy is provide.	%Recovery: Each Entry 98% - 102% Bias: Mean within 3% of nominal volume Precision: RSD ≤2% of nominal value (based on 10 replicate measurements)	By lot before first use or upon evidence of deterioration	E-Logbook
Mechanical Pipets for DOD projects.	Bias: Mean within ±2% of nominal volume. Precision: RSD ≤1% of nominal volume (based on minimum of 3 replicate measurements) [Note: for variable volume pipettes, the nominal volume is the volume of use]	**DAILY BEFORE USE**	Spreadsheet – Pipette Cal, latest version

ORGANIC COMPOUNDS AND DRO IN WATER BY MICROEXTRACTION SW3511

DOCUMENT ID: HS-EXT007, REV 1.2

Approved By: Hoai Van
Technical and Laboratory Director, Hoai Van

Date: 8/20/2020

Prepared By: Erica H Marinez
Quality Assurance Manager, Erica Marinez

Date: 08/20/2020

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1) Identification of the Method, Applicable Matrices, Scope and Applicability

1.1 Method 3511 is a procedure for extracting selected semivolatile organic compounds and diesel range organics from water. The microscale approach minimizes sample size and solvent usage, thereby reducing the supply costs, health and safety issues, and waste generated.

1.2 This method has been validated for several mono- and poly-cyclic aromatic hydrocarbons (MAHs and PAHs), and Diesel Range Organics (DRO), and can be applied to any combination of these compounds.

1.3 This method also may be used to extract selected semivolatile organic compounds (SVOCs) or Diesel Range Organics (DROs) which are slightly soluble or insoluble in water at neutral pH once their extraction performance has been demonstrated to be satisfactory using an appropriate analytical technique.

1.4 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 3500, 3600, 5000, and 8000) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

1.5 In addition, analysts and data users are advised that, except where explicitly required in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.6 Use of this method is restricted to use by, or under supervision of, appropriately experienced and trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2) Summary of Procedure

2.1 Samples are prepared by liquid liquid extraction with organic solvent in field sampling containers maximizing extraction of semivolatile and diesel range organics.

2.2 Samples should be prepared one at a time to the point of solvent addition (i.e., do not prepare a number of samples then add the solvent). Pay particular attention to minimizing the exposure of the sample and/or extract to air.

3) Definitions

3.1 Exception Report: Appropriate comments reported with the associated sample batch that addresses sample anomalies such as demonstrated sample matrix effects.

3.2 Laboratory Control Sample (LCS): A sample matrix, free from the analytes of interest, spiked with known amounts of analytes or a material containing known and verified amounts of analytes.

3.3 Laboratory Duplicates: Two sample aliquots, taken in the laboratory from a single sample bottle, and analyzed separately with identical procedures. Analyses of duplicates indicate precision associated specifically with the laboratory procedures, removing any associated variables attributed by sample collection, preservation, or storage procedures.

3.4 Matrix Spike (MS): An aliquot of sample spiked with a known concentration of the target analyte. The spiking occurs prior to sample preparation and analysis. A matrix spike is used to assess the bias of a method in a given sample matrix.

3.5 Matrix Spike Duplicate (MSD): A duplicate sample spiked with identical concentrations of target analyte(s) as the matrix spike (MS). The spiking occurs prior to sample preparation and analysis. The MS/MSD pair are used to assess method precision and bias in a given sample matrix.

3.6 Matrix: The substrate (e.g., water, soil, etc.) which may contain the analyte of interest.

3.7 Method Blank (MBLK): An interference-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

3.8 NCAR: Nonconformance Corrective Action Report (refer to SOP HS QS-003, current revision).

3.9 Organic Free Water: Deionized (DI) reagent water meeting purity characteristics of Type I laboratory distilled water (daily resistance ≥17 megohms-cm). For additional purification, the DI water is passed through an activated carbon filter.

3.10 Surrogate: An analyte added to a sample, which is unlikely to be found in any sample at significant concentration, and which is added directly to a sample aliquot in known amounts before any sample processing procedures are conducted. It is measured with the same procedures used to measure other sample components. The purpose of the surrogate analyte is to monitor method performance with each sample.

3.11 Preparation Batch: A defined set of one to 20 client samples of the same matrix, meeting the batch definition criteria, and prepared for analysis within 24 hours. The preparation batch must also contain the required method defined batch QC samples (e.g. method blank, laboratory control samples, matrix spikes, duplicates, etc.).

4) Safety

4.1 There are no significant safety issues specific to this method. However, SW-846 methods do not purport to address all safety issues associated with their use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5) Pollution Prevention and Cautions

5.1 Routine preventative maintenance must be performed and documented to assure optimum instrument performance. Refer to the current revision of SOP HS-EQ004 for preventative maintenance schedules.

5.2 Rinse glassware completely with the extraction solvent when transferring from one

container to the next.

5.3 Exposure to plastic materials is forbidden, as they are a source of phthalate contamination. Gloves, tubing, and other laboratory materials must be free of these materials.

6) Interferences

6.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method for specific guidance on quality control procedures and to Chapter Four for guidance on the cleaning of glassware.

7) Personnel Qualifications and Responsibilities

7.1 General Responsibilities - This method is restricted to use by or under the supervision of analysts experienced in the method.

7.2 Analyst - It is the responsibility of the analyst(s) to:

7.2.1 Read and understand this SOP and follow it as written. Any deviations or nonconformances must be documented and submitted to the QA Manager for approval.

7.2.2 Produce method compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP (HS-QS-009).

7.2.3 Complete the required initial demonstration of proficiency before performing this procedure without supervision.

7.2.4 Complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.

7.2.5 The analysts must submit data for peer or supervisor review.

7.3 Section Supervisor - It is the responsibility of the section supervisor to:

7.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.

7.3.2 Ensure analysts have completed the required initial demonstration of proficiency before performing this procedure without supervision.

7.3.3 Ensure analysts complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.

7.3.4 Ensure analysts produce method compliant data that meet all quality requirements using this procedure and the Data Reduction, Review and Validation SOP.

7.4 Project Manager - It is the responsibility of the Project Manager to ensure that all method requirements for a client requesting this procedure are understood by the laboratory prior to initiating this procedure for a given set of samples.

7.5 QA Manager: The QA Manager is responsible for

7.5.1 Approving deviations and nonconformances

7.5.2 Ensuring that this procedure is compliant with method and regulatory requirements,

7.5.3 Ensuring that the analytical method and SOP are followed as written through internal method and system audits.

8) Sample Collection, Handling, and Preservation

Table 0.1- Semivolatile Organics and DROs - Waters

TABLE 8.1 - Semivolatile Organics and DROs – Waters			
Sample Matrix	Container	Preservative	Holding Time
Aqueous Samples	3 - 40 mL VOA Vials with Teflon-lined lid	Cool to 6˚C	Extraction 7 days Analysis 40 days

9) Equipment and Supplies

9.1 The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

9.2 VOA vials – 40-mL capacity, disposable, pre-cleaned with Polytetrafluoroethylene (PTFE)-lined caps.

9.3 Vials – amber glass, 2-mL capacity, with PTFE-lined screw or crimp top.

9.4 Centrifuge – capable of at least 500 G's

9.5 Syringes - gastight, contaminant-free. 2.0 mL, 1.0 mL, 10 uL.

9.6 Analytical balance – capable of weighing to 0.01 g.

9.7 Pasteur glass pipettes – 1mL, disposable.

9.8 OS-500 shaker table

10) Standards and Reagents

10.1 Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

10.2 Reagent water: Organic-free water.

10.3 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for four hours in a shallow porcelain bowl. Store unused portion of sodium sulfate within a desiccator.

10.4 Methylene Chloride, CH_2Cl_2.

10.5 PAH Surrogate Solution:

10.5.1 B/N Surrogate Mix, 5000 ug/mL in methylene chloride (Restek Cat. # 31086) or equivalent.

10.5.2 PAH LVI Surrogate, 1 ug/mL: In a 50 mL volumetric flask, add approximately 40 mLs of acetone. Inject 10 uL of 5000 ug/mL B/N Surrogate Mix (10.5.1) and fill to volume with acetone.

10.6 PAH Spiking Solution:

10.6.1 PAH Standard Stock, 500 ug/mL in acetonitrile (Restek Cat.# 31841) or equivalent.

10.6.2 PAH LVI Spike, 1 ug/mL: In a 50 mL volumetric flask, add approximately 40 mLs of acetone. Inject 100 uL of 500 ug/mL PAH Standard Stock (10.6.1) and fill to volume with acetone.

10.7 PAH Internal Standard Solution:

10.7.1 SV Internal Standard, 4000 ug/mL in methylene chloride (Restek Cat. # 31006) or equivalent.

10.7.2 LVI Internal Standard, 2 ug/mL. In a 10 mL volumetric flask, add approximately 9 mLs of methylene chloride. Inject 5 uL of 4000 ug/mL SV Internal Standard (10.7.1) and fill to volume with methylene chloride.

10.8 DRO Surrogate Solution:

10.8.1 8015 Stock Surrogate, 1000 ug/mL: In a 10 mL volumetric flask, add 0.010 g of neat 2-Fluorobiphenyl Surrogate Standard. Fill to volume with Methylene Chloride and mix well.

10.8.2 LVI DRO/ORO Surrogate, 10 ug/mL: In a 5 mL volumetric flask, put approximately 4 mLs of acetone. Inject 50 uL of the 1000 ug/mL 8015 Stock Surrogate (10.8.1) and fill to the volume with acetone.

10.9 DRO Spiking Solution:

10.9.1 DRO/Motor Oil Intermediate Standard, 2000 ug/mL: In a 25 mL volumetric flask, add approximately 20 mLs of methylene chloride. Inject 1 mL of 50,000 ug/mL Diesel #2 Standard and 1 mL of 50,000 ug/mL Motor Oil Standard. Fill to volume with methylene chloride.

10.9.2 LVI DRO/ORO Spike, 100 ug/mL: In a 5 mL volumetric flask, add approximately 4 mL of acetone. Inject 250 uL of the 2000 ug/mL DRO Motor Oil Intermediate Standard (10.9.1) and fill to the volume with acetone.

11) Sample Preparation/Analysis

11.1 For each QC sample to be extracted and analyzed, prepare one vial as described in 11.2.

11.2 Each extraction batch of 20 samples will need one method blank, one laboratory control sample (LCS), and one set of matrix spike/matrix spike duplicate (MS/MSD). If there is insufficient sample volume for an MS/MSD, an LCS/LCS Duplicate may replace the MS/MSD. For each Blank, LCS/LCSD sample, fill a 40 mL glass VOA vial with a PTFE lined septum screw top with reagent water.

11.3 Working with a single field or QC sample at a time, remove the cap from the VOA vial, and use a disposable pipette to remove approximately 10 mL of water. Replace the vial cap. The volume removed should be disposed of according to the guidelines set forth by the laboratory for the disposal of laboratory wastes.

11.4 After removing the 8 mLs, weigh the capped VOA vial for each field and QC sample. Record the weight to the nearest 0.1 grams.

11.5 Remove the cap and add 100 µL of the surrogate compounds standard (PAH from section 10.5 or DRO from section 10.8) in acetone. The surrogates recommended are Nitrobenzene-d5, 2-Fluorobiphenyl, 4-Tertphenyl-d14 for PAH and 2-Fluorobiphenyl for DRO. Other compounds may be used as surrogates, depending upon the desired target analytes and project requirements.

11.5.1 It should be noted that more surrogate standard may be added to the water if the sample is suspected to be highly contaminated (i.e., the contamination may interfere with the recovery of lower concentration levels of surrogate standard).

11.5.2 The LCS, MS, and MSD samples should have 100 uL of the appropriate compounds of interest added (PAH from section 10.6 or DRO from section 10.9).

11.6 Add exactly 2.0 mL of methylene chloride (DCM) (using a class A volumetric pipette or gas-tight syringe) and approximately 10 grams of anhydrous sodium chloride to the VOA vial. Replace the vial cap. At this point, the next sample may be processed to the point of solvent addition and the subsequent steps performed for each sample batch.

11.7 Using the OS-500 shaker, shake each vial vigorously for 5 minutes, or until the sodium chloride dissolves completely.

11.8 Briefly allow the phases to settle, then centrifuge at 500 times the force of gravity (500 G's) for 15 minutes.

11.9 Using a 2.0-mL gas-tight syringe, transfer approximately 1.5 mL of the lower (DCM) layer to a 2 mL vial with a PTFE lined screw cap, taking precautions to exclude any water from the syringe. Add a small amount (~50mg) of anhydrous sodium sulfate to the vial, cap, and shake for 2 minutes.

11.10 Using a 1.0 mL gas-tight syringe, transfer exactly 1.0 mL of the dried extract to a 2 mL vial with a PTFE lined screw cap. For PAH, add 10 µL of the internal standard compounds to each vial. See Section 10.7. Other compounds may be used as internal standards, depending upon the desired target analytes and project requirements. Cap the vial and invert several times to mix the contents.

11.11 Discard the remaining contents of the VOA vials according to laboratory waste disposal guidelines. Shake off the last few drops with short, brisk wrist movements. If needed, rinse the vial with a water soluble solvent to ensure that the extraction solvent is removed. Reweigh the capped vial, and record the weight to the nearest 0.1 grams. The difference between this weight, and the weight determined in Sec. 11.6 is equal to the volume of water extracted, in milliliters.

11.12 Extracts should be stored in the freezer until analysis.

12) Troubleshooting

12.1 When requested by an analyst as part of a corrective action investigation, prepare new spike and/or surrogate standards as needed, etc.

12.2 Good technique is important to obtain consistently acceptable LCS, MS, and MSD recoveries. Good house keeping and thorough equipment and glassware cleaning is required to prevent sample contamination. Refer to Glassware Cleaning SOP (HS-GEN003) posted at the glassware cleaning area.

12.3 If an emulsion forms, allow organic layer to separate from the water phase, and if necessary, up to 10 minutes. If the emulsion interface between layers is more than 1/3 the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the solvent extract through glass wool supporting solvent-rinsed sodium sulfate into a glass collection bottle.

13) Data Acquisition

13.1 Sample preparation information is recorded into LIMS where a prep batch ID is assigned. The LIMS entered extraction data is used to calculate final analytical results

14) Calculation, and Data Reduction Requirements

14.1 See analytica1 SOP for the methods extracted.

15) Quality Control, Acceptance Criteria and Corrective Action for Out-of-Control Data

15.1 All necessary quality control samples are extracted along with the field samples.

15.2 See each analytical SOP for criteria and corrective action for out of control data.

16) Data Records Management

16.1 All data is stored both electronically and/or hard copy for 5 years or longer depending on regulations or client's request.

16.2 All analytical sequence IDs and standard preparation information must be recorded in the Run logbook. Hardcopy computer printouts of analytical sequences and raw data must be retained and initialed by the analyst (electronic initials are acceptable). To simplify standard and reagent tracking, analyst must attempt to use single lots of reagents and standards.

16.3 Complete all pertinent sections in the respective logbooks. If not-applicable then line out the section and "Z" out or "X" out all large sections of the worksheet that are not used. Make all corrections with single line through, date and initial. Make NO obliterations when manually recording data.

16.4 Logbooks are controlled. Never remove a page from a logbook. Completed logbooks are returned to the QA department when filled and no longer needed in the work area.

17) Method Performance

17.1 Method performance is determined by passing surrogates, internal standards PTs also by the performance of MDLs and other quality control standards.

17.2 The method detection limit (MDL) is established using the procedure described in the SOP *Performing and Documenting Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (CE-QA011). Method Reporting Limits are established for this method based on the low calibration point and the MDL study results

18) Waste Management

18.1 It is the laboratory's practice to minimize the amount of solvents, acids, and reagents used to perform this method wherever feasibly possible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvents and/or reagents used in this method can be minimized when recycled or disposed of properly.

18.2 The laboratory will comply with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Chemical Hygiene Plan and Lab Waste Management Plan.

19) Training

19.1 Training outline

19.1.1 Review literature (see references section). Read and understand this SOP. Also review the applicable SDS for all reagents and standards used. Following the reviews, observe the procedure as performed by an experienced analyst at least three times.

19.1.2 The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

19.1.3 Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

19.2 Training is documented following *SOP CE-QA003*).

19.3 When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

20) Summary of Changes

Table 20.1 Summary of Revision Changes			
Revision Number	**Effective Date**	**Document Editor**	**Description of Changes**
1.2	08/20/2020	G. Moulton	Sec 1: Sec1: Added scope and applicability, and Identification of the method
1.2	08/20/2020	G. Moulton	Sec 9.8: Replaced wrist shaker with OS-500 shaker table.
1.2	08/20/2020	G. Moulton	Sec 11.3: Remove 10 ml of sample.
1.2	08/20/2020	G. Moulton	Sec 11.6: Add 10 grams of Sodium Chloride.
1.2	08/20/2020	G. Moulton	Sec 5: Added pollution prevention to this sec.
1.2	08/20/2020	G. Moulton	Sec 14: Added calculation and data reduction requirement
1.2	08/20/2020	G. Moulton	Sec 15: Quality Control, Acceptance Criteria and Corrective Action for Out-of-Control Data.
1.2	08/20/2020	G. Moulton	Sec 17: Updated method performance section.
			Sec 18: Added waste management.
			Sec 19: Added training.
1.1	12/03/2019	G. Moulton	Updated cover per company standard, Updated new QA Manager.
1.1	12/03/2019	G. Moulton	Sec 17.1.1 to 17.1.3 Modified references.
1.1	12/03/2019	G. Moulton	Modified sec 14.1 data storage.
01.0	05/25/2012	J. Cady	New SOP

21) References and Related Documents

21.1 Referenced Documents

21.1.1 Current version of TNI Standard.

21.1.2 Current US Department of Defense Quality Systems Manual.

21.1.3 ANSI/ISO/IEC-17025:2017.

21.1.4 Method SW 3511, Organic Compounds in Water by Microextraction, Revision 0, November 2002.

DRO AND ORO IN WATER OR SOILS BY METHOD SW846-8015C

DOCUMENT ID: HS-GCFID003, REV 7.3

Approved By: _____ Date: 8/3/2020
Technical and Laboratory Director, Hoai Van

Prepared By: _____ Date: 08/03/2020
Quality Assurance Manager, Erica Marinez

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1) Identification of the Method, Applicable Matrices, Scope and Applicability

1.1 This methodSW846-8015C is designed to determine Diesel Range Organics (DRO) and Oil Range Organics (ORO) in extracts from aqueous or soil matrices using gas chromatography/flame ionization detection. This method can be used for the quantitative analysis of petroleum hydrocarbons in the diesel range which corresponds to the range of alkanes from C_{10} (n-decane) to C_{28} (n-octacosane), a boiling range of approximately 170ºC to 430ºC. The analysis may be extended beyond n-octacosane (C_{28}) when the environmental medium of concern, or the suspected source of the TPH, contains hydrocarbons in the heavier hydrocarbon boiling point range [Oil Range Organics or ORO, i.e., >C_{28} to C_{35} (n-pentatriacontane)].

1.1.1 Note: Method 8015C only provides guidance on performing DRO analysis (as C_{10} to C_{28}). Applicability of the method for ORO is provided in this SOP because many state programs recognize the need to analyze for the presence of heavier petroleum hydrocarbons (as ORO) in addition to DRO.

1.2 This procedure is a gas chromatography (GC) method with flame ionization detection (FID). This GC method reports the TPH into two ranges, DRO and ORO when applicable, based on retention times of the respective hydrocarbon range standards.

1.3 The limit of quantitation for DRO and ORO using this method is estimated to be 0.05 and 0.10 mg/L respectively for aqueous matrix and is estimated to be 1.7 and 3.4 mg/Kg respectively for soil matrix. Current LOD and LOQ can be found in ALS LIMS.

2) Summary of Procedure

2.1 This method is based upon analysis of water or soil methylene chloride extract using gas chromatography/ flame ionization detection (GC/FID) that measures the concentration of hydrocarbons between C_{10} and C_{35}. The method uses a diesel #2 fuel and/or motor oil as calibration standards and n-alkane markers C_{10}, C_{28} and C_{35}, are the method prescribed carbon markers to establish the boiling point range boundaries. Results are reported for boiling point ranges C_{10} to C_{28} (diesel range), and >C_{28} to C_{35} (oil range). The concentrations of each are reported as DRO and / or ORO as requested by a client. Because this procedure utilizes a motor oil standard for calibration of ORO, a combined DRO and ORO calibration standard typically yields a minimum peak response between the two materials near the C_{21} marker chromatographically. When the combined DRO / ORD standard is utilized for the initial calibration, ICV, CCV and LCS, the minimum peak response is used as the marker between the ranges to accurately quantitate both ranges.

2.2 Waters are prepared using the aqueous liquid-liquid separatory funnel extraction procedure (SW 3510C), where a 1-liter water sample is extracted using methylene chloride and concentrated to a 1.0-mL final volume (see SOP HS-EXT-009).

2.3 Soils are prepared using the automated soxhlet extraction (SW3541), where a 30-gram

soil sample is extracted using a 1:1 methylene chloride/acetone mixture and concentrated to a 1.0-mL final volume (see SOS HS-EXT-008) or microwave (SW3546) using 1:1 methylene chloride/acetone mixture (see SOP HS-EXT022).

3) Definitions

3.1 Demonstration of Capability (DOC): procedure to establish the ability of the laboratory to generate acceptable accuracy and precision which is included in many of the EPA's analytical test methods. In general, an initial DOC procedure involves the analysis of four separate Laboratory Control Samples (LCS) as prescribed by the analytical method Each LCS must meet the specified LCS acceptance limits for percent recovery, and standard deviation. Ongoing DOC requirements are met by acceptable analysis of annual NELAC accepted proficiency test (PT) samples, or by the analysis of four LCS if PT samples are not available

3.2 Exception Report: Appropriate comments reported with the associated sample batch that addresses sample anomalies such as demonstrated sample matrix effects.

3.3 Laboratory Control Sample (LCS): A sample matrix, free from the analytes of interest, spiked with known amounts of analytes or a material containing known and verified amounts of analytes.

3.4 Limit of Detection (LOD): an estimate of the minimum amount of a substance that an analytical process can reliably detect. The LOD is determined annually through the execution of a Method Detection Limit Study, and verified quarterly through the analysis of a Detectability Check Sample (DCS).

3.5 Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met.

3.6 Matrix Spike (MS): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available.

3.7 Matrix Spike Duplicate (MSD): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of recovery for each analyte.

3.8 Matrix: The substrate (e.g., water, soil, etc.) which may contain the analyte of interest.

3.9 Method Blank (MBLK): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the

analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analysis.

3.10 Method Detection Limit (MDL) study: a procedure described in 40CFR Part 136, Appendix B, that describes how to produce an MDL, a reporting element of certain EPA methods. The MDL study is one approach to determine the LOD.

3.11 NCAR: Nonconformance Corrective Action Report (refer to SOP HSQS003, current revision).

3.12 Reagent Water: Deionized (DI) reagent purified by filtration through mix resin and carbon beds. For additional purification, the DI water is passed through an activated carbon filter.

3.13 Preparation Batch: A defined set of one to 20 client samples of the same matrix, meeting the batch definition criteria, and prepared for analysis within 24 hours. The preparation batch must also contain the required determinative method defined batch QC samples (e.g. method blank, laboratory control samples, matrix spikes, duplicates, etc.).

3.14 Surrogate: An analyte added to a sample, which is unlikely to be found in any sample at significant concentration, and which is added directly to a sample aliquot in known amounts before any sample processing procedures are conducted. It is measured with the same procedures used to measure other sample components. The purpose of the surrogate analyte is to monitor method performance with each sample.

3.15 Surrogate Spike: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environmental samples and is added to them for quality control purposes.

3.16 Batch: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** is composed of one (1) to twenty (20) environmental sample of the same quality systems matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be twenty-four (24) hours. An **analytical batch** is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.

3.17 Retention Time Window: The length of time between sample injection and the appearance of a peak at the detector. The window of time is established for each analyte or group of analytes and is set for complete elution of analyte peaks. It is based upon a series of analyses and statistical calculations that establish the measured band on the chromatogram that can be associated with a specific analyte or group of analytes.

3.18 Second Source Calibration Verification (ICV): A standard obtained or prepared from a source independent of the source of standards for the ICAL. Its concentration should be at or near the middle of the calibration range. It is performed after the ICAL.

3.19 Calibration Standard (CAL): A solution prepared from the primary dilution standard solution or stock standard solutions and the surrogate analyte. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.20 Linear Calibration Range (LCR): The concentration range over which the instrument response is linear

3.21 Instrument Performance Check Sample (IPC): A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.22 Continuing Calibration Verification (CCV): A known interference free matrix spiked with a known concentration of the target analyte. The CCV is prepared from the same source that was used to prepare the calibration standards, and is used to verify that the instrument calibration is in control before and after sample analysis.

3.23 Quality Control Sample (QCS): A solution of method analytes of known concentrations that is used as the spiking solution for the LCS. The QCS is obtained from a source external to the laboratory and different from the source of calibrations standards. It is used to check laboratory performances with externally prepared test materials.

3.24 Detectability Check Sample (DCS): a sample spiked at 2 to 3 times the calculated LOD (refer to SOP HS-QS006, LOD and LOQ), or alternatively spiked near the LOQ.

3.25 Safety Data Sheets (SDS): Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

3.26 Diesel Range Organics (DRO): Gas chromatographic peaks eluting before n-Decane (nC_{10}) to n-octacosane (nC_{28}). This includes aliphatic and aromatic hydrocarbons.

3.27 Oil Range Organics (ORO): Gas chromatographic peaks eluting after n-octacosane ($>nC_{28}$) to n-Pentatriacontane (nC_{35}). This includes aliphatic and aromatic hydrocarbons.

3.28 The petroleum hydrocarbons in a sample (if any) may not encompass the entire range. There may be non - hydrocarbons in a sample that elute in the range (such as chlorinated solvents, ketones, alcohols, etc.). However, such compounds usually appear as discrete peaks and do not match typical petroleum product fingerprints. These compounds will be quantified as part of the TPH, but such sample result would be discussed as a data anomaly in a project narrative when an analyst presumption is made that such a compound may be present.

3.29 Locator (or Marker) Standard: Standards used to determine the ranges nC_{10} to nC_{28} and nC_{28} to nC_{35}. The locator mix standard must contain, but is not limited to nC_{10}, C_{28} and nC_{35} alkanes. The standards are used to determine the retention time windows for each boiling point range during the initial demonstration of proficiency procedures. The retention time marker positions are checked during every daily run. When a

marker position shift greater than ±15 seconds is observed in the retention time for a boiling point range, the results for associated chromatograms must be rechecked and recalculated as necessary.

3.30 Globally Harmonized System of Classification and Labeling of Chemicals (GHS) – common and coherent approach to classifying chemicals and communicating hazard information on labels and safety data sheets.

3.31 Safety Data Sheets (SDS): Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

3.32 DoD – United States Department of Defense.

3.33 DoD QSM – Current DoD Quality Systems Manual.

4) Safety

4.1 Lab Safety: Due to various hazards in the laboratory, safety glasses and laboratory coats or aprons must be worn at all times while in the laboratory. In addition, gloves and a face shield should be worn when dealing with toxic, caustic, and/or flammable chemicals.

4.2 Chemical Hygiene: The toxicity or carcinogenicity of each reagent used has not been precisely defined; however, each chemical used should be treated as a potential health hazard. Exposure to laboratory reagents should be reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets (MSDS) is available to all personnel involved in these analyses.

4.3 Waste Management: The principal wastes generated by this procedure are the method-required chemicals and standards. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required. Laboratory procedures in SOP SHWD001, Waste Disposal Policy, must be followed.

4.4 Pollution Prevention: The materials used in this method pose little threat to the environment when recycled and managed properly. The quantities of chemicals purchased should be based on the expected usage during its shelf life. Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards or reagents to be disposed.

4.5 Job Safety Assessment

HAZARD ASSESSMENT		
Job Task #1:	**Hazards**	**Preventative Measures**
Cooler and sample handling.	Injury due to lifting heavy coolers and placing/removing samples to/from storage locations. .	Use proper lift technique and cart to move coolers and stools/stepladder when working reaching above shoulder height in sample storage cooler.
Job Task #2:	**Hazards**	**Preventative Measures**
Sample container handling and preservation checks.	Exposure to possible hazardous chemicals.	Use of proper PPE, i.e. Lab coats, safety glasses, gloves, etc.
Job Task #3:	**Hazards**	**Preventative Measures**
Use of utility knives to cut open cooler and seals.	Cuts.	Use proper safety with auto retracting blade and proper cutting techniques. Always cut away from body.
Job Task #4:	**Hazards**	**Preventative Measures**
Unpacking coolers and searching for sample within the coolers.	Possible cuts from broken sample containers.	Wear proper protective equipment such as Kevlar kit gloves and use of broken glass containers.
Job Task #5:	**Hazards**	**Preventative Measures**
Glassware Washing.	Possible cuts from broken glassware.	Wear proper protective equipment such as Kevlar kit gloves.
Job Task #6:	**Hazards**	**Preventative Measures**
Sample Testing and/or standard and reagent/solvent use.	Exposure to possible hazardous chemicals & puncture wound with syringe.	Wear gloves, safety glasses and lab coat. Work in fume hood and avoid skin contact with solvents/acids/reagents. Know location of safety shower, first aid kits, spill kits and fire extinguisher when handling flammable material.
Job Task #7:	**Hazards**	**Preventative Measures**
Heated surface such as injector and detector.	Burn potential.	Allow surfaces time to cool down before handling. Wear gloves, safety glasses and lab coat.

5) Maintenance

5.1 Routine preventative maintenance must be performed and documented to assure optimum instrument performance. Refer to the current revision of SOP HS-EQ004 for preventative maintenance schedules.

6) Interferences

6.1 Other organic compounds, including vegetable and/or animal oils and greases, organic acids, chlorinated hydrocarbons, phenols, and phthalate esters are measurable under the conditions of this method. However, if present, the characteristic petroleum hydrocarbons will be altered.

6.2 Sample contamination due to sample preparation may be minimized by the use of disposable glassware. A reagent blank should be analyzed with each set of 20 or less samples to demonstrate that the system is free from contamination. If samples are expected to have high concentrations, it is also advised that solvent blanks be analyzed between GC runs to minimize contamination due to carryover.

6.3 High purity grade or pesticide solvents must be used to minimize contamination problems.

6.4 This method depends on correctly integrating a mass of unresolved peaks using a forced baseline. The resulting baseline, if drawn incorrectly, will have a significant effect on the concentration reported. It is imperative that chromatograms be checked (using a realistic scale relative to the chromatogram) for correct baseline extension. Blanks and/or a low level standard should be run to monitor for baseline drift.

6.5 Non-petroleum organic compounds which are soluble in methylene chloride and that have boiling points in the range of interest can be measured under the conditions of this method; however, if present, the characteristic petroleum hydrocarbon pattern will be altered. When present, these non-petroleum organic compounds will be quantified as part of the TPH; therefore, the analyst should flag the data as presumptively containing significant amounts of non-petroleum compounds.

7) Personnel Qualifications and Responsibilities

7.1 General Responsibilities - This method is restricted to use by or under the supervision of analysts experienced in the method.

7.2 Analyst - It is the responsibility of the analyst(s) to:

- 7.2.1 Each must read and understand this SOP and follow it as written. Any deviations or non-conformances must be documented and submitted to the QA Manager for approval.
- 7.2.2 Produce method compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP (HS-QS-009).
- 7.2.3 Complete the required initial demonstration of proficiency before performing

this procedure without supervision.

7.2.4 Complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.

7.2.5 The analysts must submit data for peer or supervisor review.

7.3 Section Supervisor - It is the responsibility of the section supervisor to:

7.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.

7.3.2 Ensure analysts have completed the required initial demonstration of proficiency before performing this procedure without supervision.

7.3.3 Ensure analysts complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.

7.3.4 Ensure analysts produce method compliant data that meet all quality requirements using this procedure and the Data Reduction, Review and Validation SOP.

7.4 Project Manager - It is the responsibility of the Project Manager to ensure that all method requirements for a client requesting this procedure are understood by the laboratory prior to initiating this procedure for a given set of samples.

7.5 QA Manager: The QA Manager is responsible for

7.5.1 Approving deviations and non-conformances

7.5.2 Ensuring that this procedure is compliant with method and regulatory requirements,

7.5.3 Ensuring that the analytical method and SOP are followed as written through internal method and system audits.

8) Sample Collection, Handling, and Preservation

8.1 Solid Samples: Collect as bulk solid samples in the same manner as those collected for semi-volatile analysis (4 oz glass jar, ship to lab at >0˚C to 6°C). Unused samples collected in this manner can also be used for some semi-volatile analyses, such as SW8270, SW8081 or SW8082. The holding time for solid samples is 14 days from collection to extraction and 40 days from extraction to analysis. Prior to extraction, samples should be stored at >0˚C to 6˚C. Once extracted, the extract should be tightly capped and stored at >0˚C to 6°C until the time analysis.

8.2 Aqueous samples: Collecting aqueous samples in the same manners as samples collected for semi-volatile analysis (un-preserved sample in 1 liter glass bottle, ship to lab at >0 to 6°C. After receipt, continue to store samples at >0˚C to 6°C until ready for extraction. The holding time is 7 days from collection to extraction and 40 days from extraction to analysis. Once extracted, the extracts are to be tightly capped and stored at >0˚C to 6°C until the time of analysis.

8.2.1 Note: Water samples with target compound lists eligible for microextraction by EPA Method 3511 (SOP HS-EXT007) may be collected in 40 mL glass VOA

vials with PTFE lined septum screw tops and stored at >0 to 6°C until extraction. Samples should be extracted as soon after collection as possible, but no longer than 14 days from the date of collection for sulfuric or hydrochloric acid preserved samples. If samples are not acidified, the extraction should be performed within 7 days from date of collection. Samples are prepared by liquid liquid extraction with organic solvent in field sampling containers.

9) Equipment and Supplies

9.1 Gas Chromatograph - Analytical system that includes
- 9.1.1 Split/splitless injector, column supplies, gases, and syringes.
- 9.1.2 Data system capable of storing and reintegrating chromatographic data; determining peak areas using a forced baseline, area summation, baseline projection, and performing baseline compensation
- 9.1.3 GC capable of temperature programming; equipped with variable-constant differential flow controller, agilent 6890 or equivalent.

9.2 Autosampler, Agilent 7683B, or equivalent, capable of making 1 - 5 micro liter injections.

9.3 Primary Column – Restek RTX-5 30m X 0.53mm ID 0.5um film thickness or equivalent

9.4 Flame Ionization Detector.

9.5 Volumetric flasks, class A, various sizes (1.0 through 100-ml).

9.6 100-ml Amber glass bottles with Teflon lined caps

9.7 2mL autosampler vials with crimp caps having Teflon lined septa.

9.8 Syringes: 10uL to 1000 uL gas tight syringe, Hamilton 1000, 1700 or 1800 or equivalent, ±1% accuracy.

9.9 Analytical Balance capable of accurately weighing 0.0001-grams - check daily prior to use and serviced annually.

9.10 Computer hardware: Agilent Technologies 6890N and Agilent 7683B - Auto Sampler

9.11 Computer Software: Chem station and Target

10) Standards and Reagents

10.1 Note: All purchased standards according to manufacturer specifications. Store standard solutions (remaining stock, composite, calibration and surrogate) below 6 °C in glass containers having Teflon™ lined lids or in accord with the manufacturer's recommended conditions. All purchased stock standard solutions must be replaced after reaching the manufacturer's expiration date assigned to the standard. All

laboratory prepared standard solutions must be replaced after six months or sooner if routine QC indicates a problem or if required by reference method. An assigned expiration date of a lab prepared standard cannot exceed the manufacturer's expiration date for any component used in the standard formulation. When analyzing all standards, lot numbers must be associated with the run batch or prep batch. All standard container must be labeled for content and lot numbers. Internal prepared container must also include the GHS safety labeling info. All standards, reagents and supplies must be check for purity and concentration in accordance with corporate SOP CE-GEN-CE007 and HS-QS001 (HS-QS001 is equivalent to GEN-CE007.

10.2 Methylene Chloride (MeCl2), pesticide grade or better – Document standards, reagents and supplies in inventory logbook.

10.3 Diesel Fuel #2 Composite Standard, 50,000 µg/mL in methylene chloride, Restek Cat 31258 or equivalent. Follow manufacturer's storage instructions and expiration date information. Document standards, reagents and supplies in inventory logbook.

10.4 Motor Oil Composite Stock Standard, 50,000 µg/mL in methylene chloride, Restek Cat #31464 or equivalent. Follow manufacturer's storage instructions and expiration date information. Document standards, reagents and supplies in inventory logbook.

10.5 DRO / Motor Oil Intermediate Standard, 4000 µg/mL (ppm): Prepare by addition into 12.5 ml graduated vial the following

- 10.5.1 1 mL, Diesel Fuel #2 Composite Standard, 50,000 µg/mL, available from multiple sources (10.3).
- 10.5.2 1 mL, Motor Oil Composite Standard, 50,000 µg/mL, available from multiple sources (10.4).
- 10.5.3 Bring to final volume with methylene chloride, transfer to storage vials and store at or below -10° C for up to 6 months.
- 10.5.4 Document prep in the standard prep logbook and label standard container with lot number, content, prep date and expiration date. Bottle must also contain the GHS safety label.

10.6 2-Fluorobiphenyl, 4000 µg/mL, Absolute Standards # 12009 or equivalent. Follow manufacturer's storage instructions and expiration date information. Document standards, reagents and supplies in inventory logbook.

10.7 8015 Intermediate Surrogate, 1000 µg/ml (2-Fluorobiphenyl): Prepare by addition into 1.0 ml volumetric flask vial the following

- 10.7.1 250 µL, 2-Fluorobiphenyl Standard, 4,000 µg/mL (10.6).
- 10.7.2 Bring to final volume with methylene chloride, transfer to storage vials and store at or below -10° C for up to 6 months.
- 10.7.3 Document prep in the standard prep logbook and label standard container with lot number, content, prep date and expiration date. Bottle must also contain the GHS safety label.

10.8 DRO/Motor Oil/Surrogate Calibration Standards

10.8.1 Prepare calibration levels as followed:

Table 10.8: DRO/ORO ICAL Standard Concentration

DRO/ORO ICAL Std Conc:	Std 1 50 ppm	Std 2 100 ppm	Std 3 250 ppm	Std 4 500 ppm	Std 5 1000ppm (ICV/CCV)	Std 6 1500 ppm	Std 7 2000 ppm
Surrogate STD Conc.	5	10	25	50	100	150	200
µL DRO / Motor Oil 4000 ppm (10.5)	12.5 µL	25 µL	62.5 µL	125 µL	250 µL	375 µL	500 µL
µL 1000-ppm 8015 Surr (10.7)	5 µL	10 µL	25 µL	50 µL	100 µL	150 µL	200 µL
Final volume, ml	1.0 ml	1.0 ml	1.0 ml	1.0 ml	1.0 ml	1.0 ml	1.0 ml

10.8.2 Transfer standard to autosampler vials.

10.8.3 Document prep in the standard prep logbook and label all standard vials with lot number.

10.9 DRO/Motor Oil/Surr Initial Calibration Verification Standard (DRO/MO/Surr ICV) 1000/100-ppm - Prepare the ICV from second source standards at the "Std 5" level in Table 10.8 by addition into 1.0 ml volumetric flask vial the following

10.9.1 50 µL Diesel Fuel #2 Composite Standard, 20,000 µg/mL.

10.9.2 20 µL Motor Oil Composite Stock Standard, 50,000 µg/mL.

10.9.3 10 µL 2-Fluorobiphenyl, 10000 µg/mL.

10.9.4 Bring to final volume with methylene chloride, transfer to storage vials and store at or below -10° C for up to 6 months.

10.9.5 Document prep in the standard prep logbook and label standard container with lot number, content, prep date and expiration date. Bottle must also contain the GHS safety label.

10.10 Retention Time Marker Stock (contains locators for several ranges, including C_{10}, C_{28} and C_{35}), Restek Cat 31814 or equivalent, 200 ppm for each marker. Follow manufacturer's storage instructions and expiration date information

10.10.1 Working Retention Time Marker, 20 ppm each marker (contains C_{10}, C_{28} and C_{35}).

10.10.1.1 Add 100 uL of stock marker (10.10) to 900 uL methylene chloride. Store below 6˚C.

10.10.1.2 Document prep in the standard prep logbook and label standard container with lot number, content, prep date and expiration date. Bottle must also contain the GHS safety label.

10.11 Continuing Calibration Blank (CCB): Prepare by addition into1.0 mL partially filled volumetric vial the following:

10.11.1 100 µL 2-Fluorobiphenyl Intermediate Standard (10.7).

10.11.2 Bring to final volume with methylene chloride, transfer to storage vials and store at or below -10° C for up to 6 months.

10.11.3 Document prep in the standard prep logbook and label standard container with lot number, content, prep date and expiration date. Bottle must also contain the GHS safety label.

11) Method Calibration

11.1 Typical GC Method Conditions

Table11.1 GC System Conditions

System/	Condition:
Injector Port temp:	275 ° C
Injector volume	2 µL, splitless
Septum purge flow	60 ml/min, 30 seconds after injection
Column head pressure	4 psi
GC He gas flow rate	4.0 mL/min
Init. Oven Temp.	2 min @ 75°C
Temp Program:	75 ° to 320 °C at 25° C/min
Final Temperature	320°C, hold 6.2 min
Maximum Bake Temp	320°C
FID H2 / Air Pressure	H2 @ 40 mL/min / Air @ 400 mL/min
FID Temp:	300°C
Total run time	approx. 18 minutes

11.2 Working 8015 Locator Standard Marker: Prior to running an ICAL or daily CCV, set the Retention Times Window positions for each fuel range using the Hydrocarbon marker. For the DRO range, set using the lower RT limit from 0.1-minute before C_{10} and the upper RT limit from 0.1-minute after C_{28} locator. For ORO, set using lower RT limit from 0.1-minute after C_{28} and the upper RT limit from 0.1-after C_{35}. Shifts in the absolute RT are updated using the Locator at the beginning of each daily 12 hour shift.

11.3 Initial Calibration Curve (External Calibration): 7 levels ranging from 50 ppm to 2000 ppm is performed. Prepare calibration standards from the stock solution (see section 10).

11.3.1 Inject each calibration standard using the same injection volume and technique that will be used to introduce actual samples. Tabulate peak area horizontal responses against the concentration injected using a forced baseline projection for C10 to C28, >C28 to C35 and surrogate. To use the Calibration Factor model, the response factor RSDs must be < 20% to assume linearity. If response factors are >20%, a linear calibration (not through the origin) or a quadratic fit may be used. For the linear fit, the correlation coefficient, r, must be equal to or greater than 0.995. For a quadratic fit, coefficient of determination (r2) must be greater than 0.99. For calculations, see section 15.

11.3.2 Refit of Calibration points.

11.3.2.1 After calibration curve has been process the individual calibration points against the recently create calibration curve. Curve is acceptable it each analyte achieves acceptable limits.

11.3.2.2 Acceptance for the analytes in lowest point is ±50% of the true value and all analyte in other level must achieve ±30% of the true value.

11.4 Initial Calibration Verification (ICV): A second source calibration standard is run after each initial calibration curve. Passing criteria is +/- 20 %. The ICVs for DRO and surrogate are analyzed separately in the same manner as the ICAL and CCV.

11.5 Continuing Calibration Verification (CCV)/ Continuing Calibration Blank (CCB) Pair: Verify the calibration and blank at the beginning of analytical sequence, after every 10 samples thereafter and at the end of the sequence. CCB must be analyzed immediately after the CCV. Passing criteria is +/- 20 %for all analytes and blanks less than the LOQ. Samples must be bracket by successful CCV/CCB pair.

12) Sample Preparation and Analysis

12.1 Sample Extraction: Refer to SOP HS-EXT-008, HS-EXT-009 and HS-EXT022 for both aqueous and soil samples, respectively.

12.1.1 Performance Criteria: GC run conditions and columns – section 11.

12.2 Typical Analysis Sequence:

12.2.1 Instrument blank
12.2.2 8015 Locator Standard – prior to ICAL or @ beginning of new sequence
12.2.3 ICAL Standards – with refit analysis
12.2.4 ICV is applicable after new curve
12.2.5 CCV/CCB at beginning of sequence
12.2.6 Method Blank (MB)
12.2.7 LCS
12.2.8 Sample1
12.2.9 Sample 1 MS
12.2.10 Sample 1 MSD
12.2.11 Sample 2
12.2.12 Sample 3
12.2.13 Sample 4
12.2.14 Sample 5
12.2.15 Sample 6 ...no more than 10 samples, batch including QC (LCS, MS, etc.)
12.2.16 CCV/CCB
12.2.17 Additional samples (no more than 10, including applicable QC samples)
12.2.18 Samples (1-10)
12.2.19 CCV/CCB at the end of run.

12.3 DoD samples must be analyzed using DoD LIMS codes to ensure DoD control limits from DoD QSM are applied.

13) Troubleshooting

13.1 If a very concentrated sample is analyzed, additional instrument blanks may be required to check the system for possible carry over

14) Data Acquisition

14.1 Use Agilent ChemStation™ software for chromatographic Data acquisition.
- 14.1.1 A sequence is built in ChemStation and transferred to Target DB.
- 14.1.2 The data is processed in Target DB.
- 14.1.3 The final results are imported to LIMS for reporting.

14.2 Data Collection using ChemStation™
- 14.2.1 For each new analytical sequence, open a new e-file folder for each column of FID 1, FID2 or FID3 as applicable, having a run date ID.
- 14.2.2 Data Processing using "Target DB."

14.3 Typical Sample Labeling:
- 14.3.1 CCV
- 14.3.2 FLCSW1-090611 (W=water; S= soil, F = FID)
- 14.3.3 FBLKS1-090611 (090611 = year, month, day)
- 14.3.4 0906040-01A (Sample ID)
- 14.3.5 0906040-01A MS (Matrix Spike)
- 14.3.6 0906040-01A MSD (Matrix Spike Duplicate)

15) Calculation, and Data Reduction Requirements

15.1 QC Calculations: LIMS calculates the percent recovery for various QC samples (LCS) according to the following equations:

15.1.1 % Recovery, %R (for MS and MSD Samples)

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SR = Sample Result (unspiked).
SA = Spike Amount Added (mg/L or mg/kg).

15.1.2 % Recovery, %R (for standards and LCS)

$$\%R = \frac{SSR}{SA} \times 100$$

Where:

SSR = Spiked Sample Result (mg/L or mg/kg).
SA = Spike Amount Added (mg/L or mg/kg).

15.1.3 RPD (for precision or duplicate evaluation)

$$RPD = \frac{|SR_1 - SR_2|}{½(SR_1 + SR_2)} \times 100$$

Where:
SR_1 = Sample result for duplicate 1.
SR_2 = Sample result for duplicate 2.

15.2 Sample Concentration Calculation

15.2.1 Calibration Factor (CF) and calibration RSD calculations (Target DB): Calibration Factor for DRO (sum of all the peaks that comprise the standard for the C10 to C28; for ORO- use >C28 to C35 range). Due to the use of a combined DRO/Motor Oil calibration, the minimum response between the two ranges is used for quantitation of the standards and related spiked QC standards (e.g. the LCS).

15.2.1.1 Each fuel range at the respective fuel concentration, calculate using:

$$CF = \frac{\text{Total Area within fuel Retention Time Range}}{\text{Concentration, (ug/ml)}}$$

and

$$\text{mean CF} = \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

Where:
n = number of standards analyzed

15.2.2 Calculate the standard deviation (SD) and the RSD of the calibration factors for each fuel range as:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(CF_i - \overline{CF})^2}{n-1}} \qquad RSD = \frac{SD}{\overline{CF}} \text{ x } 100$$

15.2.3 Calculation of Pearson's Product Moment Correlation Coefficient, r, used to

evaluate the goodness of fit for the linear regression.

$$r = \frac{n\sum XiYi - \sum Xi \sum Yi}{\sqrt{n(\sum Xi^2 - (\sum Xi)^2}\sqrt{n(\sum Yi^2 - (\sum Yi)^2}}$$

Where:
X = individual values for independent variable
Y = individual values for dependent variable
n = number of pairs of data.
df = n-2

15.2.4 Calculation of % drift by using the following formula:

$$\%\,\text{Drift} = \frac{C_{calc} - C_{theor}}{C_{theor}} \times 100$$

Where:
C_{calc} = Calculated concentration
C_{theor} = Theoretical concentration

15.2.5 Calculation of % difference (using the calibration factors):

$$\%\,\text{Diff} = \frac{CF - \overline{CF}}{\overline{CF}} \times 100$$

Where:
CF = the calibration factor from the CCV
$\overline{CF}$ = the mean calibration factor from the initial calibration

15.2.6 Sample Quantitation using External calibration, aqueous samples: The concentration of DRO (C_{10} to C_{28}), ORO (>C_{28} to C_{35}) in a sample can be calculated from the appropriate area using either response factors or regression analysis. Peak areas may be divided into desired carbon ranges/boiling point distribution.

$$C_S = \frac{C_C \times V_t \times D}{W_s} \times 100$$

Where:
C_s = Concentration of DRO or ORO, the defined hydrocarbon range (mg/L or mg/Kg)
C_c = Concentration from calibration curve in µg/mL

(If RF is used for calculations, this value is area response/RF)
V_t = Volume of final extract (ml) (Methylene chloride only)

D = Dilution factor or concentration factor
W_s = Weight (g) or Volume (mL) of sample extracted

15.2.7 Data Reporting Format. The following information and data should be reported:
- 15.2.7.1 The sample ID, client and laboratory
- 15.2.7.2 The sample matrix (soil, sediment, sludge, water, etc.)
- 15.2.7.3 Note any unusual problems with the samples.
- 15.2.7.4 The blank, duplicate and spike recovery and quality control data generated with the sample data.
- 15.2.7.5 The calculated concentration of hydrocarbon range as wet weight for soil, percent moisture / dry weight calculations are managed in the project:
- 15.2.7.6 DRO = C_{10} to C_{28},
- 15.2.7.7 ORO = >C_{28} to C_{35}
- 15.2.7.8 Flagged samples having presumptive compounds or samples containing significant levels of heavy petroleum products.

16) Quality Control, Acceptance Criteria and Corrective Action

16.1 Chromatographic Resolution using the Hydrocarbon Locator; RT widow verification, Absolute RT set: RT windows must verify DRO and ORO ranges set from carbon range locator standard RT data each time a new column is installed, and with initial calibration.
- 16.1.1 Purpose: Identifies the Retention Time window for the ranges of organic carbon.
- 16.1.2 Frequency: run with each initial calibration, at beginning of 12 hour shift, each 12 hrs thereafter:
- 16.1.3 Criteria: Set range for DRO and ORO using RT window data. Adjust shifts in RT by running Locator prior to 12 shift CCVs.
- 16.1.4 Corrective Action: N/A

16.2 Initial Demonstration of Capability
- 16.2.1 Purpose: Verify the ability to produce data of acceptable precision and bias for a specific instrument type, matrix, method, and analyst.
- 16.2.2 Frequency: Initially during method development, and any time there is a significant change in instrument type, personnel, methodology, or matrix.
- 16.2.3 Acceptance Criteria: Four consecutive LCS analysis meeting stated LCS criteria.
- 16.2.4 Corrective Action: Identify and correct the source of error. Reanalyze the demonstration.

16.3 Continuing Demonstration of Capability
- 16.3.1 Purpose: Verify the ability to produce data of acceptable precision and bias for a specific instrument type, matrix, method, and analyst.
- 16.3.2 Frequency: A. Annual to re-qualify analyst for analysts. If period greater than

one year has lapse since the last performance of analysis than Initial Demonstration must be performed.

16.3.3 Acceptance Criteria: Four consecutive LCS analysis meeting stated LCS criteria or successful PT study.

16.4 Initial Calibration:

16.4.1 Purpose: Establishes the calibration curve for the quantification of the analytes of interest.

16.4.2 Frequency: A new curve must be generated when the ICV or CCV criteria are not met, or after major instrument maintenance such as column replacement or changes in operating conditions.

16.4.3 Acceptance Criteria:

16.4.3.1 Initial calibration curve must have 5-points minimally for all analytes (7 are used in this procedure); linearity demonstrated when the RSD for all analytes must be ≤20 % or perform the least squares regression and generate r >0.995 for analytes where RSD is >20 %.

16.4.3.2 If non-linear fit (second order) is used, the COD ≥ 0.99 and six calibration points are required.

16.4.3.3 Refit of calibration points against generated curve.

16.4.3.3.1 Acceptance for the analytes in the lowest point is ±50% of the true value. All analytes in other levels must achieve ±30% of the true value or corrective action is needed, such as recalibration.

16.4.4 Curve Failure Corrective Action: Check standards and or perform maintenance as necessary to correct problem, then generate new curve

16.5 Initial Calibration Verification (second source).

16.5.1 Purpose: Verifies the accuracy of the ICAL using a standard prepared from a source independent of the source of the standards for the ICAL and CCV.

16.5.2 Frequency: once after an initial calibration curve

16.5.3 Criteria: The acceptance range for the second source ICV is 80 - 120 percent recovery.

16.5.4 Corrective Action: If outside these ranges, perform corrective action to solve the source of the error, and prepare and analyze a new curve.

16.6 Continuing Calibration Verification (CCV)/CCB pair

16.6.1 Purpose: Verifies that instrument response is reliable and has not changed significantly from the current ICAL.

16.6.2 Frequency: beginning of sequence, after 10 samples and at end of a sequence:

16.6.3 Criteria: The acceptance range for CCV is 80 - 120 percent recovery.

16.6.3 Corrective Action: If outside these ranges, perform corrective action to solve the source of the error, and then re-analyze all samples since the last acceptable CCV/CCB. If the CCV fails high, only the bracketed samples that are non-detect can be reported. IF CCV fails on second attempt then a new multi-point calibration must be generated.

16.7 Method Blank (MB)

16.7.1 Purpose: Assess background interference or contamination in the analytical system that may lead to high bias or false positive data.

16.7.2 Frequency: Analyze the Method Blank (MB) with each batch of 20 or less samples processed through the entire method.

16.7.3 Criteria: All analytes must be less than the quantitation limit or ½ the quantitation limit depending QA plan associated with the samples. In addition, solvent blanks should be run after samples suspected of being highly contaminated to determine if sample carryover has occurred. The method blank results must be less than the method quantitation limit, or no more than 5% of sample concentration, or 5% of regulatory limits, whichever is greater.

16.7.4 Corrective Action: If above the limit, if it is an indication of instrument drift, the baseline must be reset and the samples since the previous acceptable blank must be re-analyzed. If contamination is indicated, all affected batch samples must be reprocessed. Samples that are non-detect will not require reprocessing.

16.8 Laboratory Control Sample: The LCS is prepared from a calibration standard.

16.8.1 Purpose: Evaluates the performance of the entire analytical system, including all preparation and analysis steps. Assesses the ability of the laboratory/analyst to successfully recover the target analytes from a clean matrix. Contains all target analytes and surrogates.

16.8.2 Frequency: One per batch of 20 or less samples extracted. If the spike sample recovery is outside acceptance limits, the results of the LCS are used for determining acceptability of results.

16.8.3 Criteria: Refer to Table 24.2 for the acceptance range. DoD samples must be analyzed using DoD LIMS codes to ensure DoD control limits from DoD QSM are applied.

16.8.4 Corrective Action: The LCS results must be within the acceptance range. If outside this range perform corrective action to solve the source of the error, and re-prepare and re-analyze the sample batch unless the LCS fails high and the samples are non-detect.

16.9 Matrix Spike (If field sample is not available to perform both an MS and MSD, then perform an LCS and LCSD.

16.9.1 Purpose: Assesses the performance of the method on a particular matrix.

16.9.2 Frequency: Matrix spikes will be analyzed on a frequency of one spike for each 20 samples analyzed. If fewer than 20 samples are in a batch, at least one spike will be included. If insufficient sample is available for a MS and MSD, then an LCS duplicate must be analyzed and used for the RPD and percent recovery. When duplicate LCS's are used, the same control limits as duplicate matrix spikes will apply.

16.9.3 Criteria: Refer to Table 24.2 the acceptance range. DoD samples must be analyzed using DoD LIMS codes to ensure DoD control limits from DoD QSM are applied.

16.9.4 Corrective Action: If the spike results are outside the acceptance limits for

recovery, first determine if the cause is a system error; if so, correct the problem and repeat the MS. If not, the LCS must fall within the acceptance criteria in order for the data to be accepted. The sample results must be flagged for matrix interference.

16.10 Duplicate Samples

16.10.1 Purpose: Provides information on the heterogeneity of the sample matrix. Also determines the precision of the analytical process for that matrix.

16.10.2 Frequency: Once per preparation batch if needed.

16.10.3 Frequency: Duplicates (as MS/MSD or LCS/LCSD) are analyzed on a frequency of one duplicate for each batch of 20 or less samples extracted and analyzed. If fewer than 20 samples are in a batch, one duplicate will be analyzed.

16.10.4 Criteria: Acceptance limits for the water matrix and soil matrix are 20 % RPD. DoD samples must be analyzed using DoD LIMS codes to ensure DoD control limits from DoD QSM are applied.

16.10.5 Corrective Action: If the duplicate results are outside the acceptance limits for relative percent deviation, first determine if the cause is a system error; if so, correct the problem and repeat the duplicate. If not, the LCSD RPD must fall within the acceptance criteria in order for the data to be accepted. The sample results must be flagged to indicate the QC failure as matrix interference.

16.11 Surrogate Spikes

16.11.1 Purpose: Assess the ability of the method to successfully recover specific non-target analytes from an actual matrix; monitors recovery on a sample-specific basis.

16.11.2 Frequency: Surrogate Standards must be added prior to extraction to all samples and QC samples.

16.11.3 Criteria: Refer to Table 24.2. DoD samples must be analyzed using DoD LIMS codes to ensure DoD control limits from DoD QSM are applied.

16.11.4 Corrective Action, Surrogate Recovery failure: If surrogate recoveries fall outside acceptance limits, check for errors in calculations, TPH coelution or standard solution degradation. If obvious chromatographic interference with the surrogate is present, reanalysis may not be necessary. If chromatographic interferences are not obvious, re-extract and re-analyze the sample. If the recoveries for the re-extract are within the ranges, report the re-extract analysis. If recoveries are out again, report the first analyses. LIMS will apply the flags. Describe in the laboratory review checklist.

16.12 Method Detection Limits (MDLs) must be determined on each instrument on an annual basis (at minimum) or whenever major modifications are performed on instrumentation (ex: change detector, auto-sampler, etc.).

16.13 Limit of Detection Determination and Verification:

16.13.1 Purpose: Validates the established Detection Limit.

16.13.2 Frequency: Prior to sample analysis and verified quarterly. Verification must is performed on each instrument. The LOD is spiked at 2-3 times the detection

limit for single compound analyses and 1-4 times the detection limit for multi-analyte standards.

16.13.2.1 Note some project Quality Plans require and annual LOD between 1-2 times the MDL values for every compound. This annual study should be performed with the annual MDL study.

16.13.3 Acceptance Criteria: The apparent signal to noise ratio at the LOD must be at least three and the results must meet all method requirements for analyte identification (e.g., ion abundance, second-column confirmation, or pattern recognition.) For data systems that do not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least three standard deviations greater than the mean method blank concentrations.

16.13.4 Corrective Action: Repeat the Detection Limit Determination and LOD Verification at a higher concentration or perform and pass two consecutive LOD verifications at a higher concentration and set the LOD at the higher concentration.

16.14 Limit of Quantitation Establishment and Verification:

16.14.1 Purpose: Validates the lower quantitation limit of the analysis.

16.14.2 Frequency: Prior to sample analysis and verified quarterly.

16.14.3 Acceptance Criteria: Data must empirically demonstrate precision and bias at the LOQ.

16.14.4 Corrective Action: Identify and correct the source of error, reanalyze the LOQ. If failure persists re-evaluate the appropriateness of the LOQ.

Initial Demonstration of Proficiency – The laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operation annually and whenever new staff members are trained or significant changes in instrumentation are made.

16.15 Manual Integration: ALS procedures for Manual Integration, HS-QS-016, must be followed.

17) Data Records Management

17.1 All data is stored electronically and/or hard copy for five (5) years or ten (10) years for data to be submitted to the state of Louisiana. Operational software is maintained for the same duration.

17.1.1 Hard copy documentation is maintained via logbooks for standard and chemical tracking, extraction procedures, instrument maintenance and runlogs.

17.2 All analytical sequence IDs and standard preparation information must be recorded in

the Run logbook. Hardcopy computer printouts of analytical sequences and raw data must be retained and initialed by the analyst (electronic initials are acceptable). To simplify standard and reagent tracking, analyst must attempt to use single lots of reagents and standards.

17.3 Complete all pertinent sections in the respective logbooks. If not-applicable then line out the section and "Z" out or "X" out all large sections of the worksheet that are not used. Make all corrections with single line through, date and initial. Make NO obliterations when manually recording data.

17.4 As data is collected, the electronic files are stored on the network server. All electronic data which has been stored on the designated drive of the network server is backed up daily by the IT Manager on a tape drive.

17.5 Logbooks are controlled. Never remove a page from a logbook. Completed logbooks are returned to the QA department when filled and no longer needed in the work area.

17.6 SOP effective date is the date noted in the header. This SOP is reviewed annually and the review documented. A new effective date is given if revision is performed.

18) Contingencies for Handling Out of Control or Unacceptable Data

18.1 When method required QC exceedances occur, in every case where sample data quality are affected, the source of the QC exceedance must be determined, corrected and sample reanalysis carried out when possible.

18.2 When data is generated that is associated with a high failing CCV, it can only be reported provided the result is "not detected". The situation must be narrated in the report. Data associated with a low failing CCV cannot be reported.

18.3 When affected sample analysis can not be repeated due to limitations (i.e. sample availability, or if reanalysis can only be performed after expiration of a sample hold time), the reporting of data associated with exceeded QC data must be appropriately flagged and narrated. This documentation is necessary to define for the data user the effect of the error has upon the data quality of the results reported (e.g. E flag data indicate the result to be only an estimate).

18.4 All analysts must report sufficient comments in laboratory data review checklist for exceeded QC associated with sample results so that project management can further narrate and ensure data qualifiers (flags) are properly assigned to the reported data.

18.5 NCARs must be issued for QC system exceedances. Matrix interferences are reported using the analyte reporting comment section in LIMS or using the Laboratory Data review checklist.

19) Method Performance

19.1 Method performance is determined by passing surrogates, internal standards PTs also by the performance of MDLs and other quality control standards.

19.2 The method detection limit (MDL) is established using the procedure described in the SOP *Performing and Documenting Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (CE-QA011). Method Reporting Limits are established for this method based on the low calibration point and the MDL study results.

20) Pollution Prevention and Waste Management

20.1 It is the laboratory's practice to minimize the amount of solvents, acids, and reagents used to perform this method wherever feasibly possible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvents and/or reagents used in this method can be minimized when recycled or disposed of properly.

20.2 The laboratory will comply with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Chemical Hygiene Plan and Lab Waste Management Plan.

20.3 Laboratory procedures in SOP SHWD-001, Waste Disposal Procedures, must be followed.

21) Training

21.1 Training outline

21.1.1 Review literature (see references section). Read and understand this SOP. Also review the applicable SDS for all reagents and standards used. Following the reviews, observe the procedure as performed by an experienced analyst at least three times.

21.1.2 The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

21.1.3 Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

21.2 Training is documented following *SOP CE-QA003*).

21.3 When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

22) Summary of Changes

Table 20.1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
7.3	08/03/2020	G. Moulton	Sec 1.3:Included location of current LOD/LOQ
7.3	08/03/2020	G. Moulton	Sec 4.3: Updated waste policy ID
7.3	08/03/2020	G. Moulton	9.10 and 9.11Added computer hardware and software.
7.3	08/03/2020	G. Moulton	Sec 19: Added method performance
7.3	08/03/2020	G. Moulton	Sec 20: Added Pollution prevention and waste management.
7.3	08/03/2020	G. Moulton	Sec 21: Added a training section.
7.3	08/03/2020	G. Moulton	Updated table numbers in sec 24 and body of sop.
7.2	08/16/2019	G. Moulton	Sec 16.4.3.3.1 was corrected to match QC requirement in sections 11.3.2.2 and table 22.3
7.2	08/16/2019	G. Moulton	Sec 16.6.3: Removed unnecessary verbiage.
7.2	08/16/2019	G. Moulton	Modified sec 11.3.1
7.2	08/16/2019	G. Moulton	Sec 11.1Corrected septum purge flow
7.2	08/16/2019	G. Moulton	Modified sec 10.10.1.1 volumes for making marker.
7.2	08/16/2019	G. Moulton	Sec 9.1.3:Added equipment
7.2	08/16/2019	G. Moulton	Corrected to C10 in sec. 3.31, 15.2.1, 15.2.6, 15.2.7.6,
7.2	08/16/2019	G. Moulton	Removed sections. 3.27, 3.29, 11.2.1
7.2	08/16/2019	G. Moulton	Modified sections 3.12, 3.26, 3.32, 8.2, 11.2 grammatical error.
7.2 Section 8.2.1	08/16/2019	E. Howard	Added information for samples eligible for microextraction by SW3511.
7.2 Table 10.8	08/16/2019	E. Howard	Added concentration unit (ppm) to column headers.
7.1	11/09/2018	G. Moulton	Updated the cover page and new company format. Updated new QA Manager.
7.1	11/09/2018	G. Moulton	Modified sec 17.1
7.1	11/09/2018	G. Moulton	Modify 21.3 and 21.4.
07.0	08/31/2017	T. Yen	Signature Page – New Organic Manager, QA Manager and Lab Manager.

07.0 – Sections 10.5, 10.6, 10.7, 10.8, 10.1.	08/31/2017	T. Yen	Calibration standards prepared using mixture containing DRO. ORO and surrogate. CCB added to standard.
07.0 – Sections 11.3.2 and 16.4.3.3	08/31/2017	T. Yen	Refit check of calibration levels acceptance limits.
07.0 – Sections 12.3, 16.8.3, 16.9.3, 16.11.3 & Tables 22.2 and 22.3	08/31/2017	T. Yen	Use of DoD codes in LIMS to apply DoD QSM R5 control limits.
07.0 – Section 21	08/31/2017	T. Yen	Reference update.
07.0 – Tables 22.2 & 22.3	08/31/2017	T. Yen	Tables update.
06.2	01/21/2013	T. Yen	Signature Page – New QA Manager and Lab Manager.
06.2	01/21/2013	T. Yen	Document Footer – "A Campbell Brothers Limited Company" changed to "An ALS Limited Company" to reflect parent compar name change.
06.2 – Section 9.3	01/21/2013	T. Yen	Primary column – RTX-5.
06.2 – Section 11.1	01/21/2013	T. Yen	Changes to typical GC conditions for new column, Table 11.1.
06.2 – Section 17.2	01/21/2013	T. Yen	Attempt to use single lots of standards anc reagent per sequence to simplify traceability.
06.2 – Section 22.2	01/21/2013	T. Yen	Table 22.2 Surrogate limits updated to 60-135 %.
06.1	12/15/2011	J. Cady	Minor document revision.
06.0	01/18/2010	R. Pierrot	Major document revision.

23) References and Related Documents

23.1 Current TNI Standards.

23.2 Current Department of Defense Quality Systems Manual.

23.3 Method 8015C, "Nonhalogenated Organics using GCFID", Method Revision 3, February 2007, Test Methods for the Evaluation of Solid Waste (SW-846), USEPA OSWER.

23.4 Method 8000D, "Determinative Chromatographic Separations", Method Revision 3, July 2014, Test Methods for the Evaluation of Solid Waste (SW-846), USEPA OSWER.

24) Appendix

Table 24.1 SW 8015C DRO / ORO

Analyte – water matrix	MDL mg/L	LOQ mg/L	Analyte - solid/soil matrix	MDL mg/Kg	LOQ mg/Kg
DRO	0.02	0.05	DRO	0.5	1.7
ORO	0.02	0.10	ORO	0.5	3.4
2-Fluorobiphenyl	-	0.01	2-Fluorobiphenyl	-	0.17

Table 24.2 SW8015C DRO/ORO – Sample Surr/LCS/MS Recovery Limits at time of SOP creation and are subject to change, see LIMS for current limits. Note DoD LIMS codes and specs must be for DoD projects/samples to ensure DoD QSM limits are used, for compounds not listed in DoD QSM (current version), internal lab limits will apply.

Analyte – Water Matrix	SPK mg/L	Low	High	Analyte – Soil Matrix	SPK mg/Kg	Low	High
DRO	1.00	70	130	DRO	33.3	70	130
ORO	1.00	70	130	ORO	33.3	70	130
2-Fluorobiphenyl	0.10	60	135	2-Fluorobiphenyl	3.33	70	130
DRO - DoD	1.00	36	132	DRO - DoD	33.3	38	132
ORO - DoD	1.00	41	113	ORO - DoD	33.3	39	106
2-Fluorobiphenyl - DoD	0.10	60	135	2-Fluorobiphenyl - DoD	3.33	60	135

Table 24.3 Calibration and QC Procedures for Low Level DRO by Method 8015C

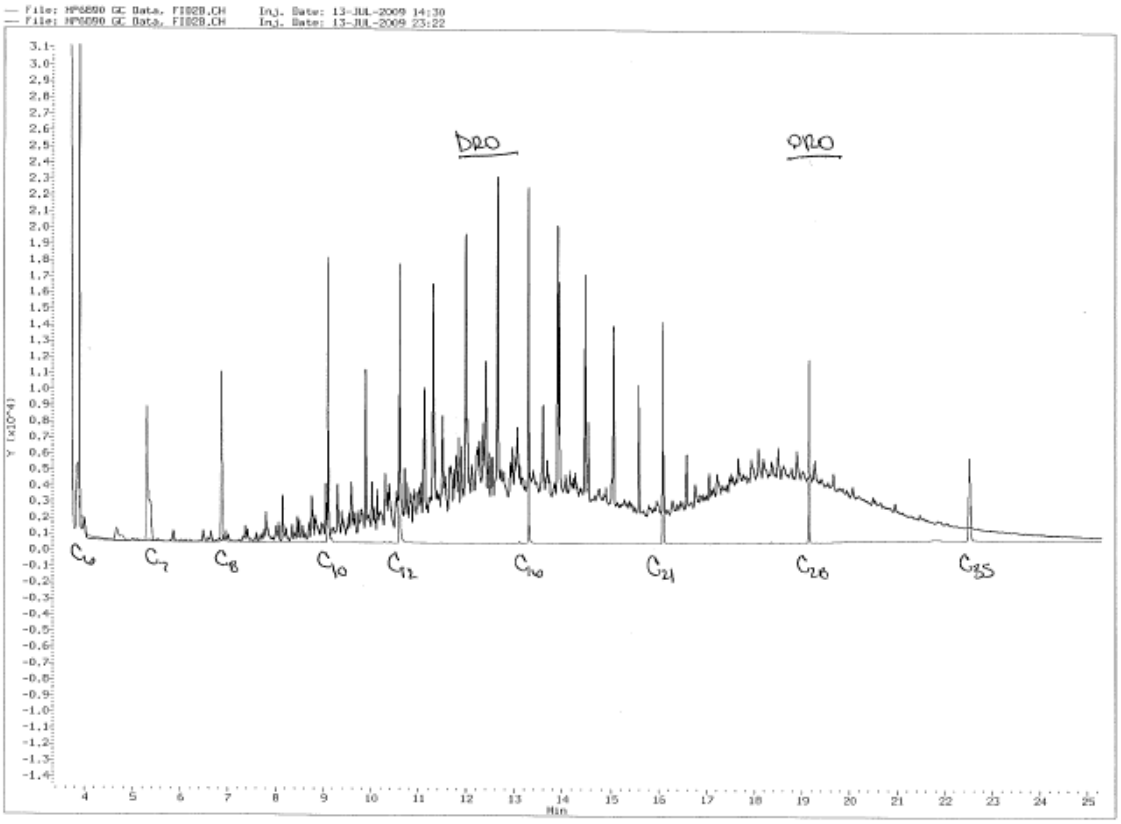
QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Hydrocarbon Locator Standard.	Prior to ICAL, and before each 12 hour shift.	Verify RT Windows, and set Absolute RT. Set range for DRO / ORO	N/A
Minimum of five-points for initial calibration for all analytes.	Initial calibration prior to sample analysis.	Calibration Factor – mean RSD for all analytes ≤20%; or Linear – r > 0.995; or Quadratic – r^2 > 0.99 (6 points shall be used for second order). Refit calibration against the newly created curve – all compounds for the lowest point must be within ±50% of true value and all other level within ±30% of true value for curve to be valid.	Correct problem then repeat initial calibration.
Second-source calibration verification (ICV).	After multi-point initial calibration.	All analytes within ±20% of expected value.	Correct problem then repeat initial calibration.
Continuing Calibration verification (CCV)/ Continuing Calibration Blank (CCB).	Beginning of analytical sequence, after 10 samples and at the end of the analysis sequence.	All analytes within ± 20% of expected value and blank with no analytes greater than the ½ LOQ,	Correct problem, then repeat initial calibration verification and reanalyze all samples since last successful calibration verification.
Method blank.	One per preparation batch (20 or less samples).	No analytes detected ≥ ½ MQL.	Correct problem, then re-extract and analyze method blank and all samples processed with the contaminated blank.
LCS	One LCS per preparation batch.	QC acceptance criteria, Table 24.2. DoD samples must be processed using DoD LIMS codes and specs to ensure DoD control limits are applied.	The LCS results must be within the acceptance range. If outside this range perform corrective action to solve the source of the error, and re-prepare and re-analyze the sample batch unless the LCS fails high and the samples are non-detect.
MS/MSD	One MS/MSD per	QC acceptance criteria,	Describe in Laboratory

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
	every preparation batch.	Table 24.2. MSD RPD ≤20%. DoD samples must be processed using DoD LIMS codes and specs to ensure DoD control limits are applied.	Review Checklist.
Duplicate (or MSD or LCSD)	One Duplicate (or MSD or LCSD) per every preparation batch.	QC acceptance criteria, RPD ≤20%. DoD samples must be processed using DoD LIMS codes and specs to ensure DoD control limits are applied.	Describe in Laboratory Review Checklist.
Surrogate	Every sample, spiked sample, standard, and method blank.	QC acceptance criteria, Table 24.2. DoD samples must be processed using DoD LIMS codes and specs to ensure DoD control limits are applied.	For all QC and field samples, correct problem, re-prepare and reanalyze samples with failing surrogates in the associated prep batch, provided sufficient sample is available. If obvious chromatographic interference with the surrogate is present, reanalysis may not be necessary. Refer to Method 8000C, Section 9.6 Requirements and describe in the Laboratory Review
Analyst demonstrate ability to generate acceptable accuracy and precision using four replicate LCS.	Once per analyst initially and annually, thereafter.	QC acceptance criteria, Table 24.2. DoD samples must be processed using DoD LIMS codes and specs to ensure DoD control limits are applied.	Recalculate results; locate and fix problem with system and then rerun demonstration and meet criteria.
MDL study.	Once per 12 month period.	Detection limits established shall be < the MQLs in Table 24.1. 40 CFR Part 136 MDL	Repeat MDL at new level to achieve 40 CFR Part 136 criteria.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
		criteria must be achieve.	
LOD Study (DCS Study)	Once per quarter	Verify detection Some QAP will require variation between 1-2X the MDL for each compound.	When a spiked analyte is not detected, increase the spiking value and analyze. Continue to increase as needed.
LOQ Study	Once per quarter	50% - 150%	When the LOQ Check sample does not pass the criteria, perform instrument maintenance and re-analyze the LOQ. If the LOQ still does not meet this criteria, please consult with the Technical Director regarding appropriate actions needed to obtain the desired precision and bias at the LOQ..

Typical Chromatograph



ANALYSIS OF DISSOLVED GASSES RSK-175

DOCUMENT ID: HS-GCFID010, REV 6.4

Approved By: Hoai. Van
Technical and Laboratory Director, Hoai Van

Date: 9/16/2020

Prepared By: Erica H Marinez
Quality Assurance Manager, Erica Marinez

Date: 09/16/2020

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1) Identification of the Method

1.1 This standard operating procedure has been prepared to provide guidance for performing dissolved gasses by method RSKSOP-175.

2) Applicable Matrix or Matrices

2.1 This method will be used for the preparation and analysis of Ground Water and Ecosystems Restoration Division of the U.S. Environmental Protection Agency and may not be specifically applicable to the activities of other organizations.

3) Limit of Detection and Quantitation

3.1 Method Detection Limits, Limits of Detection, and Limits of quantitation for this method can be found in ALS LIMS.

Scope and Application

3.2 This method is applicable to the preparation of water samples for analysis of the headspace to quantify parts per billion levels of dissolved gases in a water sample. The dissolved gasses of interest are listed in Table 4.1.

4) Summary of Procedure

4.1 A water sample is collected in the field in multiple 40-ml bottles with zero headspace and preserved to pH <2. Just prior to analysis, the sample is allowed to reach room temperature. Using a syringe filled with 10-ml of high purity helium, 10-ml of sample portion is displaced using the helium to create headspace. The sample, now having a known volume of headspace, is shaken for 5-minutes, to allow the dissolved gases to equilibrate into the headspace. After equilibration, a portion of the headspace gases are withdrawn and injected into a gas chromatograph equipped with a flame ionization detector. Using similarly prepared calibration standards, the concentration of the dissolved gas in the original water sample can be determined.

Table 4.1 Gases by RSK-175, Headspace GCFID for Aqueous Samples

Table 4.1 - Gases by RSK-175, Headspace GCFID for Aqueous Samples				
Compound	CAS No.	Formula	Molecular Wt.	LOQ-µg/L
Methane (C_1)	74-82-8	CH_4	16	0.5
Ethane (C_2)	74-84-0	C_2H_6	30	1.0
Ethene (Ethylene) (C_2)	74-85-1	C_2H_4	28	1.0
Acetylene (C_2)	74-86-2	C_2H_2	26	0.625
Propane (C_3)	74-98-6	C_3H_8	44	1.0
n-Butane (C_4)	106-97-8	C_4H_{10}	58	1.0
Isobutylene (C_4)	115-11-7	C_4H_8	56	1.3
Pentane (C_5)	109-66-0	C_5H_{12}	72	1.0
Hexane (C_6)	110-54-3	C_6H_{18}	86	1.0
Propene	115-07-1	C_3H_6	42	0.506

5) Definitions

5.1 Demonstration of Capability (DOC): procedure to establish the ability of the laboratory to generate acceptable accuracy and precision which is included in many of the EPA's analytical test methods. In general, an initial DOC procedure involves the analysis of four separate Laboratory Control Samples (LCS) as prescribed by the analytical method Each LCS must meet the specified LCS acceptance limits for percent recovery, and standard deviation. Ongoing DOC requirements are met by acceptable analysis of annual NELAC accepted proficiency test (PT) samples, or by the analysis of four LCS if PT samples are not available

5.2 Exception Report: Appropriate comments reported with the associated sample batch that addresses sample anomalies such as demonstrated sample matrix effects.

5.3 Laboratory Control Sample (LCS): A sample matrix, free from the analytes of interest, spiked with known amounts of analytes or a material containing known and verified amounts of analytes.

5.4 Limit of Detection (LOD): an estimate of the minimum amount of a substance that an analytical process can reliably detect. The LOD is determined annually through the execution of a Method Detection Limit Study, and verified quarterly through the analysis of a Detectability Check Sample (DCS).

5.5 Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met.

5.6 Matrix Spike (MS): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available.

5.7 Matrix Spike Duplicate (MSD): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of recovery for each analyte.

5.8 Matrix: The substrate (e.g., water, soil, etc.) which may contain the analyte of interest.

5.9 Method Blank (MBLK): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analysis.

5.10 Method Detection Limit (MDL) study: a procedure described in 40CFR Part 136, Appendix B, that describes how to produce an MDL, a reporting element of certain EPA methods. The MDL study is one approach to determine the LOD.

5.11 NCAR: Nonconformance Corrective Action Report (refer to SOP HSQS003, current revision).

5.12 Reagent Water: Deionized (DI) reagent purified by filtration thru mix resin and carbon beds. For additional purification, the DI water is passed through an activated carbon filter.

5.13 Preparation Batch: A defined set of one to 20 client samples of the same matrix, meeting the batch definition criteria, and prepared for analysis within 24 hours. The preparation batch must also contain the required determinative method defined batch QC samples (e.g. method blank, laboratory control samples, matrix spikes, duplicates, etc.).

5.14 Surrogate: An analyte added to a sample, which is unlikely to be found in any sample at significant concentration, and which is added directly to a sample aliquot in known amounts before any sample processing procedures are conducted. It is measured with the same procedures used to measure other sample components. The purpose of the surrogate analyte is to monitor method performance with each sample.

5.15 Surrogate Spike: A substance with properties that mimic the analyte of interest. It is

unlikely to be found in environmental samples and is added to them for quality control purposes.

5.16 Batch: Samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** is composed of one (1) to twenty (20) environmental sample of the same quality systems matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be twenty-four (24) hours. An **analytical batch** is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and cannot exceed twenty (20) samples.

5.17 Retention Time Window: The length of time between sample injection and the appearance of a peak at the detector. The window of time is established for each analyte or group of analytes and is set for complete elution of analyte peaks. It is based upon a series of analyses and statistical calculations that establish the measured band on the chromatogram that can be associated with a specific analyte or group of analytes.

5.18 Second Source Calibration Verification (ICV): A standard obtained or prepared from a source independent of the source of standards for the ICAL. Its concentration should be at or near the middle of the calibration range. It is performed after the ICAL.

5.19 Calibration Standard (CAL): A solution prepared from the primary dilution standard solution or stock standard solutions and the surrogate analyte. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

5.20 Linear Calibration Range (LCR): The concentration range over which the instrument response is linear

5.21 Instrument Performance Check Sample (IPC): A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the

performance of the instrument system with respect to a defined set of criteria.

5.22 Continuing Calibration Verification (CCV): A known interference free matrix spiked with a known concentration of the target analyte. The CCV is prepared from the same source that was used to prepare the calibration standards, and is used to verify that the instrument calibration is in control before and after sample analysis.

5.23 Quality Control Sample (QCS): A solution of method analytes of known concentrations that is used as the spiking solution for the LCS. The QCS is obtained from a source external to the laboratory and different from the source of calibrations standards. It is used to check laboratory performances with externally prepared test materials.

5.24 Detectability Check Sample (DCS): a sample spiked at 2 to 3 times the calculated LOD (refer to SOP HS-QS006, LOD and LOQ), or alternatively spiked near the LOQ.

5.25 Safety Data Sheets (SDS): Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

5.26 Globally Harmonized System of Classification and Labeling of Chemicals (GHS) – common and coherent approach to classifying chemicals and communicating hazard information on labels and safety data sheets.

5.27 Safety Data Sheets (SDS): Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

5.28 DoD – Department of Defense.

5.29 DoD QSM – DoD Quality Systems Manual Revision.

6) Safety

6.1 Lab Safety: Due to various hazards in the laboratory, safety glasses and laboratory coats or aprons must be worn at all times while in the laboratory. In addition, gloves and a face shield should be worn when dealing with toxic, caustic, and/or flammable chemicals.

6.2 Chemical Hygiene: The toxicity or carcinogenicity of each reagent used has not been precisely defined; however, each chemical used should be treated as a potential health hazard. Exposure to laboratory reagents should be reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets (MSDS) is available to all personnel involved in these analyses.

6.3 Waste Management: The principal wastes generated by this procedure are the method-required chemicals and standards. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required. Laboratory procedures in SOP SHWD001, Waste Disposal Procedures, must be followed.

6.4 Pollution Prevention: The materials used in this method pose little threat to the

environment when recycled and managed properly. The quantities of chemicals purchased should be based on the expected usage during its shelf life. Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards or reagents to be disposed.

6.5 Job Safety Assessment

HAZARD ASSESSMENT		
Job Task #1:	**Hazards**	**Preventative Measures**
Cooler and sample handling.	Injury due to lifting heavy coolers and placing/removing samples to/from storage locations.	Use proper lift technique and cart to move coolers and stools/stepladder when working reaching above shoulder height in sample storage cooler.
Job Task #2:	**Hazards**	**Preventative Measures**
Sample container handling and preservation checks.	Exposure to possible hazardous chemicals.	Use of proper PPE, i.e. Lab coats, safety glasses, gloves, etc.
Job Task #3:	**Hazards**	**Preventative Measures**
Use of utility knives to cut open cooler and seals.	Cuts.	Use proper safety with auto retracting blade and proper cutting techniques. Always cut away from body.
Job Task #4:	**Hazards**	**Preventative Measures**
Unpacking coolers and searching for sample within the coolers.	Possible cuts from broken sample containers.	Wear proper protective equipment such as Kevlar kit gloves and use of broken glass containers.
Job Task #5:	**Hazards**	**Preventative Measures**
Glassware Washing.	Possible cuts from broken glassware.	Wear proper protective equipment such as Kevlar kit gloves.
Job Task #6:	**Hazards**	**Preventative Measures**
Sample Testing and/or standard and reagent/solvent use.	Exposure to possible hazardous chemicals & puncture wound with syringe.	Wear gloves, safety glasses and lab coat. Work in fume hood and avoid skin contact with solvents/acids/reagents. Know location of safety shower, first aid kits, spill kits and fire extinguisher when handling flammable material.
Job Task #7:	**Hazards**	**Preventative Measures**
Heated surface such as injector and detector.	Burn potential.	Allow surfaces time to cool down before handling. Wear gloves, safety glasses and lab coat.
Job Task #8:	**Hazards**	**Preventative Measures**
Compressed Gas Cylinders	Injury from falling cylinders and suffocation hazard.	All cylinders must be secure to prevent falls and use cylinder dolly to transport. Use in well ventilated room.

7) Maintenance

7.1 Routine preventative maintenance must be performed and documented to assure optimum instrument performance.

7.2 Refer to the current revision of SOP HS-EQ004 for preventative maintenance schedules.

8) Interferences

8.1 Sample contamination due to sample preparation may be minimized by the use of disposable glassware. A method blank must be analyzed with each set of 20 or less samples to demonstrate that the system is free from contamination. If samples are expected to have high concentrations, it is also advised that solvent blanks be analyzed between GC runs to minimize contamination due to carryover or column/instrumental memory effects.

9) Responsibilities

9.1 General Responsibilities - This method is restricted to use by or under the supervision of analysts experienced in the method.

9.2 Analyst - It is the responsibility of the analyst(s) to:

- 9.2.1 Each must read and understand this SOP and follow it as written. Any deviations or non-conformances must be documented and submitted to the QA Manager for approval.
- 9.2.2 Produce method compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP (HS-QS-009).
- 9.2.3 Complete the required initial demonstration of proficiency before performing this procedure without supervision.
- 9.2.4 Complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 9.2.5 The analysts must submit data for peer or supervisor review.

9.3 Section Supervisor - It is the responsibility of the section supervisor to:

- 9.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.
- 9.3.2 Ensure analysts have completed the required initial demonstration of proficiency before performing this procedure without supervision.
- 9.3.3 Ensure analysts complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 9.3.4 Ensure analysts produce method compliant data that meet all quality requirements using this procedure and the Data Reduction, Review and Validation SOP.

9.4 Project Manager - It is the responsibility of the Project Manager to ensure that all method requirements for a client requesting this procedure are understood by the laboratory prior to initiating this procedure for a given set of samples.

9.5 QA Manager: The QA Manager is responsible for

- 9.5.1 Approving deviations and non-conformances
- 9.5.2 Ensuring that this procedure is compliant with method and regulatory

requirements,

9.5.3 Ensuring that the analytical method and SOP are followed as written through internal method and system audits.

10) Sample Collection, Handling, and Preservation

10.1 Aqueous samples are collected having no headspace in three 40ml VOC vials and preserved to a pH of less than 2, using 1:1 Hydrochloric acid. Samples are shipped to the laboratory >0 to 6°C. The holding time for Hydrochloric acid-preserved samples with a pH <2 is 14 days from collection to analysis. Samples received with a pH>2 have a holding time of 7 days from collection to analysis. Prior to analysis, the samples are held above freezing to 6°C.

11) Equipment and Supplies

11.1 Hamilton Gastight Syringes, or equivalent. Various sizes.

11.2 Volumetric flasks, Class A. Various sizes.

11.3 Amber glass vials with Teflon-lined screw tops (or crimp tops), 2-mLs.

11.4 Analytical Balance, capable of measuring to the nearest 0.0001g (0.1mg).

11.5 Gas Chromatograph – HP5980 GC, the system includes:

11.5.1 split/splitless injector, column supplies, gases, and auto-sampler syringes.

11.5.2 data system capable of storing and reintegrating chromatographic data;

11.5.3 temperature programmable; and variable-constant differential flow controller.

11.6 Primary Column – RT_UPLOT (Cat #19726), 30m x 0.53mm ID x 20µm film thickness

11.7 Flame Ionization Detector.

11.8 20-ml Headspace Vials, (w/ crimp caps having Teflon lined septa).

11.9 40-ml VOA Vials

11.10 Gas Tight Syringes, various sizes: 10-µl, 100-µl, 250-µl, 1.0-ml, 5-ml and 10-ml.

11.11 Ultra High Purity Nitrogen, Helium, Hydrogen and Air gas cylinders

11.12 Computer Hardware: Hewlett Packard 5890 Series II

11.13 Computer Software: Target and Chemstation

12) Standards and Reagents

12.1 Note: All purchased standards according to manufacturer specifications. Store standard solutions (remaining stock, composite, calibration and surrogate) below 6 °C in glass containers having Teflon™ lined lids or in accord with the manufacturer's recommended conditions. All purchased stock standard solutions must be replaced after reaching the manufacturer's expiration date assigned to the standard. All laboratory prepared standard solutions must be replaced after six months or sooner if routine QC indicates a problem or if required by reference method. An assigned expiration date of a lab prepared standard cannot exceed the manufacturer's

expiration date for any component used in the standard formulation. When analyzing all standards, lot numbers must be associated with the run batch or prep batch. All standard container must be labeled for content and lot numbers. Internal prepared container must also include the GHS safety labeling info. All standards, reagents and supplies must be check for purity and concentration in accordance with corporate SOP CE-GEN007 and HS-QS001 (HS-QS001 is equivalent to GEN-CE007).

12.1.1 Store standard solutions at room temperature in glass containers having Teflon™ lined lids.

12.2 Gases Standard, methane, ethane and ethane, 1000ppmV each (mole basis), Scott Specialty Gases.

12.3 Organic Free Water: Deionized (DI) reagent water meeting purity characteristics of Type I laboratory distilled water (daily resistance ≥17 megohms-cm). Additional purification includes passage through activated carbon and a nitrogen purge.

12.4 Initial Calibration Curve Standards: The following table lists the concentration of the calibration curve prepared by injecting different amounts of the reference standard (§10.1) into a 20-ml vial that contains 5-ml of headspace and 17-ml of organic free water (vial can hold approximately 22 mls). Each calibration standard is shaken for 5-minutes prior to the injection of 100-µL of the standard headspace into the GC.

Table 12.4

Table 12.4	Std 1	Std 2	Std 3	Std 4	Std 5 CCV	Std 6	Std 7
Injection volume (µL) Conc., 1000ppmV	10-µL	25-µL	50-µL	100-µL	250-µL	500-µL	1000-µL
Methane (C_1)	0.385	0.962	1.92	3.85	9.62	19.2	38.5
Ethane (C_2)	0.722	1.80	3.61	7.22	18.0	36.1	72.2
Ethene (Ethylene) (C_2)	0.674	1.68	3.37	6.74	16.8	33.7	67.4
Acetylene (C_2)	0.625	1.56	3.13	6.25	15.6	31.3	62.5
Propane (C_3)	1.06	2.65	5.29	10.6	26.5	52.9	105.9
n-Butane (C_4)	1.40	3.49	6.98	14.0	34.9	69.8	139.5
Isobutylene (C_4)	1.35	3.375	6.74	13.5	33.7	67.4	135
Pentane (C_5)	1.73	4.33	8.66	17.3	43.3	86.6	173.2
Hexane (C_6)	2.07	5.17	10.3	20.7	51.7	103.4	206.9
Injection volume (µL) Conc., 100ppmV	0.05-mL	0.10-mL	0.20-mL	0.40-mL	0.60-mL	0.80-mL	1.00-mL

Propene (C_3)	0.51	1.01	2.02	4.05	6.07	8.10	10.12

12.5 A second source calibration standard (ICV) is prepared and analyzed to validate the initial curve. The ICV is same level as the CCV. The ICV concentration is prepared near the middle of the initial calibration curve. ICV is analyzed immediately after an initial calibration to verify the curve. All analytes must be within ±20% of the true value.

13) Method Calibration

13.1 GC Method Conditions

Table 13.1 GC System Conditions

Table 13.1 - GC System Conditions		
System	C1 – C2	C3 – C6
Injector Port temp:	200°°C	200°°C
Injector volume	100 µL, splitless	100 µL, splitless
Septum purge flow	1.2 ml/min	1.2 ml/min
Column head pressure	10 psi	10 psi
GC He gas flow rate	2.2 mL/min	2.2 mL/min
Init. Oven Temp.	2.5 min @ 40oC	2.3 min @ 40oC
Temp Program:	20°/min to 190°C & hold for 2-min	25°/min to 120°C - hold for 4-min, 20°/min to 190°C - hold for 3-min
Maximum Bake Temp	200°C	190°C
FID Temp:	200°C	200°C

13.2 Initial Calibration Curve: A six level calibration is performed. Calibration standards are prepared according to Table 12.4.

13.2.1 Inject each calibration standard using the specified volume and calculate the response factor. To verify that the instrument response is linear using calibration (response) factors, the curve RSDs must be < 20%.

13.2.2 If a regression model (linear or quadratic), the correlation coefficient must be ≥ 0.995 for a linear fit and the coefficient of determination must be ≥0.99 for a quadratic fit.

13.3 Initial Calibration Verification (ICV): A second source calibration standard is run after each initial calibration curve. Passing criteria is ± 20 % within the true value for all analytes.

13.4 Continuing Calibration (CCV) is verified at the beginning of each daily sequence, after 10 injections and at the end to the sequence with a CCV standard. Passing criteria is ± 20% within the true value for all analytes.

14) Sample Preparation/Analysis

14.1 Remove samples from refrigerated storage and allow them to reach room temperature.

14.2 Sample Headspace Preparation

14.2.1 To generate headspace in the 40mL serum vial, the vial is turned upside down and a 10mL portion of sample is removed by the following helium displacement technique. The pH of the displaced volume is checked using pH paper and recorded in the logbook and Run Log.

14.2.1.1 If the pH is >2 and the sample is outside the 7-day holding time, corrective action is to notify the Project Manager that the sample is outside holding time and the analyst will create a narrative.

14.2.2 Insert through the vial septum a 22-guage needle attached to a 10mL glass syringe set a zero ml.

14.2.3 10mL of helium is pulled into a second 10-ml glass syringe having a shutoff valve and a 22-guage needle.

14.2.4 The helium filled syringe is injected through the septum up to the bottom of the vial.

14.2.5 The injected 10mL of helium displaces 10mL of water into the first glass syringe.

14.2.6 After completion of the 10mL helium injection/10mL sample displacement, both syringes and needles are carefully removed from the vial. Each vial is shaken for 5-minutes prior to the injection of 100-µL of the sample headspace into the GC.

14.2.7 A 100µL aliquot of headspace may be withdrawn and injected into the GC manually.

14.2.8 DoD samples must be analyzed using DoD LIMS codes to ensure DoD control limits from DoD QSM current revision are applied.

14.3 Analysis Sequence: The following is the used:

14.3.1 ICV (applicable after each new calibration curve)
14.3.2 CCV (at the beginning of each daily 24 hour shift and after every 10 injections)
14.3.3 Method Blank (MB)
14.3.4 LCS
14.3.5 LCS duplicate if applicable
14.3.6 Sample1
14.3.7 Sample 1 MS
14.3.8 Sample 1 MSD
14.3.9 Sample 2
14.3.10 Sample 3
14.3.11 Sample 4
14.3.12 Sample 5
14.3.13 CCV
14.3.14 Sample 20
14.3.15 CCV
14.3.16 Sample 30 samples including applicable QC samples
14.3.17 CCV
14.3.18 The sequence is closed with a CCV

15) Troubleshooting

15.1 Prepare new standards, check instrument maintenance, prepare a new curve as needed, etc.

15.2 If a very concentrated sample is analyzed, additional instrument blanks may be required to check the system for possible carry over.

16) Data Acquisition

16.1 Use Agilent ChemStation software for chromatographic data acquisition.

- 16.1.1 Build a sequence in ChemStation and auto-transfer the data to "Target".
- 16.1.2 The data is processed in "Target".
- 16.1.3 The processed "Target" data is imported into e-LIMS for data reporting.

16.2 Process Data using Sample Labeling:

- 16.2.1 GLCSW1-080621 LCS
- 16.2.2 GLCSWD1-080621 Duplicate LCS
- 14.2.3 GBLKS1-080611 (080621 = year, month, day)
- 14.2.4 0806040-01A (Sample ID)
- 14.2.5 0806040-01ADup (Sample Duplicate)
- 14.2.6 0806040-01AMS (Sample MS)

16.3 Importing Data from "Target" into the LIMS system for reporting.

- 16.3.1 Choose "Data Entry" in LIMS menu
- 16.3.2 Choose "Add", an LIMS menu icon
- 16.3.3 Choose "Instrument ID (e.g. FID4), "run start date", and "analyst".
- 16.3.4 Click on "data import" menu icon.
- 16.3.5 Input "Test Code"/"Sample Type" (
- 16.3.6 Click on the "destination file" icon and then click on the "e-LIMS file". These steps input data into e-LIMS from Target

17) Calculation, and Data Reduction Requirement

17.1 Concentration Calculation for ICAL:

Concentration (ug/L) = Stock Conc. (ppmV) x (M.W./22.4) x 273/298 x (V_{inj}(mL)/17)

17.2 Calibration Factor (CF) and calibration RSD calculations (Target DB):

17.2.1 each calibration standard at each concentration, calculate using:

$$CF = \frac{\text{Peak Area (or Height) of the Compound in the Calibration Standard}}{\text{Conc. of the Compound Injected (in } \mu\text{g/L)}}$$

$$\text{mean CF} = \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

And where n is the number of Calibration standards analyzed.

17.2.2 Calculate the standard deviation (SD) and the RSD of the calibration factors for each analyte as:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(CF_i - \overline{CF})^2}{n-1}} \qquad RSD = \frac{SD}{\overline{CF}} \times 100$$

17.3 Calculation of Linear Regression Correlation Coefficient, r

$$r = \frac{\sum XY - \frac{\sum X \sum Y}{n}}{\sqrt{\left(\sum X^2 - \frac{(\sum X)^2}{n}\right)\left(\sum Y^2 - \frac{(\sum Y)^2}{n}\right)}}$$

Where:
X = individual values for independent variable
Y = individual values for dependent variable n
= number of pairs of data.
df = n-2

17.4 Calculation of % drift by using the following formula:

17.4.1 % Drift = [(Calculated conc - Theoretical conc) x 100] / Theoretical conc.

17.5 Calculation of % difference (using the calibration factors):
17.5.1 % Difference = [(CF – mean CF) x 100] / mean CF
where; CF = the calibration factor from the CCV and
mean CF = the mean calibration factor from the initial calibration

17.6 Sample Quantitation using External calibration for aqueous samples: The concentration of the analyte in a sample can be calculated from the appropriate area using either response factors or regression analysis.

$$\text{Sample Conc.}\,(ug/L) = \frac{\text{Peak Area (or Ht) of Compound in the sample}}{\text{mean}CF} xDf$$

where: Df = Dilution factor of prepared sample

17.7 Data Reporting Format. The following information and data is reported:
17.7.1 The sample ID, client sample ID
17.7.2 The sample matrix (water), date of analysis, analyst ID
17.7.3 Notation of any unusual problems with the samples on the exception report.

17.7.4 The blank, duplicate and spike recovery and quality control data generated

with the sample data.

17.8 The LOQ for the each gas in µg/L. For LOQ see table 2.1.

17.9 QC Calculations: LIMS calculates the percent recovery for various QC samples (LCS) according to the following equations:

17.9.1 % Recovery, %R (for MS and MSD Samples)

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SR = Sample Result (unspiked).
SA = Spike Amount Added (mg/L or mg/kg).

17.9.2 % Recovery, %R (for standards and LCS)

$$\%R = \frac{(SSR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SA = Spike Amount Added (mg/L or mg/kg).

17.9.3 RPD (for precision or duplicate evaluation)

$$RPD = \frac{|SR_1 - SR_2|}{+SR_2)} \times 100$$

Where:

S
S
S
S
S
½
(
S
R
1

SR_1 = Sample result for duplicate 1.
SR_2 = Sample result for duplicate 2.

18) Quality Control, Acceptance Criteria and Corrective Action

18.1 Initial Demonstration of Capability

18.1.1 Purpose: Verify the ability to produce data of acceptable precision and bias for a specific instrument type, matrix, method, and analyst.

18.1.2 Frequency: Initially during method development, and any time there is a significant change in instrument type, personnel, methodology, or matrix or a period greater than one year has lapsed since last performance of analysis.

18.1.3 Acceptance Criteria: Four consecutive LCS analysis meeting stated LCS criteria.

18.1.4 Corrective Action: Identify and correct the source of error. Reanalyze the demonstration.

18.2 Continuing Demonstration of Capability

18.2.1 Purpose: Verify the ability to produce data of acceptable precision and bias for a specific instrument type, matrix, method, and analyst.

18.2.2 Frequency: A. Annual to re-qualify analyst for analysts. If period greater than one year has lapse since the last performance of analysis than Initial Demonstration must be performed.

18.2.3 Acceptance Criteria: Four consecutive LCS analysis meeting stated LCS criteria or successful PT study.

18.3 Initial Calibration:

18.3.1 Purpose: Establishes the calibration curve for the quantification of the analytes of interest.

18.3.2 Frequency: A new curve must be generated when the ICV or CCV criteria are not met, or after major instrument maintenance such as column replacement or changes in operating conditions.

18.3.3 Acceptance Criteria:

18.3.3.1 Initial calibration curve must have 5-points minimally for all analytes (7 are used in this procedure); linearity demonstrated when the RSD for all analytes must be ≤20 % or perform the least squares regression and generate r >0.995 for analytes where RSD is >20 %.

18.3.3.2 If non-linear fit (second order) is used, the COD ≥ 0.99 and six calibration points are required.

18.3.3.3 Refit of calibration points against generated curve.

18.3.3.4 All analytes in the lowest point must agree within ±50% of the true value and analytes in all other levels must be within ±30% of the true

18.3.4 Curve Failure Corrective Action: Check standards and or perform maintenance as necessary to correct problem, then generate new curve.

18.4 Initial Calibration Verification (second source).

18.4.1 Purpose: Verifies the accuracy of the ICAL using a standard prepared from a source independent of the source of the standards for the ICAL and CCV.

18.4.2 Frequency: once after an initial calibration curve

18.4.3 Criteria: The acceptance range for the second source ICV is 80 - 120 percent recovery.

18.4.4 Corrective Action: If outside these ranges, perform corrective action to solve the source of the error, and prepare and analyze a new curve.

18.5 Continuing Calibration Verification (CCV)

18.5.1 Purpose: Verifies that instrument response is reliable and has not changed significantly from the current ICAL.

18.5.2 Frequency: beginning of sequence, after 10 samples and at end of a sequence:

18.5.3 Criteria: The acceptance range for CCV is 80 - 120 percent recovery.

18.5.4 Corrective Action: If outside these ranges, perform corrective action to solve the source of the error, and then re-analyze all samples since the last acceptable CCV. If the CCV fails high, only the bracketed samples that are non-detect can be reported. IF CCV fails on second attempt then a new multi-point calibration must be generated.

18.6 Initial and Continuing Calibration Blanks (ICB/CCB):

18.6.1 Frequency: The ICB is run after the ICV in the evaluation of each new initial calibration. The CCB must be run at the beginning of analysis, after every 20 samples injections (including QC samples) and at the end of the analytical sequence.

18.6.2 Acceptance Criteria:

18.6.2.1 All analytes must be less than the MQL.

18.6.2.2 ICB/CCB Corrective Action: If the ICB or CCB do not meet the detection level criteria, < ½ MQL, identify the problem (i.e. system contamination, sample carryover, or instrument drifting). Re-analyze the CCB and any samples since the last passing CCB that have detections >MQL, once the problem has been addressed.

18.7 Method Blank:

18.7.1 Frequency: Analyze the method blank at a frequency of one per preparation batch of 20 or less samples.

18.7.2 Acceptance Criteria: All analytes of interest must be ≤ ½ MQL.

18.7.3 Method Blank Contamination Corrective Action: Reanalyze the Method Blank to confirm failure. If the blank is still unacceptable, identify the source of the contamination. All samples in the associated preparation batch must be re-prepared and re-analyzed (including all appropriate QC samples).If samples cannot be re-run because of insufficient sample or other similar circumstances, an NCAR must be initiated and issued to project management and to the QAD. The NCAR must be detailed enough for preparation of the project narrative and all appropriate data flags are entered into LIMS for the final report preparation. Data reported with an associated contaminated method blank must be flagged with a “B”, indicating the occurrence.

18.7.4 Criteria: All analytes must be less than the quantitation limit or ½ the quantitation limit depending QA plan associated with the samples. In addition, solvent blanks should be run after samples suspected of being highly contaminated to determine if sample carryover has occurred. The method blank results must be less than the method quantitation limit, or no more than 5% of sample concentration, or 5% of regulatory limits, whichever is greater.

18.7.5 Corrective Action: If above the limit, if it is an indication of instrument drift, the baseline must be reset and the samples since the previous acceptable blank must be re-analyzed. If contamination is indicated, all affected batch samples must be reprocessed. Samples that are non-detect will not require reprocessing.

18.8 Laboratory Control Sample:

18.8.1 Purpose: Evaluates the performance of the entire analytical system, including all preparation and analysis steps. Assesses the ability of the laboratory/analyst to successfully recover the target analytes from a clean matrix. Contains all target analytes and surrogates.

18.8.2 Frequency: One per batch of 20 or less samples extracted. If the spike sample recovery is outside acceptance limits, the results of the LCS are used for determining acceptability of results.

18.8.3 Criteria: Refer to table 26.1 for the acceptance range. DoD samples must be analyzed using DoD LIMS codes to ensure DoD control limits from DoD QSM are applied.

18.8.4 Corrective Action: The LCS results must be within the acceptance range. If outside this range perform corrective action to solve the source of the error, and re-prepare and re-analyze the sample batch unless the LCS fails high and the samples are non-detect.

18.9 Matrix Spike

18.9.1 Frequency: the MS frequency must be at least one MS/MSD pair per 20 samples per matrix. If fewer than 20 samples are in a batch, at least one spike will be included. If insufficient sample is available for a MS and MSD, then an LCS duplicate must be analyzed and used for the RPD and percent recovery. When duplicate LCS's are used, the same control limits as duplicate matrix spikes will apply.

18.9.2 Acceptance Criteria: Refer to Table 26.1 the acceptance range. DoD samples must be analyzed using DoD LIMS codes to ensure DoD control limits from DoD QSM are applied.

18.9.3 MS % Recovery Criteria Failure Corrective Action: If the MS has recoveries which are outside the target range, the poor recoveries in the MS may be due to matrix effects. The LCS, surrogate recoveries must all be evaluated in order to determine if matrix interference is present or if method performance is poor. Note that the MS are used to evaluate the matrix effect, not to control the analytical process. If the Matrix Spike is found to be out of control for the same analyte, a matrix effect is likely confirmed (assuming the LCS passes).

18.10 Sample Duplicate

18.10.1 Frequency: The duplicate frequency must be at least one duplicate per 20 samples per matrix.

18.10.2 Acceptance Criteria: The duplicate recovery criterion is ≤ 20% RPD. DoD samples must be analyzed using DoD LIMS codes to ensure DoD control limits from DoD QSM are applied.

18.10.3 Corrective Action: f the duplicate results are outside the acceptance limits for relative percent deviation, first determine if the cause is a system error; if so, correct the problem and repeat the duplicate. If not, the LCSD RPD must fall within the acceptance criteria in order for the data to be accepted. The sample results must be flagged to indicate the QC failure as matrix interference.

18.11 Method Detection Limits (MDLs) must be determined on each instrument on an annual basis (at minimum) or whenever major modifications are performed on instrumentation (ex: change detector, auto-sampler, etc.).

18.12 Limit of Detection Determination and Verification:

18.12.1 Purpose: Validates the established Detection Limit.

18.12.2 Frequency: Prior to sample analysis and verified quarterly. Verification must is performed on each instrument. The LOD is spiked at 2-3 times the detection limit for single compound analyses and 1-4 times the detection limit for multi-analyte standards.

18.12.3 Acceptance Criteria: The apparent signal to noise ratio at the LOD must be at least three and the results must meet all method requirements for analyte identification (e.g., ion abundance, second-column confirmation, or pattern recognition.) For data systems that do not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least three standard deviations greater than the mean method blank concentrations.

18.12.4 Corrective Action: Repeat the Detection Limit Determination and LOD Verification at a higher concentration or perform and pass two consecutive LOD verifications at a higher concentration and set the LOD at the higher concentration.

18.13 Limit of Quantitation Establishment and Verification:

18.13.1 Purpose: Validates the lower quantitation limit of the analysis.

18.13.2 Frequency: Prior to sample analysis and verified quarterly.

18.13.3 Acceptance Criteria: Data must empirically demonstrate precision and bias at the LOQ.

18.13.4 Corrective Action: Identify and correct the source of error, reanalyze the LOQ. If failure persists re-evaluate the appropriateness of the LOQ.
Initial Demonstration of Proficiency – The laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operation annually and whenever new staff members are trained or significant changes in instrumentation are made.

18.14 Manual Integration: ALS procedures for Manual Integration, HS-QS-016, must be followed.

19) Data Records Management

19.1 All data is stored electronically and/or hard copy for5 years or 10 years for the state of Louisiana.

19.2 All analytical sequence IDs and standard preparation information must be recorded in the Run logbook. Hardcopy computer printouts of analytical sequences and raw data must be retained and initialed by the analyst (electronic initials are acceptable). To simplify standard tracking, analyst must attempt to use one lot of reagents and standards with each batch.

19.3 Complete all pertinent sections in the respective logbooks. If not-applicable then line out the section. “Z” out or “X” out all large sections of the worksheet that are not used.

Make all corrections with single line through, date and initial. Make NO obliterations when manually recording data.

19.4 Logbooks are controlled. Never remove a page from a logbook. Completed logbooks are returned to the QA department when filled and no longer needed in the work area.

19.5 The effective date this SOP is the date in the header or last signature date, whichever is most recent.

20) Contingencies for Handling Out of Control Data

20.1 When method required QC exceedances occur, in every case where sample data quality are affected, the source of the QC exceedance must be determined, corrected and sample reanalysis carried out when possible.

20.2 When affected sample analysis cannot be repeated due to limitations (i.e. sample availability, or if reanalysis can only be performed after expiration of a sample hold time), the reporting of data associated with exceeded QC data must be appropriately flagged and narrated. This documentation is necessary to define for the data user the effect of the error has upon the data quality of the results reported (e.g. E flag data indicate the result to be only an estimate).

20.3 All analysts must report sufficient comments in laboratory data review checklist for exceeded QC associated with sample results so that project management can further narrate and ensure data qualifiers (flags) are properly assigned to the reported data.

20.4 NCARs must be issued for QC system exceedances. Matrix interferences are reported using the analyte reporting comment section in e-LIMS or using the Laboratory Data review checklist.

21) Method Performance

21.1 Method performance is determined by passing surrogates, internal standards PTs also by the performance of MDLs and other quality control standards.

21.2 The method detection limit (MDL) is established using the procedure described in the SOP *Performing and Documenting Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (CE-QA011). Method Reporting Limits are established for this method based on the low calibration point and the MDL study results.

21.3 Refer to Appendices in this SOP.

22) Pollution Prevention

22.1 It is the laboratory's practice to minimize the amount of solvents, acids, and reagents used to perform this method wherever feasibly possible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvents and/or reagents used in this method can be minimized when recycled or disposed of properly.

22.2 The laboratory will comply with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Chemical Hygiene Plan and Lab Waste Management Plan.

22.3 Laboratory procedures in SOP SHWD001, Waste Disposal Procedures, must be followed.

23) Training

23.1 Training outline

23.1.1 Review literature (see references section). Read and understand this SOP. Also review the applicable SDS for all reagents and standards used. Following the reviews, observe the procedure as performed by an experienced analyst at least three times.

23.1.2 The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

23.1.3 Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

23.2 Training is documented following *SOP CE-QA003*).

23.3 When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

24) Summary of Changes

Table 24.1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
6.4	09/16/2020	G. Moulton	Sec 1: added Identification of the method. Modified sec 1.1 to include actual method number
6.4	09/16/2020	G. Moulton	Sec 2: added Applicable matrix
6.4	09/16/2020	G. Moulton	Sec 11.12 and 11.13: Added computer hardware and software.
6.4	09/16/2020	G. Moulton	Updated sec 6 to say just safety
6.4	09/16/2020	G. Moulton	Sec 7: Updated to say Maintenance
6.4	09/16/2020	G. Moulton	Sec 21: Modified method performance.
6.4	09/16/2020	G. Moulton	Sec 22: Added Pollution prevention and waste management.

6.4	09/16/2020	G. Moulton	Sec 23: Added Training.
6.4	09/16/2020	G. Moulton	Change appendix to say Tables, Diagrams, Flowcharts and Validation Data. Updated table numbers.
6.3 Sec 8.1	07/26/2019	E. Howard	Added holding time for samples with pH >2.
6.3 Sec 12.1.1	07/26/2019	E. Howard	Added procedure to check pH of displaced sample and corrective action for samples greater than pH 2 and outside 7 day holding time. Section 12.4 rendered unnecessary and deleted.
6.3 Sec 19.1	07/26/2019	E. Howard	Reference missing. Referred to the reader to Appendices.
6.2 Sec. 2.1	02/06/2019	G. Moulton	Removed nitrogen and replaced with helium in sec 2.1. Corrected vial size to 40 ml Vial.
Sec 12.2, 12.4 to 12.4.18	02/06/2019	G. Moulton	Sample CCV frequency every 10 injections.
6.1	11/09/2018	G. Moulton	Updated the cover page and new company
6.1	11/09/2018	G. Moulton	Modified sec 17.1
6.1	11/09/2018	G. Moulton	Modify 21.2 and 21.3.
6.0	11/30/2016	T. Yen	New Lab Director and Organic Manager.
6.0 – Section 4.5	11/30/2016	T. Yen	Job safety assessment added.
6.0 – Sections 11.2.2 & 16.3.3.1.	11/30/2016	T. Yen	Initial calibration %RSD set to ≤20%.
6.0 – Sections 11.3 & 16.4.3.3.	11/30/2016	T. Yen	ICV acceptance limits set to ±20 of true concentration for each analyte.
6.0 – Sections 11.4 & 16.5.3.	11/30/2016	T. Yen	CCV acceptance limits set to ±20 of true concentration for each analyte. CCV frequency set to before analysis, after every ten sample and the end of an analytical
6.0 – Section 12.3.7	11/30/2016	T. Yen	For DoD sample, must use DOC LIMS codes and specs.
6.0 – Section 12.5	11/30/2016	T. Yen	After analysis of samples pH must be checked and documented.
6.0 – Sections 16.8.3, 16.9.2 & 16.10.2,	11/30/2016	T. Yen	Use DoD LIMS codes and specs for field samples, QC Samples and blanks.
6.0 – Tables 22.1 and 22.2.	11/30/2016	T. Yen	Use DoD LIMS codes and specs for field samples, QC Samples and blanks. QC and Calibration Summary update.
5.0	06/30/2013	T. Yen	Revert to use of Method RSK 175
4.0	09/01/2012	J. Cady	Revised to use Method PA-DEP 3686, Rev.0, April 2012.

3.0	08/05/2011	I. Williams	Major format revision.

25) References and Related Documents

25.1 Kampbell, D.H, Vandegrift, S.A., "Analysis of Dissolved Methane, Ethane and Ethylene in Ground Water by a Standard Gas Chromatographic Technique", Journal of Chromatographic Science, Volume 36, pp 253-256, May 1998. for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, EPA-600/4-79-020, Revision 5.4, 1994.

25.2 Current DoD Quality Systems Manual.

25.3 Current TNI Standards.

26) Tables, Diagrams, Flowcharts and Validation Data

Table 26.1 Dissolved Gases by Headspace Analysis by RSK-175 at time of SOP creation and are subject to change, see LIMS for current limits. Note DoD LIMS codes and specs must be for DoD projects/samples to ensure DoD QSM limits are used, for compounds not listed in DoD QSM(current version) internal lab limits will apply.

Table 26.1 - Dissolved Gases by Headspace Analysis of waters, RSK-175.					
Analyte – waters	SPK, µg/L	LCS (%Low)	LCS (% High)	MS (% Low)	MS (% High)
Methane (C_1)	9.62	75	125	70	130
Ethane (C_2)	18.0	75	125	70	130
Ethene (Ethylene) (C_2)	16.8	75	125	70	130
Acetylene (C_2)	15.6	75	125	70	130
Propane (C_3)	52.9	75	125	70	130
n-Butane (C_4)	139.5	75	125	70	130
Isobutylene (C_4)	33.7	75	125	70	130
Pentane (C_5)	173.2	75	125	70	130
Hexane (C_6)	103.4	75	125	70	130
Propene (C_3)	4.049	75	125	70	130

Table 26.2 Summary of Calibration and QC Procedures for RSK – 175

Table 26.2 - Summary of Calibration and QC Procedures for RSK – 175			
QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action

Minimum of five-points for initial calibration for all analytes.	Initial calibration (ICAL) prior to sample analysis.	Linear – mean RSD for all analytes <20%; or Linear – least squares regression, R > 0.995; or Non-linear – COD > 0.99 (6 points shall be used for second order). Linear calibration requires minimum of 5 point and quadratic requires 6 points.	Correct problem then repeat initial calibration.
Second-source (ICV) calibration verification.	Once per each initial calibration curve.	All analytes within ±20% of expected value.	Correct problem then repeat initial calibration.
Calibration verification.	Daily, before sample analysis, after every 10 samples and at the end of the analysis sequence.	All analytes within ±20% of expected value.	Correct problem, then repeat ICAL verification and reanalyze all samples since last successful calibration verification.
Method blank.	One per preparation batch.	Any analytes detected must be < 1/2 LOQ.	Correct problem, then re-prepare and analyze method blank and all affected samples processed with the contaminated blank.
LCS/LCSD	LCS for all analytes, one LCS per preparation batch.	Recovery: ±25% of expected value; LCSD RPD <30%. DoD samples must be processed using DoD LIMS codes and specs to ensure DoD control limits are applied.	Correct problem then re-analyze the LCS and all samples in the affected batch.

Table 26.2 - Summary of Calibration and QC Procedures for RSK – 175

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action

MS/MSD	One MS/MSD per every 20 project samples.	Recovery: ±30% of expected value; MSD RPD <30%. DoD samples must be processed using DoD LIMS codes and specs to ensure DoD control limits are applied.	Describe in Laboratory Review Checklist.
Duplicate (for sample, or as MSD, or as LCSD).	One duplicate per every 20-project samples.	Duplicate RPD <30%. DoD samples must be processed using DoD LIMS codes and specs to ensure DoD control limits are applied.	Describe in Laboratory Review Checklist.
Analyst demonstrates ability to generate acceptable accuracy and precision using four replicate LCS.	Once per analyst initially and annually thereafter.	QC acceptance criteria for LCS (±25%, RPD <30%).	Recalculate results; locate and fix problem with system and then rerun demonstration and meet criteria.

Anions by Ion Chromatography

EPA 300.0/SW846-9056A/SW846-9056

DOCUMENT ID: HS-IC001, REV 9.3

Approved By: Hoai. Van
Technical and Laboratory Director, Hoai Van

Date: 03/05/2020

Prepared By: Erica H Marinez
Quality Assurance Manager, Erica Marinez

Date: 03/05/2020

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1) Identification of the Method and Applicable Matrices

1.1 This Standard Operating Procedure is used to determine the following common anions in water samples (wastewater, surface water, ground water, and non-potable water).

Bromide	Nitrite as N
Chloride	Nitrate/Nitrite as N
Fluoride	Ortho-Phosphate as P
Nitrate as N	Sulfate
Chlorate	

1.2 This analysis is applicable to aqueous samples, and soil sample leachates.

2) Scope Application and Summary of the Method

2.1 The sample is pumped through two different ion exchange columns, then a suppressor device, and into a conductivity detector. The two ion exchange columns, a pre-column or guard column and a separator column, are packed with low-capacity, strongly basic anion exchange resin. Ions are separated into discreet bands based on their affinity for the exchange sites of the resin. The suppressor is an ion exchange-based device that reduces the background conductivity of the eluent to a low or negligible level and also converts the anions in the sample to their more conductive acid forms. The separated anions in their acid forms are measured using an electrical-conductivity cell. Anions are identified based on their retention times compared to known standards. Quantitation is accomplished by measuring the peak height or area and comparing it to a calibration curve generated from known standards.

2.2 Soluble anions from soil samples are determined by the analysis of a 1:10 by weight DI water leachate of the sample and recorded in the prep batchs.

3) Definitions

3.1 Batch: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** is composed of one (1) to twenty (20) environmental sample of the same quality systems matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be twenty-four (24) hours. An **analytical batch** is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.

3.2 Continuing Calibration Blank (CCB): Reagent water, or appropriate solvent, containing no analytes of interest.

3.3 Calibration Standard (CAL): A solution prepared from the primary dilution standard solution or stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration

3.4 Continuing Calibration Verification (CCV): The verification of the ICAL that is required during the course of analysis at periodic intervals. The CCV applies to both external standard and internal standard calibration techniques, as well as to linear and non-

linear calibration models.

3.5 Demonstration of Capability (DOC): procedure to establish the ability of the laboratory to generate acceptable accuracy and precision which is included in many of the EPA's analytical test methods. In general, an initial DOC procedure involves the analysis of four separate Laboratory Control Samples (LCS) as prescribed by the analytical method Each LCS must meet the specified LCS acceptance limits for percent recovery, and standard deviation. Ongoing DOC requirements are met by acceptable analysis of annual NELAC accepted proficiency test (PT) samples, or by the analysis of four LCS if PT samples are not available

3.6 Detectability Check Sample (DCS): a sample spiked at 2 to 3 times the calculated LOD (refer to SOP HS-QS006, LOD and LOQ), or alternatively spiked near the LOQ.

3.7 Exception Report: Appropriate comments reported with the associated sample batch that addresses sample anomalies such as demonstrated sample matrix effects.

3.8 Laboratory Control Sample (LCS): A sample matrix, free from the analytes of interest, spiked with known amounts of analytes or a material containing known and verified amounts of analytes.

3.9 Limit of Detection (LOD): an estimate of the minimum amount of a substance that an analytical process can reliably detect. The LOD is determined annually through the execution of a Method Detection Limit Study, and verified quarterly through the analysis of a Detectability Check Sample (DCS).

3.10 Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met.

3.11 Linear Calibration Range (LCR): The concentration range over which the instrument response is linear, Study must be performed every six-months.

3.12 Matrix Spike (MS): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available.

3.13 Matrix Spike Duplicate (MSD): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of recovery for each analyte.

3.14 Matrix: The substrate (e.g., water, soil, etc.) which may contain the analyte of interest.

3.15 Method Blank (MBLK): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at

concentrations that impact the analytical results for sample analysis.

3.16 Method Detection Limit (MDL) study: a procedure described in 40CFR Part 136, Appendix B, that describes how to produce an MDL, a reporting element of certain EPA methods. The MDL study is one approach to determine the LOD.

3.17 NCAR: Nonconformance Corrective Action Report (refer to SOP HSQS003, current revision).

3.18 Quality Control Sample (QCS): A solution of method analytes of known concentrations that is used as the spiking solution for the LCS. The QCS is obtained from a source external to the laboratory and different from the source of calibrations standards. It is used to check laboratory performances with externally prepared test materials.

3.19 Reagent Water: Deionized (DI) reagent purified by filtration thru mix resin and carbon beds. For additional purification, the DI water is passed through an activated carbon filter with characteristics of Type I laboratory distilled water (daily resistance ≥17 megohms-cm).

3.20 Preparation Batch: A defined set of one to 20 client samples of the same matrix, meeting the batch definition criteria, and prepared for analysis within 24 hours. The preparation batch must also contain the required determinative method defined batch QC samples (e.g. method blank, laboratory control samples, matrix spikes, duplicates, etc.).

3.21 Retention Time Window: The length of time between sample injection and the appearance of a peak at the detector. The window of time is established for each analyte or group of analytes and is set for complete elution of analyte peaks. It is based upon a series of analyses and statistical calculations that establish the measured band on the chromatogram that can be associated with a specific analyte or group of analytes.

3.22 Second Source Calibration Verification (ICV): A standard obtained or prepared from a source independent of the source of standards for the ICAL. Its concentration should be at or near the middle of the calibration range. It is performed after the ICAL but prior to analyzing samples.

4) Safety

4.1 Lab Safety: Due to various hazards in the laboratory, safety glasses and laboratory coats or aprons must be worn at all times while in the laboratory. In addition, gloves and a face shield should be worn when dealing with toxic, caustic, and/or flammable chemicals.

4.2 Chemical Hygiene: The toxicity or carcinogenicity of each reagent used has not been precisely defined; however, each chemical used should be treated as a potential health hazard. Exposure to laboratory reagents should be reduced to the lowest possible

level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets (MSDS) is available to all personnel involved in these analyses.

4.3 Waste Management: The principal wastes generated by this procedure are the method-required chemicals and standards. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required. Laboratory procedures in SOP HS-SAF-001, Waste Disposal Procedures, must be followed.

4.4 Pollution Prevention: The materials used in this method pose little threat to the environment when recycled and managed properly. The quantities of chemicals purchased should be based on the expected usage during its shelf life. Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards or reagents to be disposed.

4.5 Job Safety Assessment

HAZARD ASSESSMENT		
Job Task #1:	**Hazards**	**Preventative Measures**
Sample handling.	Injury due lifting and placing samples on storage locations and broken sample containers.	Use proper lift technique and cart to move coolers and stools/stepladder when working reaching above shoulder height in sample storage cooler. When transporting samples always use sample carrier or properly inspected cart. Wear proper PPE when handling sample container and have spill kits available.
Job Task #2:	**Hazards**	**Preventative Measures**
Sample Testing and/or standard and reagent/solvent use.	Exposure to possible hazardous chemicals.	Wear gloves, safety glasses and lab coat. Work in fume hood and avoid skin contact with solvents/acids/reagents. Know location of safety shower, first aid kits, spill kits and fire extinguisher when handling flammable material.

5) Cautions

5.1 Routine preventative maintenance must be performed and documented to assure optimum instrument performance. Refer to the current revision of SOP HS-EQ004 for preventative maintenance schedules.

6) Interferences

6.1 Frequently compare calibration standard chromatograms to those of the column test chromatogram (received when the column was purchased) to insure proper separation and similar response ratios between the target analytes is observed.

6.2 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in an ion chromatogram. These interferences can lead to false

positive results for target analytes as well as reduced detection limits as a consequence of elevated baseline noise.

6.3 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

6.4 Any anion that is only weakly retained by the column may elute in the retention time window of fluoride and potentially interfere. At concentrations of fluoride above 1.5 mg/L, this interference may not be significant; however, it is the responsibility of the analyst to generate precision and accuracy information in each sample matrix.

6.5 Close attention should be given to the potential for carry over peaks from one analysis that will affect the proper detection of analytes of interest in a second, subsequent analysis. It is the responsibility of the analyst to confirm that no late eluting peaks have carried over into a subsequent analysis thereby compromising the integrity of the analytical results.

6.6 Acetate, formate and other monovalent organic acid anions elute early and interfere with fluoride. Retention times of anions may differ when large amounts of acetate are present. Therefore this method is not recommended for leachates of solid samples where acetate is used for pH adjustment. Because acetate interferes, analysis of TCLP leachates for fluoride should be avoided.

6.7 When this method is used to analyze unfamiliar samples for any of the above anions, anion identification should be supported by the use of a fortified sample matrix covering the anions of interest.

6.8 Bromide and nitrite react with most oxidants employed as disinfectants. The utility of measuring these anions in treated water should be considered prior to conducting the analysis.

7) Personnel Qualifications and Responsibilities

7.1 General Responsibilities - This method is restricted to use by or under the supervision of analysts experienced in the method.

7.2 Analyst - It is the responsibility of the analyst(s) to:

- 7.2.1 Each must read and understand this SOP and follow it as written. Any deviations or non-conformances must be documented and submitted to the QA Manager for approval.
- 7.2.2 Produce method compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP (HS-QS-009).
- 7.2.3 Complete the required initial demonstration of proficiency before performing this procedure without supervision.
- 7.2.4 Complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 7.2.5 The analysts must submit data for peer or supervisor review.

7.3 Section Supervisor - It is the responsibility of the section supervisor to:

- 7.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.

7.3.2 Ensure analysts have completed the required initial demonstration of proficiency before performing this procedure without supervision.
7.3.3 Ensure analysts complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
7.3.4 Ensure analysts produce method compliant data that meet all quality requirements using this procedure and the Data Reduction, Review and Validation SOP.

7.4 Project Manager - It is the responsibility of the Project Manager to ensure that all method requirements for a client requesting this procedure are understood by the laboratory prior to initiating this procedure for a given set of samples.

7.5 QA Manager: The QA Manager is responsible for
7.5.1 Approving deviations and non-conformances
7.5.2 Ensuring that this procedure is compliant with method and regulatory requirements,
7.5.3 Ensuring that the analytical method and SOP are followed as written through internal method and system audits.

8) Sample Collection, Handling, and Preservation

8.1 Water samples are collected in plastic or glass. Volume collected should be sufficient to insure a representative sample, allow for replicate analysis, and minimize waste disposal.

8.2 Sample preservation and holding times for the anions are as follows:

Table 8.2 Common Anions, Analyte Preservation and Holding Time

Compound	Container	Preservative	Holding Time
Bromide	P,G	Cool to >0 to 6 ° C	28 days
Chloride	P,G	Cool to >0 to 6 ° C	28 days
Fluoride	P,G	Cool to >0 to 6 ° C	28 days
Nitrate as N	P,G	Cool to >0 to 6 ° C	48 hours
Nitrite as N	P,G	Cool to >0 to 6 ° C	48 hours
Nitrate + Nitrite as N	P,G	pH<2 w/ H2SO4, Cool to >0 to 6 ° C	28 days
Dissolved Ortho-Phosphate as P	P,G	Cool to >0 to 6 ° C	48 hours
Sulfate	P,G	Cool to >0 to 6 ° C	28 days
Chlorate	P,G	Cool to >0 to 6 ° C	28 days

Note: If the determined value for the combined Nitrate + Nitrite, as N, is >0.5mg/L, the sample must be reanalyzed, unpreserved, within holding time. This may require re-sampling.

9) Equipment and Supplies

9.1 Ion chromatograph:

9.1.1 Dionex ICS-2100

9.1.1.1 Dionex AS Autosampler
9.1.1.2 Dionex EO-Eluent Organizer
9.1.1.3 Dionex EluGen® Cartridges,
9.1.1.4 Eluent Pumps
9.1.1.5 Anion suppressor device: Dionex Anion Self-Regenerating Suppressor (ASRS Ultra II 4-mm, P/N 061561). The ASRS should be set to perform electrolytic suppression at a current setting of 112-mA using an external source DI water mode. Insufficient baseline stability may be observed using the ASRS in recycle mode.
9.1.1.6 Anion Guard Columns: Dionex IonPac® AG18 (4x50-mm, P/N 063154) or Dionex IonPac® AG18 (4x50-mm, P/N 060551) or equivalent. These columns functions as a protector of the analytical column.
9.1.1.7 Anion Analytical Columns: Dionex IonPac® AS18 (4x250-mm, P/N 063148) or Dionex IonPac® AS18 (4x250-mm, P/N 060549) or equivalent.
9.1.1.8 Carbonate Removal Device (CRD 200 – 4mm, P/N 062983)
9.1.1.9 Electrical Conductivity Detectors
9.1.1.10 Dionex Chromeleon Data System – Data acquisition and processing software.

9.1.2 Dionex Integrion HPIC
9.1.2.1 Dionex AS Autosampler
9.1.2.2 Dionex ICS-Series VWD
9.1.2.3 Dionex EluGen® Cartridge

9.2 In order to achieve comparable detection limits, the IC system must be properly maintained and must be capable of yielding a baseline with no more than 5 nS noise/drift per minute of monitored response over the background conductivity.

9.3 Nitrogen, zero grade or better.

9.4 Analytical balance, ±0.1 mg sensitivity (used to accurately weigh reagents).

9.5 Autosampler Vials, 1.5 ml capacity with Teflon lined crimp top.

9.6 Syringes, plastic, disposable, 10 mL - used during sample preparation.

9.7 Pipets, fixed, or variable, volume Eppendorf, various sized, calibrations verified per HS-EQ003.

9.8 Bottles, high-density polyethylene (HDPE), opaque or glass, amber, various sizes. For sampling and storage of calibration solutions.

9.9 Micro beakers, plastic, disposable - used during sample preparation.

9.10 Syringe filters, 30-mm Nylon, 0.45-µm.

10) Standards and Reagents

10.1 Note: All purchased standards according to manufacturer specifications. Store all standard solutions (remaining stock, composite and calibration) below 6 °C in glass containers having Teflon™ lined lids or in accord with the manufacturer's

recommended conditions. All purchased stock standard solutions must be replaced after reaching the manufacturer's expiration date assigned to the standard. All laboratory prepared standard solutions must be replaced after six months or sooner if routine QC indicates a problem or if required by reference method. An assigned expiration date of a lab prepared standard cannot exceed the manufacturer's expiration date for any component used in the standard formulation. When analyzing or preparing samples, all standards, lot numbers must be associated with the run batch or prep batch.

10.2 DI Water: Deionized (DI) water meeting purity characteristics of Type I laboratory distilled water (resistance >17 megohms-cm, anion free water). Water should contain particle sizes no greater than 0.20µm. Filter as necessary.

10.3 Stock Standard Solution, multi-anion 100-500 mg/L: Stock standards are purchased as certified solutions: Bromide, Fluoride, Nitrate as N, Nitrite as N and o- Phosphate as P all at 100 mg/L; Chloride and Sulfate at 500 mg/L.

10.3.1 Adhere to the manufacturer determined expiration date.

10.4 Second Source Stock Standard Solution, multi-anion 100-500 mg/L: Second source stock standards are purchased as certified solutions from a different sources as section 10.3 (i.e., different vendor, or if from the same vendor, obtain a different lot): Bromide, Fluoride, Nitrate as N, Nitrite as N and o- Phosphate as P all at 100 mg/L; Chloride and Sulfate at 500 mg/L.

10.4.1 Adhere to the manufacturer determined expiration date.

10.5 Working Calibration Standards – prepared from appropriate dilutions of the Stock Standard Solution (section10.3).

10.5.1 In a 100-mL volumetric flask, add the indicated amount of stock to ~50mL of DI water and dilute to volume.

10.5.2 Prepare fresh at each use.

Table 10.5 Initial Calibration Standards, Low-Level Curve

These standards are prepared in 100 mL volumetric flasks								
Anion	Stock (10.3) mL	Br^- mg/L	Cl^- mg/L	Fl^- mg/L	NO_3^- mg/L	NO_2^- mg/L	SO_4^{2-} mg/L	PO_4^{3-} mg/L
Level 1	0.1	0.1	0.5	0.1	0.1	0.1	0.5	0.1
Level 2	0.4	0.4	2.0	0.4	0.4	0.4	2.0	0.4
Level 3*	2.0	2.0	10.0	2.0	2.0	2.0	10.0	2.0
Level 4**	4.0	4.0	20.0	4.0	4.0	4.0	20.0	4.0
Level 5***	10	10.0	50.0	10.0	10.0	10.0	50.0	10.0
Level 6	20	20.0	100	20.0	20.0	20.0	100	10.0

*Low Level CCV.

**LCS/LCSD, MS/MSD and ICV are at 4ppm/20ppm.

***High level CCV.

10.6 Calibration Verification Standards (ICV/LCS/CCV) are prepared at the same concentration as the Levels in Calibration Standard (Table 10.5)

10.6.1 The CCV is prepared from the Stock Standard Solution (10.3)

10.6.2 The ICV is prepared from the Second Source Stock Standard Solution (110.4).

11) Calibration and Standardization

11.1 Perform Support Equipment Calibration Checks:

11.1.1 Balance Calibration Checks must be performed prior to balance use as per SOP HS-EQ001, current revision.

11.1.2 Quarterly Pipet Calibration checks must be current for the micro-pipets when they are used to measure portions of DI water or standard solutions required in this procedure. Quarterly pipet calibration checks are performed according to SOP HS-EQ003, current revision.

11.2 Operating Conditions for IC analysis: The analytical approach involves the use of a guard and analytical column. The IC operating conditions are given as Table 11.2 below:

Table 11.2 Perform Support Equipment Calibration Checks:

IC Conditions	Column: IonPac® AG20, AS20
Flow rate:	1.0 mL/minute
Injection volume:	20 µL
Makeup gas:	Helium
Detection:	conductivity detector

11.2.1 Note: Once optimized and calibrated, the same IC conditions must be used for analysis of all standards, samples, blanks and QC samples.

11.3 Initial Calibration Curve: External standard calibration is used. Six standards are used at the concentrations outlined in Table 10.5.

11.4 The calibration is processed using the linear calibration model:

11.4.1 For a linear calibration curve (y = ax + b), the analyst should not force the line through the origin, but leave the intercept calculated. In addition, do not include the origin (0,0) as a calibration point. In order to be used for quantitative purposes, a correlation coefficient, r, must be greater than or equal to 0.995. For non-linear fit using least square fit, r2 must be greater than or equal to 0.990.

11.4.2 Retention Time Windows: The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for each analyte. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.5 Initial Calibration Verification (ICV): Verify each new Initial Calibration using a second source standard (ICV) at or near the midpoint of the curve. Agreement with the new curve should be ±10% of the true value of the second source standard.

11.6 Continuing Calibration Verification (CCV):

11.6.1 Verify calibration by injecting a CCV standard (10) prior to conducting any sample analyses. A CCV must also be injected at intervals of not more than once every ten samples and at the end of the analysis sequence. CCVs must be analyzed at two levels on days when a full multipoint calibration is not preformed. Analyst must alternate the CCV level between high and low standards.

11.6.2 If the response of any analyte varies from the expected values by more than ± 10%, then the test must be repeated using fresh standard. If the results are still more than ± 10%, then an entirely new calibration curve must be prepared for that analyte.

11.7 Continuing Calibration Blank (CCB): This blank is run after the CCV to evaluate whether carryover from previous samples or a CCV has occurred or whether the calibration has drifted. The CCB should be < ½ the PQL.

12) Sample Preparation/Analysis

12.1 Sample Preparation – recommend pre-filter all samples using a 0.45 µ filter. Document filter lots used in sample sequence log along with all standards and reagents, such as eluent.

12.2 IC analysis of aqueous samples -

12.2.1 Transfer a 1-ml aliquot of filtered sample (or diluted sample) into autosampler vial and load onto the instrument autosampler. Create an analytical sequence for all samples and required QC samples. The autosampler will load approximately 100 µL into the sample loop and auto-inject a 20 µL aliquot of the loaded sample. This process is repeated for each sample in the sequence.

12.2.2 Identification of an analyte occurs when a peak from a sample falls within the retention time window of the target analyte.

12.2.3 If the resulting chromatogram fails to produce adequate resolution, except for preserved samples or if identification of specific anions is questionable, analyze a matrix spike of the sample to confirm the anion identification.

12.3 IC analysis of soil samples:

12.3.1 Weigh out 5 grams of soil sample into a digestion tube. Record to nearest 0.1g in logbook. Add 50 mL DI water to sample. Cap and shake vigorously for 2 – 3 minutes. Centrifuge the sample afterwards or let it settle. Decant a sufficient volume of liquid and filter using a 0.45µ membrane filter. Document prep in pre batch containing sample weight, water volume and filter lots and analyze as in sections 12.2.1 thru 12.2.3. A 10x preparation factor is applied to yield an mg/Kg solid result.

12.3.1.1 Note: The nature of the sample matrix may require that varying sample amount are used in this step. In such cases, a 1:10 ratio of

sample to DI water must be maintained. Any deviation must be recorded in the sample preparation batch in LIMS.

12.4 Example calculations for constituent concentration are provided section 15.

12.5 If the responses exceed the calibration range of the system, dilute the sample and reanalyze. NOTE: Using the sequence scanner in LIMS will flag by sample ID those RPDs outside 30% with a code #120.

12.6 If during analysis, there is a need to manually integrate the peak (due to high salt concentration, co-elution, etc.), refer to CE-QA002 Corporate SOP for Manual Integration, or to HS-QS016 Houston Laboratory SOP for Manual Integration, whichever is most current.

12.7 If any carryover is suspected due to a higher anion sample just preceding the sample, then the sample is rerun after a CCV/CCB to check for potential carryover effect. If the concentration of the run matches, then it can be used as confirmation. If it is less than the original, then the rerun is reported.

12.8 Each sample analysis must be bracketed with an acceptable initial calibration, calibration verification standard(s) and initial calibration blank (every 10 samples).

12.9 Build an analytical sequence table with the Dionex Chromeleon software and initiate instrument operation. The Typical Analytical Sequence:

- 12.9.1 Initial Calibration curve samples, including the ICV or
- 12.9.2 Initial CCV/CCB (alternating between a high and low standard on day without initial multipoint calibration)
- 12.9.3 Method Blank (MBLK)
- 12.9.4 LCS
- 12.9.5 Client sample
- 12.9.6 Client Matrix Spike
- 12.9.7 Client Matrix Spike Duplicate
- 12.9.8 Client samples (5)
- 12.9.9 Initial CCV/CCB (alternating between a high and low standard on day without initial multipoint calibration)
- 12.9.10 Client samples (10 or less)
- 12.9.11 Initial CCV/CCB (alternating between a high and low standard on day without initial multipoint calibration)

13) Troubleshooting and Maintenance

13.1 Review of Retention Time data: Shifts in retention time is inversely proportional to concentration. Nitrate, phosphate and sulfate will exhibit the greatest degree of change, although all anions can be affected. In some cases this peak migration may produce poor resolution or make peak identification difficult.

- 13.1.1 Should more complete resolution be needed between any two co-eluting peaks be required, the eluent can be diluted. This will spread out the run, however, and will cause late eluting anions to be retained even longer.
- 13.1.2 The analysts must verify that this dilution does not negatively affect performance by repeating and passing all the QC criteria in Section 16.

13.1.3 As a specific precaution, upon dilution of the eluent, a peak for bicarbonate may be observed within the retention time window for bromide that will negatively impact the analysis.

13.1.4 Eluent dilution will reduce the overall response of an anion due to chromatographic band broadening which will be evident by shortened and broadened peaks. This will adversely affect the LODs for each analyte.

13.2 When a change of >15% for the RT for sulfate is observed, it may indicate the guard column requires attention. Clean or replace the column.

14) Data Reduction and Reporting

14.1 Data is collected with "Chromeleon" data acquisition software. This software provides the sequence log of run order for the data to be collected from the IC detector.

14.1.1 For each new analytical sequence, a new folder is opened (e.g. IC-1).

14.1.2 Chromeleon processes the calibration curve and all associated sample and QC data.

15) Calculations

15.1 QC Calculations: LIMS calculates the percent recovery for various QC samples (LCS) according to the following equations:

15.1.1 % Recovery, %R (for MS and MSD Samples)

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SR = Sample Result (unspiked).
SA = Spike Amount Added (mg/L or mg/kg).

15.1.2 % Recovery, %R (for standards and LCS)

$$\%R = \frac{SSR}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SA = Spike Amount Added (mg/L or mg/kg).

15.1.3 RPD (for precision or duplicate evaluation)

$$RPD = \frac{|SR_1 - SR_2|}{½(SR_1 + SR_2)} \times 100$$

Where:
SR_1 = Sample result for duplicate 1.

SR_2 = Sample result for duplicate 2.

15.2 Sample Concentration Calculation

15.2.1 Aqueous sample

Conc (mg/L) = Instr reading (mg/L) * DF

Where DF = Dilution Factor

15.2.2 Solid Sample

Conc (mg/kg) = Instr reading (mg/L) * DF * PrepFac

Where DF = Dilution Factor
PrepFac = Prepation Factor, normally 10 (0.5 g to 50 mL DI water)

50 /0.5 = 10

16) Quality Control, Acceptance Criteria and Corrective Action

16.1 Initial Demonstration of Capability (IDOC)

16.1.1 Purpose: Verify the ability to produce data of acceptable precision and bias for a specific instrument type, matrix, method, and analyst.

16.1.2 Frequency: Initially during method development, and any time there is a significant change in instrument type, personnel, methodology, or matrix

16.1.3 Acceptance Criteria: Four aliquots at one (1) to four (4) time the limit of quantitation and analyzed according to the method either concurrently or over a period of day. Calculate mean recovery and standard deviation for each analyte of interest. Compare recovery and standard deviation to the corresponding acceptance criteria for precision and accuracy in the method (if applicable) or to lab-generated acceptance limits. If any one compound does not achieve acceptance criteria, the performance is unacceptable for

16.1.4 Corrective Action: Identify and correct the source of error. Reanalyze the demonstration.

16.2 Continuing Demonstration of Capability

16.2.1 Purpose: Verify the ability to produce data of acceptable precision and bias for a specific instrument type, matrix, method, and analyst.

16.2.2 Frequency: A. Annual to re-qualify analyst for analysts. If period greater than one year has lapse since the last performance of analysis than Initial Demonstration must be performed.

16.2.3 Acceptance Criteria: Four consecutive LCS analysis meeting stated LCS criteria or successful PT study.

16.3 Retention Time Window Width:

16.3.1 Purpose: Ensures that the chromatographic system is operating reliably and that system conditions have been optimized for the target analytes in the standards and sample matrix to be analyzed.

16.3.2 Frequency: At method development and after major instrument maintenance (i.e. column replacement, temperature program changes)

16.3.3 Acceptance Criteria: RT Window is determined as ±3 times the standard deviation of the RT for the analyte of interest obtained from the ICAL and several CCVs analyzed over a 24 hour period. However, the experience of the analyst should weigh heavily in interpreting chromatograms.

16.3.4 Corrective Action: N/A

16.4 Initial Calibration:

16.4.1 Purpose: Establishes the calibration curve for the quantification of the analytes of interest.

16.4.2 Frequency: A new curve must be generated when the ICV or CCV criteria are not met, or after major instrument maintenance such as column replacement or changes in operating conditions.

16.4.3 Acceptance Criteria:

16.4.3.1 Initial calibration curve must have 5-points minimally for all analytes (7 are used in this procedure); generate r >0.995

16.4.3.2 If non-linear fit (second order) is used, the COD ≥ 0.99 and six calibration points are required.

16.4.4 Curve Failure Corrective Action: Check standards and or perform maintenance as necessary to correct problem, then generate new curve

16.5 Initial Calibration Verification (ICV).

16.5.1 Purpose: Establishes the calibration curve for the quantification of the analytes of interest.

16.5.2 Frequency: Prior to sample analysis, following significant instrument maintenance, and as required by instrument QC performance.

16.5.3 Acceptance Criteria: The new ICAL curve must have a correlation coefficient equal to or greater than 0.995 with a minimum of 6 calibration points

16.5.4 Corrective Action: Identify and correct the source of error. Perform the ICAL again and reanalyze all affected samples.

16.6 Retention Time Window Position:

16.6.1 Purpose: Assists in the identification of analytes of interest.

16.6.2 Frequency: Set the absolute RT position for each analyte of interest using the mid-point of the ICAL. Reset the absolute RT position for each analyte of interest daily using the first CCV analyzed each day.

16.6.3 Acceptance Criteria: The RT must be ±10% of the previous RT window.

16.6.4 Corrective Action: Re-analyze the CCV. If the acceptance criteria are not met on re-analysis, determine the source of error and perform corrective action.

16.7 Continuing Calibration Verification (CCV)

16.7.1 Purpose: Verifies that instrument response is reliable and has not changed significantly from the current ICAL. On days when multipoint calibration is not performed, analyst must alternate CCV levels between a high and low level standards.

16.7.2 Frequency: beginning of sequence, after every 10 sample injections and at end of a sequence.

16.7.3 Criteria: The acceptance range for CCV is 90 - 110 percent recovery.

16.7.4 Corrective Action: If outside these ranges, perform corrective action to solve

the source of the error, and then re-analyze all samples since the last acceptable CCV. If the CCV fails high, only the bracketed samples that are non-detect can be reported.

16.8 Calibration Blank (CCB):

16.8.1 Purpose: Determines the zero point of the calibration curve for all initial and continuing calibrations. Please place CCB after CCV in the analytical sequence.

16.8.2 Frequency: At the beginning of each sequence, after every 10 samples and at the end of each sequence.

16.8.3 Acceptance Criteria: No analytes detected > ½ LOQ

16.8.4 Corrective Action: Identify and correct the source of error. Reanalyze all affected samples.

16.9 Method Blank (MB)

16.9.1 Purpose: Assess background interference or contamination in the analytical system that may lead to high bias or false positive data.

16.9.2 Frequency: Analyze the Method Blank (MB) with each batch of 20 or less field samples processed through the entire method within a normal work shift.

16.9.3 Criteria: All analytes must be less than the quantitation limit or ½ the quantitation limit depending QA plan associated with the samples. In addition, solvent blanks should be run after samples suspected of being highly contaminated to determine if sample carryover has occurred. The method blank results must be less than the method quantitation limit, or no more than 5% of sample concentration, or 5% of regulatory limits, whichever is greater.

16.9.4 Corrective Action: If above the limit, if it is an indication of instrument drift, the baseline must be reset and the samples since the previous acceptable blank must be re-analyzed. If contamination is indicated, all affected batch samples must be reprocessed. Samples that are non-detect will not require reprocessing.

16.10 Laboratory Control Sample (LCS) or Lab Fortified Blank (LFB): The LCS is prepared from a calibration standard.

16.10.1 Purpose: Evaluates the performance of the entire analytical system, including all preparation and analysis steps. Assesses the ability of the laboratory/analyst to successfully recover the target analytes from a clean matrix. LCS must contain all target analytes.

16.10.2 Frequency: Analyze the LCS/LFB with each batch of 20 or less field samples processed through the entire method within a normal work shift.

16.10.3 Criteria: Refer to table 22.2 for the acceptance range.

16.10.4 Corrective Action: The LCS/LFB results must be within the acceptance range. If outside this range perform corrective action to solve the source of the error, and re-prepare and re-analyze the sample batch unless the LCS/LFB fails high and the samples are non-detect.

16.11 Matrix Spike, Matrix spike duplicate (If field sample is not available to perform both an MS and MSD, then perform an LCS and LCSD.

16.11.1 Purpose: Assesses the performance of the method on a particular matrix.

16.11.2 Frequency: Matrix spikes will be analyzed at the frequency of one spike for

each 10 samples analyzed by Method 300.0 and one spike for each 20 samples analyzed by Method 9056A. If fewer than 20 samples are in a batch, at least one spike will be included for method 9056A and If fewer than 10 samples are in a batch, at least one spike will be included for Method 300.0. If insufficient sample is available for a MS and MSD, then an LCS duplicate must be analyzed and used for the RPD and percent recovery. When duplicate LCS's are used, the same control limits as duplicate matrix spikes will apply.

16.11.3 Acceptance Criteria: Spike recovery and RPD criteria are specified in the Table 22.2.

16.11.4 MS/MSD % Recovery Criteria Failure Corrective Action: If the MS and MSD have recoveries which are outside the target range, the poor recoveries in the MS and MSD may be due to matrix effects. The LCS, surrogate recoveries and calibration results must all be evaluated in order to determine if matrix interference is present or if method performance is poor. Note that the MS and MSD are used to evaluate the matrix effect, not to control the analytical process. If both the Matrix Spike and Matrix Spike Duplicate are found to be out of control for the same analyte, a matrix effect is likely confirmed (assuming the LCS passes). If recoveries of the MS/MSD pair are suspicious (laboratory error, etc) another set of MS/MSD must be re-extracted with the sample batch. For instance, if both matrix spikes exhibit low recovery but good precision then it can be assumed that matrix interference is present. However, if precision between the MS and the MSD is poor, technique error must be eliminated as a possible source of error before the data can be accepted. If matrix interference is highly suspected corrective action is not necessary.
MS/MSD RPD Criteria Failure Corrective Action: If the RPD fails, the data must be evaluated for error and perform sample/batch QC reprocessing if necessary

16.12 Duplicate Samples

16.12.1 Purpose: Provides information on the heterogeneity of the sample matrix. Also determines the precision of the analytical process for that matrix.

16.12.2 Frequency: Once per preparation batch.

16.12.3 Frequency: Duplicates (as MS/MSD or LCS/LCSD) are analyzed on a frequency of one duplicate for each batch of 10 or less samples extracted and analyzed.

16.12.4 Criteria: Acceptance limits for the water matrix and soil matrix are 20 % RPD.

16.12.5 Corrective Action: If the duplicate results are outside the acceptance limits for relative percent deviation, first determine if the cause is a system error; if so, correct the problem and repeat the duplicate. If not, the LCSD RPD must fall within the acceptance criteria in order for the data to be accepted. The sample results must be flagged to indicate the QC failure as matrix interference.

16.13 Method Detection Level (MDL) or Detection Limit Procedure

16.13.1 Purpose: To establish the method detection limit, see SOP HS-QS006 for detail on MDL, LOD and LOQ procedures.

16.13.2 Frequency: Establish the initial MDL of an instrument by process a minimum of 7 spiked aliquots at the appropriate matrix spike level and 7 method blank samples through all steps of the method. The samples used for the MDL must

be prepared in at least three batches on three separate calendar dates and analyzed on three separate calendar dates. After analysis determine the MDLs (spiked MDL) and MDLb (blank MDL). Select the highest MDL as the initial MDL. MDL must be determined for each analyte per matrix per method.

16.13.3 Ongoing Data Collection: On a quarterly basis, two MDL spikes must be prepared at the MDL spiking level and analyzed. Ensure minimum of seven spiked samples and seven method blanks are completed for the annual verification. If only one instrument is in use, a minimum of seven spikes are still required.

16.13.3.1 If new instrument is added to group of instruments, analyze a minimum of two spike replicates and two method blanks. If both blank MDL and are below the MDL then instrument is considered valid. Combine new spied samples with existing MDL and recalculate the MDL. If the recalculated MDL does not vary by the specified factor then existing MDL is validated. If either one of these conditions are not met, then than the MDL must be regenerated.

16.13.4 Annual Verification

16.13.4.1 Recalculate the MDLs and MDLb from the spike samples and method blank from the last twenty four months, but only data with the same spiking level. Include initial MDL if data was within 24 months.

16.13.4.2 If the verified MDL is the greater of MDLs or MDLb. If the verified MDL is within 0.5 to 2.0 times the existing MDL and fewer than 3% of the method blank have numerical results above the existing MDL, then the existing MDL may be left unchanged. Otherwise adjust the MDL to the new verified MDL.

16.13.5 Current MDLs may be found in the Limits tab of each testcode in LIMS.

16.14 Limit of Detection (LOD) Verification

16.14.1 Purpose: Validates the established Detection Limit.

16.14.2 Frequency: Prior to sample analysis and verified quarterly Verification must is performed on each instrument. The LOD is spiked at 2-3 times the detection limit for single compound analyses and 1-4 times the detection limit for multi-analyte standards. Sample must be taken through all preparatory steps such as digestion, extraction clean-up, etc.

16.14.2.1 With each MDL study, all compound must be confirmed at a concentration equal to 1-2 time the calculated MDL. To achieve this confirmation multiple concentration may need to be analyzed. Remaining quarterly checks may be performed at 2-3 times the MDL until the next MDL study.

16.14.3 Acceptance Criteria: The apparent signal to noise ratio at the LOD must be at least three and the results must meet all method requirements for analyte identification (e.g., ion abundance, second-column confirmation, or pattern recognition.) For data systems that do not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least three standard deviations greater than the mean method blank concentrations.

16.14.4 Corrective Action: Repeat the Detection Limit Determination and LOD

Verification at a higher concentration or perform and pass two consecutive LOD verifications at a higher concentration and set the LOD at the higher concentration.

16.14.5 Current LOD values may be found in LIMS under the QA Section in the Limit Manager feature.

16.15 Limit of Quantitation (LOQ) Establishment and Verification:

16.15.1 Purpose: Validates the lower quantitation limit of the analysis. Can be performed at 1-2 X the LOQ. Sample must be taken through all preparatory steps such as digestion, extraction clean-up, etc.

16.15.2 Frequency: Prior to sample analysis and verified quarterly.

16.15.3 Acceptance Criteria: Data must empirically demonstrate precision and bias at the LOQ using LCS control limits.

16.15.4 Corrective Action: Identify and correct the source of error, reanalyze the LOQ. If failure persists re-evaluate the appropriateness of the LOQ.
Initial Demonstration of Proficiency – The laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operation annually and whenever new staff members are trained or significant changes in instrumentation are made.

16.15.5 LOQ at time of SOP creation is found in Table 22.1 of this SOP. For latest LOQ confirmation values, see Limit Manager feature in LIMS under the QA Section.

16.16 Data anomalies must be reported using batch Data Review exception reporting or via NCAR reporting. NCARs must be submitted to the department supervisor or QA manager.

16.17 Linear Calibration Range (LCR) - The LCR must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by ±10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

17) Data Records Management

17.1 All data is stored electronically and/or hard copy for 5 years, or 10 years for the state of Louisiana. Data will also be held longer per client's request.

17.2 All analytical sequence IDs and standard preparation information must be recorded in the Run logbook. Hardcopy computer printouts of analytical sequences and raw data must be retained and initialed by the analyst (electronic initials are acceptable). To simplify standard and reagent tracking, analyst must attempt to use single lots of reagents and standards.

17.3 Complete all pertinent sections in the respective logbooks. If not-applicable then line

out the section and "Z" out or "X" out all large sections of the worksheet that are not used. Make all corrections with single line through, date and initial. Make NO obliterations when manually recording data.

17.4 Logbooks are controlled. Never remove a page from a logbook. Completed logbooks are returned to the QA department when filled and no longer needed in the work area.

17.5 SOP effective date is the date noted in the header or last signature date, whichever is most recent.

18) Contingencies for Handling Out of Control Data

18.1 When method required QC exceedances occur, in every case where sample data quality are affected, the source of the QC exceedance must be determined, corrected and sample reanalysis carried out when possible.

18.2 When affected sample analysis can not be repeated due to limitations (i.e. sample availability, or if reanalysis can only be performed after expiration of a sample hold time), the reporting of data associated with exceeded QC data must be appropriately flagged and narrated. This documentation is necessary to define for the data user the effect of the error has upon the data quality of the results reported (e.g. E flag data indicate the result to be only an estimate).

18.3 All analysts must report sufficient comments in laboratory data review checklist for exceeded QC associated with sample results so that project management can further narrate and ensure data qualifiers (flags) are properly assigned to the reported data.

18.4 NCARs must be issued for QC system exceedances. Matrix interferences are reported using the analyte reporting comment section in LIMS or using the Laboratory Data review checklist.

19) Corrective Action for Out-Of-Control Data

19.1 See table 24.3 and section 16 of this SOP for Corrective actions for handling out of control data.

20) Training

20.1 Training to perform the procedures for this method should take the following into consideration:

20.1.1 Review literature (see references section). Read and understand this SOP. Also review the applicable SDS for all reagents and standards used. Following the reviews, observe the procedure performed by an experienced analyst at least three times.

20.1.2 The next training step is to assist in the procedure under the guidance of an

experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

20.1.3 Perform initial Demonstration of Capability (IDOC) study as described above for water samples. Summaries of the IDOC are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IDOC studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

20.2 Training is documented following *SOP CE-QA003*).

20.3 When the analyst training is documented by the supervisor on internal training documentation forms (HS-QAFORM010 and HS-QAFORM038) the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

21) Method Performance

21.1 Method performance is determined by:

21.1.1 The performance of MDL, LOD, AND LOQ study.

21.1.2 Quality control standards in each batch of data.

21.1.3 Performance Evaluation Samples.

22) Summary of Changes

Table 22.1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
9.3	03/05/2020	G. Moulton	Added Training in section 20
9.3	03/05/2020	G. Moulton	Updated section on method performance
9.3	03/05/2020	G. Moulton	updated section on corrective action for out of control data sec 19
9.3	03/05/2020	G. Moulton	Updated table numbers due to addition of more headers in the SOP.
9.3	03/05/2020	G. Moulton	Removed no longer needed verbiage on equipment and instrument no longer in use in section 9.
9.3	03/05/2020	G. Moulton	Removed repeated definitions in section 3.
9.3	03/05/2020	G. Moulton	Removed task 3 form section 4 in job safety assessment.
9.3	03/05/2020	G. Moulton	Corrected sec 11.3 to say six standards.
9.3	03/05/2020	G. Moulton	Added chlorate to list of elements in section 1.
9.2	11/20/2018	G. Moulton	Updated to new cover page and added new QA Manager
9.2	11/20/2018	G. Moulton	Modified headers of sec 1 and 2
9.2	11/20/2018	G. Moulton	Modified sec 17.1 storage time for data.
9.2	11/20/2018	G. Moulton	Modified sec 21.6 and 21.7
09.2- Section	10/15/2018	C.Stoike	Duplicate frequency defined for one in every 10 field

16.12.3			samples (10%)
09.2- Sections 3.11 & 16.17	10/15/2018	T. Yen	Linear Dynamic Range (LDR) study every 6 months or with major instrument modification.
09.2- Section 16.9.2	10/15/2018	T. Yen	Method Blank (MB) frequency defined as for every batch of 20 or less field samples during normal work shift.
09.2- Section 16.10.2	10/15/2018	T. Yen	Lab Control Sample/Lab Fortified Blank frequency defined as for every batch of 20 or less field samples during normal work shift.
09.1- Section 10.5	06/30/2017	T. Yen	New CCV levels identified on Table 10.5.
09.1- Section 11.6, 12.9 & 16.7	06/30/2017	T. Yen	Alternating between high and low CCV on days when initial calibration was not preformed.
09.1- Section 16.2.2	06/30/2017	T. Yen	DOC period on one calendar year or IDOC must be repeated.
09.1- Section 16.13	06/30/2017	T. Yen	LOD ate1-2 x for certain projects.
09.1- Section 21	06/30/2017	T. Yen	References updated.
09.1- Section 22	06/30/2017	T. Yen	Table 22.7 update with MDL, LOD and Linear Range criteria and corrective action.
09.0	05/15/2015	T. Yen	New SOP format, Lab Director and Inorganics Manager.
09.0 – Sections 3.14, 3.15, 3.23, 3.26	05/15/2015	T. Yen	Surrogate use removed.
09.0 – Sections 16.11 & 16.12	05/15/2015	T. Yen	QC frequency for 300.0 at 10%.
09.0- Section 22	05/15/2015	T. Yen	Updated references.
08.2	08/15/2013	T. Yen	Document format change.
08.2	08/15/2013	T. Yen	Signature Page – QA Manager and Lab Director
08.2 –Sections 12.1 & 12.3.1	08/15/2013	T. Yen	Document syringe and filter lot numbers.
08.2 –Sections 16.14	08/15/2013	T. Yen	New section on linear dynamic range.
08.2 -Section 17.2	08/15/2013	T. Yen	Analyst must make an effect not to use multiple lots of a reagents, solvents, standards or spikes in the preparation or the analytical batch.
08.2 -Section 17.5	08/15/2013	T. Yen	SOP effective date defined.
08.2 – Section 22	08/15/2013	T. Yen	Appendices updated.
08.1	12/15/2011	J. Cady	Minor document revision.
08.0	01/15/2011	R. Pierrot	Updated document to new format. Added level 6 to the calibration table. Revised Section 16 to clarify requirements. Revised the soil preparation procedure to reflect the laboratory practice of 5 grams to 50 mL (12.3.1). Added language allowing the variation in sample amounts for soil preps, as required by matrix. Added the option for variable volume pipettes (9.7)

23) References and Related Documents

23.1 Method 300.0, Determination of Inorganic Anions by Ion Chromatography, USEPA, EMSL – ORD, Cincinnati, Ohio, Revision 2.1, August 1993.

23.2 Method 9056A, Determination of Inorganic Anions by Ion Chromatography, USEPA OSWER, Test Methods for Evaluating Solid Waste Physical/Chemical Methods, Revision 1, February 2007.

23.3 Method 9056, Determination of Inorganic Anions by Ion Chromatography, USEPA OSWER, Test Methods for Evaluating Solid Waste Physical/Chemical Methods, Revision 0, September 1994.

23.4 Dionex Reference Library, May 2006 (CD-ROM)

23.5 ICS3000 Ion Chromatograph Operator's Manual, Rev 01, May 2005, Dionex Corporation, Sunnyvale, CA.

23.6 Current TNI Standards.

23.7 Current Department of Defense Quality Systems Manual.

23.8 EPA MDL Procedure, **Definition and Procedure for the Determination of the Method Detection Limit, Revision 2,** EPA 821-R-16-006. December 2016.

24) Tables, Diagrams, Flowcharts and Validation Data

Table 24.1 300.0 Anion Calibration Acceptance Limits, including ICV

Analyte – water matrix	Low CCV mg/L	SPK mg/L	Low %	High %
Bromide	4.0	10.	90	110
Chloride	20.0	50.0	90	110
Fluoride	4.0	10	90	110
Nitrate-N	4.0	10	90	110
Nitrite-N	4.0	10	90	110
Ortho-Phosphate-P	4.0	10	90	110
Sulfate	20.0	50	90	110
Nitrate/Nitrite – N	8.0	20	90	110

For MDLs (DLs) see QA or LIMS for latest MDLs.

Table 24.2 300.0 Aqueous Spike Levels and Acceptance Limits

Analyte – solid matrix	LCS & MS Spike, mg/L	Low %	High %	RPD %
Bromide	4.0	90	110	20
Chloride	20.0	90	110	20

Fluoride	4.0	90	110	20
Nitrate-N	4.0	90	110	20
Nitrite-N	4.0	90	110	20
Ortho-Phosphate-P	4.0	90	110	20
Sulfate	20.0	90	110	20
Nitrate/Nitrite – N	8.0	90	110	20

For MDLs (DLs) see QA or LIMS for latest MDLs.

Table 24.3 300.0 Solid Spike Levels and Acceptance Limits

Analyte – solid matrix	LCS & MS Spike, mg/L	Low %	High %	RPD %
Bromide	40	90	110	20
Chloride	200	90	110	20
Fluoride	40	90	110	20
Nitrate-N	40	90	110	20
Nitrite-N	40	90	110	20
Ortho-Phosphate-P	40	90	110	20
Sulfate	200	90	110	20
Nitrate/Nitrite – N	80	90	110	20

For MDLs (DLs) see QA or LIMS for latest MDLs.

Table 24.4 9056A Anion Calibration Acceptance Limits, including ICV

Analyte – water matrix	Low Level, mg/L	High Level, mg/L	Low %	High %
Bromide	4.0	10.	90	120
Chloride	20.0	50.0	90	120
Fluoride	4.0	10	90	120
Nitrate-N	4.0	10	90	120
Nitrite-N	4.0	10	90	120
Ortho-Phosphate-P	4.0	10	90	120
Sulfate	20.0	50	90	120
Nitrate/Nitrite – N	8.0	20	90	120

For MDLs (DLs) see QA or LIMS for latest MDLs.

Table 24.5 9056A Aqueous Spike Acceptance Limits

Analyte – solid matrix	LCS & MS Spike, mg/L	Low %	High %	RPD %
Bromide	4.0	80	120	20
Chloride	20.0	80	120	20
Fluoride	4.0	80	120	20

Nitrate-N	4.0	80	120	20
Nitrite-N	4.0	80	120	20
Ortho-Phosphate-P	4.0	80	120	20
Sulfate	20.0	80	120	20
Nitrate/Nitrite – N	8.0	80	120	20

For MDLs (DLs) see QA or LIMS for latest MDLs.

Table 24.6 9056A Solid Spike Acceptance Limits

Analyte – solid matrix	LCS & MS Spike, mg/L	Low %	High %	RPD %
Bromide	40	80	120	20
Chloride	200	80	120	20
Fluoride	40	80	120	20
Nitrate-N	40	80	120	20
Nitrite-N	40	80	120	20
Ortho-Phosphate-P	40	80	120	20
Sulfate	200	80	120	20
Nitrate/Nitrite – N	80	80	120	20

For MDLs (DLs) see QA or LIMS for latest MDLs.

Table 24.7 Summary of Calibration and QC Procedures for EPA Method 300.0 / SW9056A

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Minimum five - point initial calibration for all analytes.	Initial calibration prior to sample analysis.	r ≥0.995	Correct problem then repeat initial calibration. No samples shall be analyzed until ICAL has passed.
Retention Time window position establishment	Once per multipoint calibration.	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA
Second-source (ICV) calibration verification, all analytes.	Once immediately following three-point initial calibration.	All analytes within ± 10% of expected value.	Correct problem and/or prepare fresh ICV, then rerun ICV. If that fails, repeat initial calibration. No samples shall be analyzed until ICV has passed.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Retention Time (RT) window width	At method set-up and after major maintenance (e.g., column change).	RE width is ±3 times standard deviation for each analyte RT over the 24-hour period	Calculated for each analyte.
Retention time window verified for each analyte.	Each calibration verification	± 10% of previous RT.	Prepare and analyze a fresh calibration curve
Calibration verification (CCV and CCB)	CCV and CCB daily before samples and then after every 10 injections and at the end of the analysis sequence. CCV levels must be alternated between the high and low level standards on days when no initial calibration is performed.	All reported analytes within ± 10% of expected value for CCV; analytes in CCB < ½ PQL.	Correct problem, repeat calibration verification and reanalyze all samples since last successful calibration verification.
Demonstration of ability to generate acceptable accuracy and precision using four replicate LCS.	Annually, Once per analyst.	Recovery ±10% of expected value	Recalculate results; locate and fix problem with system, then rerun the demonstration for those analytes that did not meet criteria.
Method blank.	One method blank must be analyzed for every 20 or less field samples	No analytes detected above <1/2 LOQ	Correct problem, and then re-analyze method blank and all samples processed with the contaminated blank.
LCS for all analytes.	One LCS per analytical batch of 20 or less field samples. .	Recovery at ± 10% of expected value for method 300.0. Recovery at ±20% of expected value for SW9056A	Correct problem, and then re-analyze the LCS and all samples in the affected analytical batch.
MS	One MS per every 20 or less field samples per matrix. For Method EPA300.0, one in every 10 or less field samples must be spiked.	Recovery ± 10% of expected value for EPA300.0, and ±20% for SW9056A	Describe in Laboratory Review Checklist.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
LCD/MSD	One duplicate (or MSD) per every 20 or less field samples per matrix. For Method EPA300.0, one in 10 or less field samples must be spiked.	RPD <20%	Describe in Laboratory Review Checklist.
MDL Study	Once per 6 months.	Follow procedure in EPA publication EPA 821-R-16-006, **Definition and Procedure for the Determination of the Method Detection Limit, Revision 2.**	Repeat MDL level spike twice every quarter. Compile data annually with spike standards and method blanks.
LOQ/LOD Study	Once per 3 months.	In LOD must be greater than MDL and less than or equal to PQL. Generally performed ate 2-4 times the MDL concentration. Note some project QA Plans require the LOD to be at 1-2 the MCL concentration. LOQ may be analyzed at 1 or 2 times the LOQ. All compounds must achieve LCS control limits.	LOD does not have acceptance limits, but all method analytical criteria must be achieved. Repeat LOQ if LCS limits are not achieved.
Linear Calibration Range (LCR). If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.	The LCR must be determined initially and verified every six months or whenever a significant change is made in the instrumentation.	If any verification data exceeds the initial values by ±10%, linearity must be reestablished.	Repeat LRC if limits are not achieved or revised Linear range in LIMS. Not even if linear is confirm to be greater than upper calibration, lab will not report greater than upper calibration limit.

HOT BLOCK DIGESTION OF AQUEOUS METALS SAMPLES BY METHOD SW846-3010A-EPA 200.8

DOCUMENT ID: HS-MET002, REV 9.4

Approved By: Hoai. Van
Technical and Laboratory Director, Hoai Van

Date: 03/05/2020

Prepared By: Erica H Marinez
Quality Assurance Manager, Erica Marinez

Date: 03/05/2020

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1) Scope and Applicability

1.1 This document describes the hotblock digestion procedure for water, extracts (SPLP, TCLP & DI Water), elutriate and seawater samples requiring analysis for total metals. Two equivalent digestion procedures are described in this document, both using nitric and hydrochloric acids. The preferred digestion uses 16 mL hotblock tubes with 10 mL of sample, as it is more efficient, significantly reduces consumable costs, and supports miniaturization using 60 mL sample bottles. A digestion using 50 mL hotblock tubes is also included. These digestion procedures are not applicable for the analysis of total mercury. Refer to mercury specific analytical methods for other digestion procedures applicable to mercury analysis. This procedure is the ALS default water digestion procedure and is based on methods described in EPA 200.8, and EPA SW-846 3010A.

1.2 This procedure is based upon the procedures in method SW3010A and EPA 200.8 Rev 5.4 for the preparation of aqueous samples (surface, ground and non-potable waters) and TCLP and SPLP extracts for determination of metals by ICP-MS. The method is applicable for the following total (recoverable) metals: minerals (K, Ca, Fe, Na and Mg) and trace metals (Ag, Au, Al, Sb, As, Ba, Be, B, Bi, Cd, Cr, Co, Cu, Ge, Li, Mn, Mo, Ni, Pb, Pd, Rh, Se, Sr, Sn, Ti, Th, Tl, V, Zn, P, W, Zn, U, and Y).

Note – Bismuth (Bi), Germanium (Ge), Lithium (Li), and Yttrium (Y) are purchased separately in their own spiking mix. Quality Control samples must be prepared separately from the Quality Control samples receiving the standard spike mix.

2) Summary of Procedure

2.1 A 50mL or 10mL aliquot of aqueous sample, following the addition of concentrated nitric acid and concentrated hydrochloric acid, is slowly refluxed in a covered digestion tube on a hot block digester. This step may be repeated with additional portions of nitric acid and hydrochloric acid should the sample be colored, where the additional acid is required to turn the digestate to light in color or until its color has stabilized. The final reflux step includes reducing the digestate to a low volume. After completion of reflux, the digestate is removed from the hot block and allowed to cool. After cooling, the digestate is adjusted to a final volume of 50mL or 10mL. Should the digestate have suspended material after refluxing, cooling, and final volume adjustment, the digestate will be gently decanted or pipetted from the digestion tube to avoid clogging of the ICPMS delivery system.

3) Definitions

3.1 Batch: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** is composed of one (1) to twenty (20) environmental sample of the same quality systems

matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be twenty-four (24) hours. An **analytical batch** is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.

3.2 Demonstration of Capability: The analysis of QC samples in series to verify the ability to produce data of acceptable precision and bias.

3.3 DI: Abbreviation for Deionized water

3.4 Exception Report: Appropriate comments reported with the associated sample batch that addresses sample anomalies such as demonstrated sample matrix effects.

3.5 HCl: Abbreviation for Hydrochloric acid

3.6 HNO_3: Abbreviation for Nitric acid

3.7 Laboratory Control Sample (LCS): A sample matrix, free from the analytes of interest, spiked with known amounts of analytes or a material containing known and verified amounts of analytes.

3.8 Limit of Detection (LOD): an estimate of the minimum amount of a substance that an analytical process can reliably detect. The LOD is determined annually through the execution of a Method Detection Limit Study, and verified quarterly through the analysis of a Detectability Check Sample (DCS).

3.9 Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met.

3.10 Linear Dynamic Range (LDR): High-level check standard periodically analyzed to verify the linearity of the calibration curve at the upper end.

3.11 Low-level calibration check standard (LL-CCV): A reference standard that contains a quantity of analyte equal to or less than the reporting limit.

3.12 Matrix: The substrate (e.g., water, soil, etc.) which may contain the analyte of interest.

3.13 Matrix Spike (MS): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available.

3.14 Matrix Spike Duplicate (MSD): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of recovery for each analyte.

3.15 Method Blank (MBLK): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at

concentrations that impact the analytical results for sample analysis.

3.16 Method Detection Limit (MDL) study: a procedure described in 40CFR Part 136, Appendix B, that describes how to produce an MDL, a reporting element of certain EPA methods. The MDL study is one approach to determine the LOD.

3.17 NCAR: Nonconformance Corrective Action Report (refer to SOP HSQS003, current revision).

3.18 Post Digestion Spike Addition (PDS): An analyte spike added to a portion of prepared sample to verify absence or presence of matrix effects.

3.19 Preparation Batch: A defined set of one to 20 client samples of the same matrix, meeting the batch definition criteria, and prepared for analysis within 24 hours. The preparation batch must also contain the required determinative method defined batch QC samples (e.g. method blank, laboratory control samples, matrix spikes, duplicates, etc.).

3.20 Reagent Water: Deionized (DI) reagent purified by filtration through mixS resin and carbon beds. For additional purification, the DI water is passed through an activated carbon filter.

3.21 Second Source Calibration Verification (ICV): A standard obtained or prepared from a source independent of the source of standards for the ICAL. Its concentration should be at or near the middle of the calibration range. It is performed after the ICAL.

3.22 Safety Data Sheet (SDS): Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

4) Health and Safety Warnings

4.1 Lab Safety: Due to various hazards in the laboratory, safety glasses and laboratory coats or aprons must be worn at all times while in the laboratory. In addition, gloves and a face shield should be worn when dealing with toxic, caustic, and/or flammable chemicals.

4.2 Chemical Hygiene: The toxicity or carcinogenicity of each reagent used has not been precisely defined; however, each chemical used should be treated as a potential health hazard. Exposure to laboratory reagents should be reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets (MSDS) is available to all personnel involved in these analyses.

4.3 Waste Management: The principal wastes generated by this procedure are the method-required chemicals and standards. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required. Laboratory procedures in SOP HS-SAF-001, Waste Disposal Procedures, must be followed.

4.4 Pollution Prevention: The materials used in this method pose little threat to the environment when recycled and managed properly. The quantities of chemicals purchased should be based on the expected usage during its shelf life. Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards or reagents to be disposed.

4.5 Job Safety Assessment

HAZARD ASSESSMENT		
Job Task #1:	**Hazards**	**Preventative Measures**
Cooler and sample handling.	Injury due to lifting heavy coolers and placing/removing samples to/from storage locations. .	Use proper lift technique and cart to move coolers and stools/stepladder when working reaching above shoulder height in sample storage cooler.
Job Task #2:	**Hazards**	**Preventative Measures**
Sample container handling and preservation checks.	Exposure to possible hazardous chemicals.	Use of proper PPE, i.e. Lab coats, safety glasses, gloves, etc.
Job Task #3:	**Hazards**	**Preventative Measures**
Use of concentrated acid.	Chemical burns and acid fume exposure.	Use of proper PPE, i.e. Lab coats, safety glasses, gloves, etc. Face shield must be used when using concentrated acid. All acid must be handled in fume hoods
Job Task #4:	**Hazards**	**Preventative Measures**
Sample Testing and/or standard and reagent/solvent use.	Exposure to possible hazardous chemicals.	Wear gloves, safety glasses and lab coat. Work in fume hood and avoid skin contact with solvents/acids/reagents. Know location of safety showers, first aid kits, spill kits and fire extinguishers when handling flammable material.
Job Task #5:	**Hazards**	**Preventative Measures**
Burn hazard from heated hotblocks.	Burns from heated surfaces.	Use of proper PPE, i.e. Lab coats, safety glasses, gloves, etc. and keep hand and arm away from hot surfaces.

5) Cautions

5.1 Routine preventative maintenance must be performed and documented to assure optimum instrument performance. Refer to the current revision of SOP HS-EQ004 for preventative maintenance schedules.

6) Interferences

6.1 Contamination

Contaminants present in reagents, plastic, and other sample processing equipment may cause interferences or yield artifacts. All these materials must be routinely monitored and demonstrated to be free of interferences by analyzing Method Blanks.

Most plastic supplies leach metals when heated with acidic solutions. It is critical to use the plastic supplies listed be monitored for contamination. The inserts (reflux covers) and caps for the tubes, and the filter used with the digestion must be acid washed to prevent potential sources of contamination.

6.2 Interferences are discussed in the SOP for ICP-MS, HS-MET003. Suspended matter, typically silicates, may require filtration after completion of the digestion to prevent clogging of the ICPMS.

Samples with high levels of ferrous iron may produce an orange-colored precipitate when water soluble ferrous iron oxidizes to the insoluble ferric state (i.e. Fe^{2+} ---> Fe^{3+}); this reaction is not always immediate and may only be noticeable after the sample has been acidified for several days. Samples with this type of precipitate must be shaken vigorously prior to digestion or analysis to re-suspend this precipitate in order to obtain a representative sub-sample.

These digestion procedures are not intended to fully solubilize all particulate metals in the sample, especially when the sample is high in organic matter or minerals. These procedures are empirical, and provide a conservative measure of environmentally or ecologically available metals.

This method is suitable for the digestion of aqueous samples containing silver concentrations of up to 0.1 mg/L (Reference: US EPA 200.2). Samples containing higher levels of silver must be diluted prior to digestion by this procedure.

The solubility and stability of barium is limited in the presence of free sulfate using this method (Reference: US EPA 200.2).

7) Personnel Qualifications and Responsibilities

7.1 General Responsibilities - This method is restricted to use by or under the supervision of analysts experienced in the method.

7.2 Analyst - It is the responsibility of the analyst(s) to:

- 7.2.1 Each must read and understand this SOP and follow it as written. Any deviations or non-conformances must be documented and submitted to the QA Manager for approval.
- 7.2.2 Produce method compliant data that meets all quality requirements using

this procedure and the Data Reduction, Review and Validation SOP (HS-QS009).

7.2.3 Complete the required initial demonstration of proficiency before performing this procedure without supervision.

7.2.4 Complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.

7.2.5 The analysts must submit data for peer or supervisor review.

7.3 Section Supervisor - It is the responsibility of the section supervisor to:

7.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.

7.3.2 Ensure analysts have completed the required initial demonstration of proficiency before performing this procedure without supervision.

7.3.3 Ensure analysts complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.

7.3.4 Ensure analysts produce method compliant data that meet all quality requirements using this procedure and the Data Reduction, Review and Validation SOP.

7.4 Project Manager - It is the responsibility of the Project Manager to ensure that all method requirements for a client requesting this procedure are understood by the laboratory prior to initiating this procedure for a given set of samples.

7.5 QA Manager: The QA Manager is responsible for

7.5.1 Approving deviations and non-conformances

7.5.2 Ensuring that this procedure is compliant with method and regulatory requirements,

7.5.3 Ensuring that the analytical method and SOP are followed as written through internal method and system audits.

8) Sample Collection, Handling, and Preservation

8.1 Aqueous samples are acidified to pH <2 with HNO_3 and stored in plastic or glass. The holding time is 180 days.

8.2 If samples are not acidified in the field or if pH > 2, samples should be acidified, mixed, and held for 24 hours, and then verified to be pH < 2 just before withdrawing an aliquot for digestion. If for some reason, such as high alkalinity, the sample pH is verified to be > 2, more acid must be added and the sample held for an additional 24 hours until verified to be pH < 2.

8.3 Dissolved metals which are not field filtered will be filtered in the lab as soon as possible.

8.3.1 Certain clients require method blanks, LCS and MS/MSD to prepared and filtered through a 0.45 um filter prior to digestion, see Supervisor or QA for additional into. Document all filter lots used in digestion in the LIMS Prep Requirements.

9) Equipment and Supplies

9.1 Hot Block digester capable of maintaining a temperature of 90 to 95°C. The recommended hotblock is manufactured by ALS Minerals in North Vancouver (120 position x 10 mL or 60 position x 50 mL).

9.2 Disposable 60-mL graduated digestion tubes with caps (volume markings up to 50-ml, in 5 ml increments, accuracy verified per SOP HS-EQ003), Environmental Express Cat # SC475 or equivalent, each lot must be documented to ensure filter and is free of metal.

9.3 The standard ALS hotblock has 17.0 mm diameter well size (16.5 mm diameter hotblocks have also been produced). Using either the 16.5 mm or 17.0 mm hotblock, this method does not cause significant volume change to samples when used with Evergreen 214-2380-030 tubes and Sarstedt REF. 65.816 inserts.

9.3.1 Calibrated tube marked with 9, 10, and 11 mL volumes. Tare a balance with an Evergreen (214-2380-030) tube and weigh 9 g of water, and mark a line with a permanent marker. Repeat with 10 g and 11 g of water. The calibrated tube will have lines for each of 9, 10, and 11 mL volumes. Transfer sample using pipette or cylinder.

9.4 Disposable ribbed watch glasses for 50 mL tubes, Environmental Express Cat # SC505.

9.5 Disposable ribbed watch glasses for 17 mL tubes, available from ALS Minerals.

9.6 Appropriate Class A volumetric flasks, various sizes, 10, 25, 50, 100-mL, etc.

9.7 Eppendorf pipettes and tips or equivalent, various delivery volumes, accuracy per SOP HS-EQ003.

9.8 Bottle top dispensers, various delivery volumes, accuracy per SOP HS-EQ003.

9.9 Centrifuge.

9.10 HDPE bottles – 60, 125 and 250 mL from vendor such as ThermoFisher or equivalent.

9.11 PPE such as gloves, lab coats, safety glasses and face shield.

9.12 25 mm, hardened ashless filters, Whatman 541 or equivalent, Whatman Cat# 1541-125, Fisher Scientific Cat# 09-851-D (MEOL 4340059). Used for large particle removal (> 1 mm) for the 50 mL digestion. These require acid washing (refer to Section 9.1.3 for acid washing instructions).

9.13 Polypropylene funnels, 2 ½ inches, Evergreen Scientific 208-5136-030, Fisher Scientific Cat# 05-555-6. Cat# 208-5136-030 (MEOL 4010096). Used for filtration for the 50 mL digestion

10) Standards and Reagents

10.1 Store all purchased standards according to manufacturer specifications. All purchased stock standard solutions must be replaced after reaching the manufacturer's expiration date assigned to the standard. All laboratory prepared standard solutions must be replaced after six months or sooner if routine QC indicates a problem or if required by reference method. An assigned expiration date of a lab prepared standard cannot exceed the manufacturer's expiration date for any component used in the standard formulation. When analyzing or preparing samples, all standard IDs must be documented in the designated location (i.e. LIMS batches, controlled spreadsheets, paper logbooks, run logs, etc.) to allow traceability back to the lot number. Upon receipt, all standards, reagents and supplies must be checked for purity and concentration in accordance with SOPs GEN-CE007 and HS-QS001 (HS-QS001 is equivalent to GEN-CE007).

10.2 Ultra Pure reagent water.

10.3 Concentrated HNO_3 (Ultra Trace metal grade).

10.4 Concentrated HCl (Ultra Trace metal grade).

10.5 LCS and MS Spike Solution (NIST traceable): A 24-element standard is used (Absolute Standards, Cat # 59153 or equivalent). Each element is at a concentration of 10.0 ppm, with the exception of five mineral elements (K, Ca, Fe, Na and Mg) at 1000 ppm. The nineteen trace elements at 10.0 ppm are: Ag, Al, As, Ba, Be, Cd, Cr, Co, Cu, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn and Ti. When additional trace metals are required (e.g. Sr, Sn, etc.), 10 ppm spiking standards are prepared from 1000 ppm reference sources.

10.6 Bi, Li, Ge and Y standard at 1000 ppm

10.6.1 10 ppm Spike Mix – Add 1 mL of the 1000 ppm stock to a 100 mL volumetric flask and volume up to 100mL using DI water. Document preparation in the Standard Preparation logbook and label the storage container with the standard ID number and expiration date.

11) Method Calibration

11.1 Perform support equipment calibration checks per SOP HS-EQ003. Balances require daily calibration checks prior to use. Pipettes require quarterly calibration checks and then additional daily checks prior to use for DOD projects. This daily check must be performed on the days the standards are prepared which will be used for DoD samples even if standard preparation occurs on a different day than sample preparation. Standards made using pipettes that were not checked on the day of standard

preparation are not eligible to use for DoD samples. Fresh standards would need to be prepared after performing calibration checks for all pipettes used in the process. Therefore, it is recommended that daily pipette checks are performed every time prepared standards are made.

12) Sample Preparation

12.1 50 mL Sample Digestion by Method 3010A

12.1.1 Total Metals Aliquots

12.1.1.1 Transfer a 50-mL representative aliquot of the well-mixed aqueous sample to a labeled digestion tube. Document the pH of each sample in the prep log to ensure less than 2 and pH paper lot. If pH is greater than 2 check bottle to ensure correct sample container. If container is correct preserve same and hold for 24 hours. Document acid lot used for preservation.

12.1.1.2 Method Blank (MB) Preparation: A 50-mL portion of DI water is added to a digestion cup. The LCS is now ready for the digestion.

12.1.1.3 LCS Preparation: A 50-mL portion of DI water is added to a digestion cup. A 0.25-ml portion of LCS/MS Spike Solution is added to the digestion cup. The LCS is now ready for the digestion. The LCSD is prepared in the same manner.

12.1.1.3.1 For Bi, Ge and Y, samples and spike must be prep separately and spike with the spiking solution from10.6. Spiking with 0.25mL in a 50 mL sample aliquot.

12.1.1.4 MS Preparation: A 50-mL portion of randomly chosen client water sample is added to a digestion cup. A 0.25-mL portion of LCS/MS Spike Solution is added to the digestion cup and label tube the sample ID and MS. The MS is now ready for the digestion. The MSD is prepared in the same manner. Pour a third 50 ml aliquot of the chosen spike sample in to digestion tube and label tube with sample ID, do not spike this sample.

12.1.1.4.1.1 Label tubes with client sample LIMS generated label include the sample ID & digestion date. Label associated QC Samples.

12.1.1.4.1.2 MBLKW1-date (metals method blank, 1st soil batch of day);

12.1.1.4.1.3 MLCSW1-date (metals soil LCS, 1st soil batch of day);

12.1.1.4.1.4 Sample ID- MS-date (metals sample MS);

12.1.1.4.1.5 Sample ID- MSD-date; (metals sample MSD).

12.1.1.5 Repeat subsampling for the other samples up to another 19 additional samples for a maximum of 20 samples per batch.

12.1.1.6 LCS/MS spike solutions must be added to the aqueous sample portion in the digestion vessel prior to the addition of any digestion reagents.

12.1.1.7 Batch is now ready for digestion following procedure in Section 12.1.4. Note: when a sample contains oil or has a significant organic odor, use of smaller, well-mixed portion may be required due to the matrix. Document the reason for the use of a smaller portion.

12.1.2 Dissolved Metals Aliquots-

12.1.2.1 For dissolved metals samples that have not been field filtered, samples must be filtered through a 0.45 um membrane filter and then preserved with 1:1 HNO_3 to a pH <2. Sample must be held for 24 hours prior to digestion. If filtering samples in the lab, record the filter lot number in the LIMS Prep Requirements.

12.1.2.2 For dissolved metals sample that have not been field filtered, samples must be filtered through a 0.45 um membrane filter and sample preserved with 1:1 HNO_3 to less than 2. Sample must be held for 24 hours prior to digestion. If filtering samples in the lab record filter Lot Number in prep batched.

12.1.2.3 Prepare method blank by filtering DI water if samples are filtered in the lab. If samples are field filter used Di water.

12.1.2.4 Prepare separate batches for dissolved, total and leachates.

12.1.2.5 Prepare MB, LCS, LCSD (If needed), MS/MSD and samples in the same manner as Section 12.1.1.1 to 12.1.1.7.

12.1.2.6 Batch is now ready for digestion following procedure in Section 12.1.4.

12.1.3 TCLP/SPLP Leachates and DI water leachate aliquots.

12.1.3.1 TCLP/SPLP extract are digested using 5 mL of extract diluted to 50mL, 10X dilution.

12.1.3.2 Separate batches are needed to each type of leachate.

12.1.3.3 Each batch will consists of the leach blank, method blank, LCS and MS and sample up to twenty samples. Prepare spikes and sample as instructed in Section 12.1.1.1 to 12.1.1.7.

12.1.3.4 Batch is now ready for digestion following procedure in Section 12.1.4.

12.1.4 Sample Digestion by Method 3010A for 50 mL sample volume.

12.1.4.1 Add 1.5 mL concentrated HNO_3 to each digestion cup. Cover each cup with a watch glass and place the rack of cups into the hotblock. Adjust the hot block temperature to 90 -95° C. Do not allow the digesting samples to boil, but slowly evaporate them to 2.5-mL. Do not allow sample to go dry, if sample does go dry discard sample and re-prepare sample in new batch. Note lot of

acid added in prep log. Place calibrated thermometer in clean tube with 50 mL of water in random slot, rotating daily.

12.1.4.2 Remove the rack of digestion cups briefly from the hot block to allow cooling and inspect for adequate color stabilization of the digestates. Add another 1.5 mL portion of concentrated HNO_3. Cover the tubes again with the watch glass and return the rack to the hot block. Repeat the step as necessary until the color has stabilized and the volume has reduced to < 5 mL. Sample Digestion volume must not go to dryness. If it does, the digestion must be repeated.

12.1.4.3 If colors stabilization has occurred (e.g. dark digestates are now light), no further digestion is required. If color stabilization has not occurred continuing heating and adding additional acid ass necessary until light in color or does not change in appearance with continuing refluxing and the volume has reduced to < 5 mL. Remove from heat and cool. Note in pre log comment if additional acid volume was added.

12.1.4.4 Add 2.5mL of concentrated HCl, cover the digestion cup, and reflux for an additional 15 minutes to dissolve any precipitate or residue resulting from evaporation.

12.1.4.5 Wash down the tube walls and watch glass with DI and adjust the final volume to 50-mL with DI. Allow sample to settle. If needed to remove silicates and other insoluble material that could clog the ICP-MS, allow the sample to settle before gently decanting or pipetting aliquots for analysis.

12.1.4.6 Create a batch ID in LIMS and log samples and QC samples into LIMS and all reagents, standards and supplies used.

12.2 Sample Digestion by Method 3010A for 10 mL Sample Volume

12.2.1 Total Metals and Field-filtered Dissolved Metals

12.2.1.1 Check the pH of each sample. If pH is >2, preserve the sample by adding concentrated Nitric Acid to bring the pH <2. Samples must be held for a minimum of 24 hours prior to digestion. The pH must be rechecked immediately prior to digestion. If the pH is >2 after the 24 hours, the sample must be preserved again to pH <2 and held another 24 hours. Record the acid used each time additional preservation was required. Once the pH is <2 after holding 24 hours, digestion can proceed.

12.2.1.2 Mix the sample by shaking well. Transfer a 10 mL aliquot to a labeled digestion tube.

12.2.1.3 Method Blank (MB) Preparation: A 10-mL portion of DI water is added to a digestion cup labeled MB. The MB is now ready for the digestion.

12.2.1.4 Laboratory Control Sample (LCS) Preparation: A 10-mL portion of DI water is added to a digestion cup. A 0.05-mL

portion of LCS/MS Spike Solution is added to the digestion cup. The LCS is now ready for digestion. If LCS Duplicate (LCSD) is required, prepare a second tube in the same manner.

12.2.1.4.1 For Bi, Ge and Y, samples and QC must be prepared separately and spiked with the spiking solution from Section 10.6. Add 0.05 mL into a 10 mL DI aliquot.

12.2.1.5 Matrix Spike (MS) Preparation: A 10-mL portion of a randomly chosen customer sample is added to a digestion cup. A 0.05-mL portion of LCS/MS Spike Solution is added to the digestion cup and the cup is labeled with both the sample ID and MS. The MS is now ready for digestion. The MS Duplicate (MSD) is prepared in the same manner. Pour a third 10 mL aliquot of this chosen customer sample into a digestion cup and label with the sample ID. Do not spike this sample. This will be available to the analyst as a Post Digestion Spike (PDS) sample, if needed.

12.2.1.6 Repeat subsampling for the other samples up to another 19 additional samples for a maximum of 20 samples per batch.

12.2.1.7 The LCS/MS spike solutions must be added to the aqueous sample portion in the digestion vessel prior to the addition of any digestion reagents.

12.2.1.8 Batch is now ready for digestion following procedure in Section 12.2.4.

Note: When a sample contains oil or has a significant organic odor, use of smaller, well mixed portion may be required due to the matrix. Document the reason for use of smaller portion.

12.2.2 Lab-filtered Dissolved Metals

12.2.2.1 For dissolved metals samples that have not been field filtered, samples and a filter blank (DI water) must be filtered through a 0.45 um membrane filter and preserved with concentrated HNO_3 to pH <2. Record the filter lot, Reagent ID for the acid, and the final pH.

12.2.2.2 Samples must be held for a minimum of 24 hours prior to digestion. The pH must be rechecked immediately prior to digestion. If the pH is >2 after the 24 hours, the sample must be preserved again to pH <2 and held another 24 hours. Record the acid used each time additional preservation was required. Once the pH is <2 after holding 24 hours, digestion can proceed.

12.2.2.3 Lab filtered samples will require a LIMS batch separate from other metals samples (i.e. Total metals, TCLP leachates, etc.).

12.2.2.4 Prepare MB, LCS, LCSD (If needed), MS/MSD and samples in the same manner as Section 12.2.1.2 to 12.2.1.7.

12.2.2.5 Batch is now ready for digestion following procedure in Section 12.2.4.

12.2.3 TCLP/SPLP Leachates and DI water leachate.

12.2.3.1 TCLP/SPLP extract are digested using 1 mL of extract diluted to 10 mL.

12.2.3.2 Separate batch is needed to each type of leachate.

12.2.3.3 Each batch will consists of the leach blank, method blank, LCS and MS and sample up to twenty samples.

12.2.3.4 Batch is now ready for digestion following procedure in Section 12.2.4.

12.2.4 Sample Digestion by Method 3010A for 10 mL sample volume.

12.2.4.1 Adjust the hot block temperature such that the covered thermometer in the block reaches 90-95˚C. Rotate the thermometer to different hot block cells daily.

12.2.4.2 Add 0.2 mL concentrated HNO_3 to each digestion cup. Cover each cup with a watch glass and place the rack of cups into the hot block. Do not allow the digesting samples to boil, but slowly evaporate them to ~2-mL. Do not allow samples to go dry. If a sample goes dry, discard the cup and re-prepare the sample in a new batch.

12.2.4.3 Add 0.1mL of concentrated HCl, cover the digestion cup, and reflux for an additional 15 minutes to dissolve any precipitate or residue resulting from evaporation.

12.2.4.4 Wash down the tube walls and watch glass with DI and adjust the final volume to 10mL with DI. Allow sample to settle. If needed to remove silicates and other insoluble material that could clog the ICP-MS, allow the sample to settle before gently decanting or pipetting aliquots for analysis.

12.2.4.5 LIMS generated labels may now be affixed to the corresponding cups. Labels are heat sensitive and will turn black if applied to tubes prior to digestion.

12.2.4.6 Create a batch ID in LIMS. Enter samples and QC samples on the Samples tab in the batch. Document reagents, standards, supplies and equipment on the Prep Requirements tab in the batch.

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12.3 50 mL Sample Volume digestion by Method 200.8

12.3.1 All samples are digested for Total Recoverable Analysis.

12.3.2 Transfer a 50-mL representative aliquot of the well-mixed aqueous sample to a digestion tube. Document the pH of sample to ensure less than 2. If pH is greater than 2 check bottle to ensure correct sample container. If container is correct preserve same and hold for 24 hours. Prepare batch MB, LCS, LCSD, MS & MSD as below. Place calibrated thermometer in clean tube with 50 mL of water in random slot, rotating daily.

12.3.2.1 Method Blank (MB) Preparation: A 50-mL portion of DI water is added to a digestion cup. The LCS is now ready for the digestion.

12.3.2.2 LCS Preparation: A 50-mL portion of DI water is added to a digestion cup. A 0.25-ml portion of LCS/MS Spike Solution is added

to the digestion cup. The LCS is now ready for the digestion. The LCSD is prepared in the same manner.

12.3.2.2.1 For Bi, Ge and Y, samples and spike must be prep separately and spike with the spiking solution from10.6. Spiking with 0.25mL in a 50 mL sample aliquot

12.3.2.3 MS Preparation: A 50-mL portion of randomly chosen client water sample is added to a digestion cup. A 0.25-mL portion of LCS/MS Spike Solution is added to the digestion cup and label tube the sample ID and MS. The MS is now ready for the digestion. The MSD is prepared in the same manner. Pour a third 50 ml aliquot of the chosen spike sample in to digestion tube and label tube with sample ID, do not spike this sample.

12.3.2.4 The LCS/MS spike solutions must be added to the aqueous sample portion in the digestion vessel prior to the addition of any digestion reagents.

Note: When a sample contains oil or has a significant organic odor, use of smaller, well mixed portion may be required due to the matrix. Document the reason for use of smaller portion.

12.3.2 The LIMS sample label must be placed on the sample tube. This label includes the sample ID & digestion date. Label associated QC Samples as

12.3.2.1 MBLKW1-date (metals method blank, 1st soil batch of day);
12.3.2.2 MLCSW1-date (metals soil LCS, 1st soil batch of day);
12.3.2.3 Sample ID- MS-date (metals sample MS);
12.3.2.4 Sample ID- MSD-date; (metals sample MSD).

12.3.3 Sample digestion

12.3.3.1 Adjust the hot block temperature such that the covered thermometer in the block reaches approximately 95˚C.

12.3.3.2 Add 0.5 mL of concentrated HNO_3 and 0.25 mL of concentrated HCl to each digestion cup.

12.3.3.3 Place the rack of cups into the hotblock inside a fume hood. Cover each cup with a watch glass. Reduce sample volume to ~10 mL by gentle heating. Sample must not go to dryness. If sample does go to dryness, the digestion must be repeated for that sample.

12.3.3.4 Remove from heat and allow digestion cups to cool.

12.3.3.5 Wash down the tube walls with DI water and adjust the final volume to 50 mL with DI water. If necessary, allow insoluble material to settle. The digested sample is now ready for analysis.

12.3.3.6 Create a batch ID in LIMS. Enter samples and QC samples on the Samples tab in the batch. Document reagents, standards and supplies on the Prep Requirements tab in the batch.

12.4 10 mL Sample Volume digestion by Method 200.8

12.4.1 All samples are digested for Total Recoverable Analysis.

12.4.2 Transfer a 10-mL representative aliquot of the well-mixed aqueous sample to a digestion tube. Document the pH of sample to ensure less than 2. If pH is greater than 2 check bottle to ensure correct sample container. If container is correct preserve same and hold for 24 hours. Prepare batch MB, LCS, LCSD, MS & MSD as below. Place calibrated thermometer in clean tube with 10 mL of water in random slot, rotating daily.

12.4.2.1 Method Blank (MB) Preparation: A 10-mL portion of DI water is added to a digestion cup. The LCS is now ready for the digestion.

12.4.2.2 LCS Preparation: A 10-mL portion of DI water is added to a digestion cup. A 0.05-mL portion of LCS/MS Spike Solution is added to the digestion cup. The LCS is now ready for the digestion. The LCSD is prepared in the same manner.

12.4.2.2.1 For Bi, Ge and Y, samples and spike must be prepared separately and spike with the spiking solution from10.6. Spiking with 0.05mL in a 10 mL sample aliquot

12.4.2.3 MS Preparation: A 10-mL portion of randomly chosen client water sample is added to a digestion cup. A 0.05-mL portion of LCS/MS Spike Solution is added to the digestion cup and label tube the sample ID and MS. The MS is now ready for the digestion. The MSD is prepared in the same manner. Pour a third 10 ml aliquot of the chosen spike sample in to digestion tube and label tube with sample ID, do not spike this sample.

12.4.2.4 The LCS/MS spike solutions must be added to the aqueous sample portion in the digestion vessel prior to the addition of any digestion reagents.

Note: When a sample contains oil or has a significant organic odor, use of smaller, well mixed portion may be required due to the matrix. Document the reason for use of smaller portion.

12.4.3 The LIMS sample label must be placed on the sample tube. This label includes the sample ID & digestion date. Label associated QC Samples as

12.4.3.1 MBLKW1-date (metals method blank, 1st soil batch of day);

12.4.3.2 MLCSW1-date (metals soil LCS, 1st soil batch of day);

12.4.3.3 Sample ID- MS-date (metals sample MS);

12.4.3.4 Sample ID- MSD-date; (metals sample MSD).

12.4.4 Sample digestion

12.4.4.1 Adjust the hot block temperature such that the covered thermometer in the block reaches approximately 95˚C.

12.4.4.2 Add 0.1 mL concentrated HNO_3 and 0.05 mL of concentrated HCl to each digestion cup.

12.4.4.3 Place the rack of cups into the hotblock inside a fume hood. Cover each cup with a watch glass. Reduce sample volume

to ~2 mL by gentle heating. Sample must not go to dryness. If sample does go to dryness, the digestion must be repeated for that sample.

12.4.4.4 Remove from heat and allow digestion cups to cool.

12.4.4.5 Wash down the tube walls with DI water and adjust the final volume to 10-mL with DI water. If necessary, allow insoluble material to settle. The digested sample is now ready for analysis.

12.4.4.6 Create a batch ID in LIMS. Enter samples and QC samples on the Samples tab in the batch. Document reagents, standards, supplies and equipment on the Prep Requirements tab in the batch.

13) Troubleshooting

13.1 Prepare new standards, check instrument maintenance, prepare a new curve as needed, etc.

13.2 Proper use and maintenance of pipettes is important to achieve good technique and obtain good LCS, MS, and MSD recoveries.

13.3 Monitor digestion volumes carefully. Any digestate that goes to dryness must be discarded and repeated.

14) Data Acquisition

14.1 Sample preparation data recorded in preparation logbooks is manually entered into the LIMS for later use in analytical and QC calculations. LIMS assigns a prep batch number for the data entered. Record the LIMS prep batch number in the prep log. The original and final sample volumes are entered into LIMS.

15) Calculation, and Data Reduction Requirements

15.1 QC Calculations: LIMS calculates the percent recovery for various QC samples (LCS) according to the following equations:

15.1.1 % Recovery, %R (for MS and MSD Samples)

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SR = Sample Result (unspiked).
SA = Spike Amount Added (mg/L or mg/kg).

15.1.2 % Recovery, %R (for standards and LCS)

$$\%R = \frac{SSR}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SA = Spike Amount Added (mg/L or mg/kg).

15.1.3 RPD (for precision or duplicate evaluation)

$$RPD = \frac{|SR_1 - SR_2|}{½(SR_1 + SR_2)} \times 100$$

Where:
SR_1 = Sample result for duplicate 1.
SR_2 = Sample result for duplicate 2.

15.2 LIMS uses the digestion data (sample volumes) entered to perform calculations and reporting after analysis has been completed.

16) Quality Control, Acceptance Criteria and Corrective Action

16.1 Initial Demonstration of Capability
- 16.1.1 Purpose: Verify the ability to produce data of acceptable precision and bias for a specific instrument type, matrix, method, and analyst.
- 16.1.2 Frequency: Initially during method development, and any time there is a significant change in instrument type, personnel, methodology, or matrix
- 16.1.3 Acceptance Criteria: Four consecutive LCS analysis meeting stated LCS criteria.
- 16.1.4 Corrective Action: Identify and correct the source of error. Reanalyze the demonstration.

16.2 Continuing Demonstration of Capability
- 16.2.1 Purpose: Verify the ability to produce data of acceptable precision and bias for a specific instrument type, matrix, method, and analyst.
- 16.2.2 Frequency: Annual to re-qualify analyst for analysts.
- 16.2.3 Acceptance Criteria: Four consecutive LCS analysis meeting stated LCS criteria or successful PT study.

16.3 Initial Calibration:
- 16.3.1 See associated analytical SOP.

16.4 Initial Calibration Verification (second source).

16.4.1 See associated analytical SOP.

16.5 Continuing Calibration Verification (CCV)
16.5.1 See associated analytical SOP.

16.6 Method Blank (MB)
16.6.1 Purpose: Assess background interference or contamination in the analytical system that may lead to high bias or false positive data.
16.6.2 Frequency: Analyze the Method Blank (MB) with each batch of 20 or less samples processed through the entire method for 3010A and 10 or less samples processed through the entire method for 200.8
16.6.3 Criteria: Refer to relevant section in the ICPMS SOP, HS-MET-003.
16.6.3.1 all analytes of interest must < 1/2 MQL, and common lab contaminants and major cations must be < MQL.
16.6.3.2 Other approved QA program requirements must be followed when the acceptable blank contamination specified in the approved quality assurance project plan differs from the above.
16.6.3.3 If an analyte does exceed the MQL in the MB, the analyte level in the MB must be less than 5% of the regulatory limit associated with the analyte or analyte level in the MB must be less than 5% of the sample result for the same analyte, whichever is greater.
16.6.4 Method Blank Contamination Corrective Action: refer to determinative method SOP HS -MET003.

16.7 Laboratory Control Sample: The LCS is prepared from a calibration standard.
16.7.1 Purpose: Evaluates the performance of the entire analytical system, including all preparation and analysis steps. Assesses the ability of the laboratory/analyst to successfully recover the target analytes from a clean matrix. Contains all target analytes and surrogates.
16.7.2 Frequency: One per batch of 20 or less samples extracted by 3010A or one per batch of 10 or less samples extracted by 200.8. If the spike sample recovery is outside acceptance limits, the results of the LCS are used for determining acceptability of results.
16.7.3 Criteria: Refer to relevant section in the determinative method SOP HS-MET003 (SW-6020, ICPMS).
16.7.4 Corrective Action: The LCS results must be within the acceptance range. If outside this range perform corrective action to solve the source of the error, and re-prepare and re-analyze the sample batch unless the LCS fails high and the samples are non-detect.
16.7.5 Note: When a field sample is not available to perform both an MS and MSD, then include an LCSD with the LCS.

16.8 Matrix Spike (If field sample is not available to perform both an MS and MSD, then perform an LCS and LCSD.
16.8.1 Purpose: Assesses the performance of the method on a particular

matrix.

16.8.2 Frequency: Matrix spikes will be analyzed at a frequency of one spike and spike duplicate for each 20 samples by 3010A or at a frequency of one spike and spike duplicate for each 10 samples by 200.8. If insufficient sample is available for a MS and MSD, then an LCS duplicate must be analyzed and used for the RPD and percent recovery. When duplicate LCS's are used, the same control limits as duplicate matrix spikes will apply.

16.8.3 Criteria: Refer to relevant section in the determinative method SOP HS-MET003 (SW-6020A-EPA200.8, ICPMS).

16.8.4 Corrective Action: If the spike results are outside the acceptance limits for recovery, first determine if the cause is a system error; if so, correct the problem and repeat the MS. If not, the LCS must fall within the acceptance criteria in order for the data to be accepted. The sample results must be flagged for matrix interference.

16.9 Duplicate Samples

16.9.1 Purpose: Provides information on the heterogeneity of the sample matrix. Also determines the precision of the analytical process for that matrix.

16.9.2 Frequency: Once per preparation batch.

16.9.3 Frequency: Duplicates (as MS/MSD or LCS/LCSD) are analyzed on a frequency of one duplicate for each batch of 20 or less samples extracted by 3010A and one duplicate for each batch of 10 or less samples extracted by 200.8.

16.9.4 Criteria: Refer to relevant section in the determinative method SOP HS-MET003 (SW-6020A-EPA200.8, ICPMS).

16.9.5 Corrective Action: If the duplicate results are outside the acceptance limits for relative percent deviation, first determine if the cause is a system error; if so, correct the problem and repeat the duplicate. If not, the LCSD RPD must fall within the acceptance criteria in order for the data to be accepted. The sample results must be flagged to indicate the QC failure as matrix interference.

16.10 Limit of Detection Determination and Verification:

16.10.1 Purpose: Validates the established Detection Limit.

16.10.2 Frequency: Prior to sample analysis and verified quarterly. Verification must is performed on each instrument. The LOD is spiked at 2-3 times the detection limit for single compound analyses and 1-4 times the detection limit for multi-analyte standards.

16.10.3 Acceptance Criteria: The apparent signal to noise ratio at the LOD must be at least three and the results must meet all method requirements for analyte identification (e.g., ion abundance, second-column confirmation, or pattern recognition.) For data systems that do not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least three standard deviations greater than the mean method blank concentrations.

16.10.4 Corrective Action: Repeat the Detection Limit Determination and LOD Verification at a higher concentration or perform and pass two consecutive LOD verifications at a higher concentration and set the LOD at the higher concentration.

16.11 Limit of Quantitation Establishment and Verification:

16.11.1 Purpose: Validates the lower quantitation limit of the analysis.

16.11.2 Frequency: Prior to sample analysis and verified quarterly.

16.11.3 Acceptance Criteria: Data must empirically demonstrate precision and bias at the LOQ.

16.11.4 Corrective Action: Identify and correct the source of error, reanalyze the LOQ. If failure persists re-evaluate the appropriateness of the LOQ.

Initial Demonstration of Proficiency – The laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operation annually and whenever new staff members are trained or significant changes in instrumentation are made.

17) Data Records Management

17.1 All data is stored electronically and/or hard copy for 5 years or 10 years for the state of Louisiana.

17.2 All analytical sequence IDs and standard preparation information must be recorded in the Run logbook. Hardcopy computer printouts of analytical sequences and raw data must be retained and initialed by the analyst (electronic initials are acceptable). To simplify standard and reagent tracking, analyst must attempt to use single lots of reagents and standards.

17.3 Complete all pertinent sections in the respective logbooks. If not-applicable then line out the section and “Z” out or “X” out all large sections of the worksheet that are not used. Make all corrections with single line through, date and initial. Make NO obliterations when manually recording data.

17.4 Logbooks are controlled. Never remove a page from a logbook. Completed logbooks are returned to the QA department when filled and no longer needed in the work area.

17.5 SOP effective date is the date noted in the header or last signature date, whichever is most recent.

18) Contingencies for Handling Out of Control Data

18.1 When method required QC exceedances occur, in every case where sample data quality are affected, the source of the QC exceedance must be determined, corrected and

sample reanalysis carried out when possible.

18.2 When affected sample analysis cannot be repeated due to limitations (i.e. sample availability, or if reanalysis can only be performed after expiration of a sample hold time), the reporting of data associated with exceeded QC data must be appropriately flagged and narrated. This documentation is necessary to define for the data user the effect of the error has upon the data quality of the results reported (e.g. E flag data indicate the result to be only an estimate).

18.3 All analysts must report sufficient comments in laboratory data review checklist for exceeded QC associated with sample results so that project management can further narrate and ensure data qualifiers (flags) are properly assigned to the reported data.

18.4 NCARs must be issued for QC system exceedances. Matrix interferences are reported using the analyte reporting comment section in LIMS or using the Laboratory Data review checklist.

19) Method Performance

19.1 Refer to analytical Method SOP HS-MET003.

20) Summary of Changes

Table 20.1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
9.3	03/05/2020	E. Marinez	Grammatical, punctuation and non-clerical formatting corrections.
9.3 Sec 3	03/05/2020	E. Marinez	Alphabetized Definitions section
9.3 Sections 3.14, 3.15	03/05/2020	E. Marinez	Removed definitions for Surrogate and Surrogate spike as they are unrelated to this SOP.
9.3 Sec 10.3, 10.4	03/05/2020	E. Marinez	Removed references to 1:1 acids. Only Concentrated acids are used.
9.3 Sec 11.1	03/05/2020	E. Marinez	Clarified section regarding calibration

Revision Number	Effective Date	Document Editor	Description of Changes
			checks. Elaborated on DoD requirement for daily pipette check in relation to standard preparation.
9.3 Sec 12.1.4.1	03/05/2020	E. Marinez	Sample reduction to 2.5 mL
9.3 Sec 12.1.4.2	03/05/2020	E. Marinez	Sample reduction to 1.5mL
9.3 Sec 12.1.4.4, 12.2.4.2, 12.2.4.3	03/05/2020	E. Marinez	Corrected acid quantity.
9.3 Sec 12.2.1	03/05/2020	E. Marinez	Corrected section to match procedure.
9.3 Sec 12.4.6	03/05/2020	E. Marinez	Corrected final volume.
9.3 Sec 12.3.3, 12.4.4, Appendix A	03/05/2020	E. Marinez	Corrected section to reflect proportionately reduced acid volumes and clarified temperature requirements since watchglasses are being used.
9.3 Sec 21	03/05/2020	E. Marinez	Included Reference to 200.2
9.2	06/19/2019	E. Howard	Appendix A Added: Brief Work Instruction
9.1	10/15/2018	G. Moulton	Updated to new cover page and added new QA Manager
9.1 Sec 9.3.1	10/15/2018	G. Moulton	Numbered 9.3.1
9.1 Sec 12.3 and 21.4	10/15/2018	G. Moulton	Modified References
9.1 Sec 17.1	10/15/2018	G. Moulton	Modified storage time for data.
09.1 – Section 9.4	08/15/2018	T. Yen	Push filter removed. Sample allow to settle.
09.1 – Sections 12.1, 12.2, 12.3 & 12.4	08/15/2018	T. Yen	Adjust acid volume to be in port potion to 3010A and 200.8.
09.1 – Section 16	08/15/2018	T. Yen	QC frequency updated.
09.1 – Section 21	08/15/2018	T. Yen	Reference updated.
09.0	02/15/2017	T. Yen	Added procedure for 10 mL digestion.

Revision Number	Effective Date	Document Editor	Description of Changes
09.0 – Section 21	02/15/2017	T. Yen	Update method reference.
08.0	02/28/2016	T. Yen	New SOP Format.
08.0 – Section 1.2.	02/28/2016	T. Yen	Li, Bi, Ge and Y prep requires separate spike.
08.0 – Section 4.5.	02/28/2016	T. Yen	Job safety assessment added.
08.0 – Section 8.3 – 12. 4 dissolved samples	02/28/2016	T. Yen	Certain clients required lab filtered dissolved samples to include MB, LCS and MS/MSD to be filtered thru 45 um filter before acidification and digestion.
08.0 – Section 10.8	02/28/2016	T. Yen	Li, Bi, Ge and Y standards.
08.0 – Section 12.2.	02/28/2016	T. Yen	Temperature corrected for 200.8 and reduction volume changed. 3010A and 200.8 digestion separated
08.0 – Section 12.7.7.	02/28/2016	T. Yen	Li, Bi, Ge and Y digestion.
07.2	01/31/2013	T. Yen	Signature Page – New QA Manager and Lab Director.
07.2	01/31/2013	T. Yen	Document Footer – "A Campbell Brothers Limited Company" changed to "An ALS Limited Company" to reflect parent company name change.
03.3 – Sections 10.2 – 10.3	01/31/2013	T. Yen	Acids must be of trace metal grade or better.
03.3 – Sections 10.6 & 10.7	01/31/2013	T. Yen	Spike 0.25 mL of spiking solution from Section 10.4 for to 50 mL aliquot of LCS and MS/MSD.
03.3 – Section 10.8	01/31/2013	T. Yen	New - TCLP Spiking solution.

Revision Number	Effective Date	Document Editor	Description of Changes
03.3 – Section 12.1	01/31/2013	T. Yen	Document pH. If greater than 2 take corrective action.
03.3 – Section 12.4	01/31/2013	T. Yen	If sample must be filtered, then the MB and LCS must be filtered must also be filtered.
03.3 – Sections 16.3 and 16.4	01/31/2013	T. Yen	TCLP spike prepared by spiking 50 mL of leachate blank, leachate LCS, and leachate MS/MSD using 0.5 mL of TCLP spiking mix from 10.8
03.3 – Section 17.2	01/31/2013	T. Yen	Statement about attempt to use one lot of reagent or standard to make standard/reagent tracking easier.
07.1	01/20/2012	J. Cady	Minor document revision.
06.0	03/31/2011	I. Williams	Major template revision.

21) References and Related Documents

21.1 Method 3010A, Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy", Test Methods for Evaluating Solid Waste Physical/Chemical Methods, Revision 1, July 1992, USEPA OSWER.

21.2 Method 200.8, Determination of Trace Metals in Waters and Wastes by ICP/MS, (Section 11.2 – Aqueous Sample Preparation – Total Recoverable Metals, Revision 5.4, 1994, USEPA EMSL ORD, Cincinnati, Ohio.

21.3 Method 200.2, Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements, Revision 2.8, 1994, USEPA EMSL ORD, Cincinnati, Ohio.

21.4 Current TNI Standards.

21.5 Current Department of Defense Quality Systems Manual.

22) Appendix

Appendix A: Brief Work Instruction for SOP HS-MET002

Sample digestion by Method 3010A or 200.8 for 10mL sample volume

Note: This Brief Work Instruction does not contain all information necessary to prepare samples for metals analysis. The full procedure in SOP HS-MET002 must be followed as written.

Excerpt from HS-MET002, Revision 9.3

12.2.4 Sample Digestion by Method 3010A for 10 mL sample volume.

12.2.4.1 Adjust the hot block temperature such that the covered thermometer in the block reaches 90-95˚C. Rotate the thermometer to different hot block cells daily.

12.2.4.2 Add 0.2 mL concentrated HNO3 to each digestion cup. Cover each cup with a watch glass and place the rack of cups into the hot block. Do not allow the digesting samples to boil, but slowly evaporate them to ~2-mL. Do not allow samples to go dry. If a sample goes dry, discard the cup and re-prepare the sample in a new batch.

12.2.4.3 Add 0.1mL of concentrated HCl, cover the digestion cup, and reflux for an additional 15 minutes to dissolve any precipitate or residue resulting from evaporation.

12.2.4.4 Wash down the tube walls and watch glass with DI and adjust the final volume to 10mL with DI. Allow sample to settle. If needed to remove silicates and other insoluble material that could clog the ICP-MS, allow the sample to settle before gently decanting or pipetting aliquots for analysis.

12.2.4.5 LIMS generated labels may now be affixed to the corresponding cups. Labels are heat sensitive and will turn black if applied to tubes prior to digestion.

12.2.4.6 Create a batch ID in LIMS. Enter samples and QC samples on the Samples tab in the batch. Document reagents, standards, supplies and equipment on the Prep Requirements tab in the batch.

Excerpt from HS-MET002, Revision 9.3

12.4.4 Sample digestion by Method 200.8 for 10mL sample volume

12.4.4.1 Adjust the hot block temperature such that the covered thermometer in the block reaches approximately 95˚C.

12.4.4.2 Add 0.1 mL concentrated HNO3 and 0.05 mL of concentrated HCl to each digestion cup.

12.4.4.3 Place the rack of cups into the hotblock inside a fume hood. Cover each cup with a watch glass. Reduce sample volume to ~2 mL by gentle heating. Sample must not go to dryness. If sample does go to dryness, the digestion must be repeated for that sample.

12.4.4.4 Remove from heat and allow digestion cups to cool.

12.4.4.5 Wash down the tube walls with DI water and adjust the final volume to 10-mL with DI water. If necessary, allow insoluble material to settle. The digested sample is now ready for analysis.

12.4.4.6 Create a batch ID in LIMS. Enter samples and QC samples on the Samples tab in the batch. Document reagents, standards, supplies and equipment on the Prep Requirements tab in the batch.

SOP For The Analysis of Metals By Inductively Coupled Plasma Mass-Spectrometry, Methods SW846-6020A/EPA 200.8

DOCUMENT ID: HS-MET003, REV 8.5

Approved By: Hoai Van
Technical and Laboratory Director, Hoai Van

Date: 03/05/2020

Prepared By: Erica H Marinez
Quality Assurance Manager, Erica Marinez

Date: 03/05/2020

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METALS BY INDUCTIVELY COUPLED PLASMA MASS-SPECTROMETRY – METHOD SW846 6020A / EPA 200.8

1) Scope and Applicability

1.1 Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of µg/L concentrations of a large number of elements in water samples and in waste extracts or digests. When dissolved constituents are required, samples must be filtered and acid-preserved prior to analysis. No digestion is required prior to analysis for dissolved elements in water samples. Acid digestion is required for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are required.

1.2 ICP-MS has been applied to the determination of over 60 elements in various matrices. Method detection limits, Method Quantitation Limits and linear ranges will vary with the matrices, instrumentation, and operating conditions.

1.3 SW-846 Method 6020A is used to determine the analytes listed in Table 22.1. The table lists more elements than the current version of Method 6020A and EPA method 200.8. The additional elements are included based upon results of demonstrations of precision and accuracy and completion of method detection limit studies for aqueous and solid matrix.

1.4 Internal standards are used for each analyte determined by ICP-MS. The internal standards used are ^{6}Li, ^{72}Ge, ^{115}In, and ^{209}Bi.

1.5 This method is applicable for the calculation of Hardness as $CaCO_3$ as prescribed in Method 2340 B utilizing calcium and magnesium result from this procedure.

2) Summary of Procedure

2.1 Prior to analysis, samples which require total ("acid-leachable") values must be digested using appropriate sample preparation methods (such as SW-846 Methods 3010A, 3050B or EPA Method 200.8.

2.2 Method 6020A and Method 200.8 describe the multi-elemental determination of analytes by ICP-MS. The method measures ions produced by a radio frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

3) Definitions

3.1 Demonstration of Capability (DOC): procedure to establish the ability of the laboratory

to generate acceptable accuracy and precision which is included in many of the EPA's analytical test methods. In general, an initial DOC procedure involves the analysis of four separate Laboratory Control Samples (LCS) as prescribed by the analytical method Each LCS must meet the specified LCS acceptance limits for percent recovery, and standard deviation. Ongoing DOC requirements are met by acceptable analysis of annual NELAC accepted proficiency test (PT) samples, or by the analysis of four LCS if PT samples are not available. DOC must be performed annually, if not performed within one calendar year, analyst must repeat initial demonstration prior to sample analysis

3.2 Exception Report: Appropriate comments reported with the associated sample batch that addresses sample anomalies such as demonstrated sample matrix effects.

3.3 Laboratory Control Sample (LCS): A sample matrix, free from the analytes of interest, spiked with known amounts of analytes or a material containing known and verified amounts of analytes.

3.4 Limit of Detection (LOD): an estimate of the minimum amount of a substance that an analytical process can reliably detect. The LOD is determined annually through the execution of a Method Detection Limit Study, and verified quarterly through the analysis of a Detectability Check Sample (DCS).

3.5 Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met.

3.6 Matrix Spike (MS): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available.

3.7 Matrix Spike Duplicate (MSD): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of recovery for each analyte.

3.8 Matrix: The substrate (e.g., water, soil, etc.) which may contain the analyte of interest.

3.9 Method Blank (MBLK): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analysis.

3.10 Method Detection Limit (MDL) study: a procedure described in 40CFR Part 136, Appendix B, that describes how to produce an MDL, a reporting element of certain EPA methods. The MDL study is one approach to determine the LOD.

3.11 NCAR: Nonconformance Corrective Action Report (refer to SOP HSQS003, current revision).

3.12 Reagent Water: Deionized (DI) reagent purified by filtration thru mix resin and carbon beds. For additional purification, the DI water is passed through an activated carbon filter.

3.13 Preparation Batch: A defined set of one to 20 client samples of the same matrix, meeting the batch definition criteria, and prepared for analysis within 24 hours. The preparation batch must also contain the required determinative method defined batch QC samples (e.g. method blank, laboratory control samples, matrix spikes, duplicates, etc.).

3.14 Surrogate: An analyte added to a sample, which is unlikely to be found in any sample at significant concentration, and which is added directly to a sample aliquot in known amounts before any sample processing procedures are conducted. It is measured with the same procedures used to measure other sample components. The purpose of the surrogate analyte is to monitor method performance with each sample.

3.15 Surrogate Spike: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environmental samples and is added to them for quality control purposes.

3.16 Batch: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** is composed of one (1) to twenty (20) environmental sample of the same quality systems matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be twenty-four (24) hours. An **analytical batch** is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.

3.17 Retention Time Window: The length of time between sample injection and the appearance of a peak at the detector. The window of time is established for each analyte or group of analytes and is set for complete elution of analyte peaks. It is based upon a series of analyses and statistical calculations that establish the measured band on the chromatogram that can be associated with a specific analyte or group of analytes.

3.18 Second Source Calibration Verification (ICV): A standard obtained or prepared from a source independent of the source of standards for the ICAL. Its concentration should be at or near the middle of the calibration range. It is performed after the ICAL.

3.19 Calibration Standard (CAL): A solution prepared from the primary dilution standard solution or stock standard solutions and the surrogate analyte. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.20 Linear Calibration Range (LCR): The concentration range over which the instrument response is linear

3.21 Instrument Performance Check Sample (IPC): A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.22 Continuing Calibration Verification (CCV): A known interference free matrix spiked with a known concentration of the target analyte. The CCV is prepared from the same source that was used to prepare the calibration standards, and is used to verify that the instrument calibration is in control before and after sample analysis.

3.23 Quality Control Sample (QCS): A solution of method analytes of known concentrations that is used as the spiking solution for the LCS. The QCS is obtained from a source external to the laboratory and different from the source of calibrations standards. It is used to check laboratory performances with externally prepared test materials.

3.24 Detectability Check Sample (DCS): a sample spiked at 2 to 3 times the calculated LOD (refer to SOP HS-QS006, LOD and LOQ), or alternatively spiked near the LOQ.

3.25 Globally Harmonized System of Classification and Labeling of Chemicals (GHS) – common and coherent approach to classifying chemicals and communicating hazard information on labels and safety data sheets.

3.26 Safety Data Sheets (SDS): Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

4) Health and Safety Warnings

4.1 Lab Safety: Due to various hazards in the laboratory, safety glasses and laboratory coats or aprons must be worn at all times while in the laboratory. In addition, gloves and a face shield should be worn when dealing with toxic, caustic, and/or flammable chemicals.

4.2 Chemical Hygiene: The toxicity or carcinogenicity of each reagent used has not been precisely defined; however, each chemical used should be treated as a potential health hazard. Exposure to laboratory reagents should be reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets (MSDS) is available to all personnel involved in these analyses.

4.3 Waste Management: The principal wastes generated by this procedure are the method-required chemicals and standards. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required. Laboratory procedures in SOP HS-SAF-001, Waste Disposal Procedures, must be followed.

4.4 Pollution Prevention: The materials used in this method pose little threat to the environment when recycled and managed properly. The quantities of chemicals purchased should be based on the expected usage during its shelf life. Standards and reagents should be prepared in volumes consistent with laboratory use to minimize

the volume of expired standards or reagents to be disposed.

4.5 Job Safety Assessment

HAZARD ASSESSMENT		
Job Task #1:	**Hazards**	**Preventative Measures**
Cooler and sample handling.	Injury due to lifting heavy coolers and placing/removing samples to/from storage locations. .	Use proper lift technique and cart to move coolers and stools/stepladder when working reaching above shoulder height in sample storage cooler.
Job Task #2:	**Hazards**	**Preventative Measures**
Sample container handling and preservation checks.	Exposure to possible hazardous chemicals.	Use of proper PPE, i.e. Lab coats, safety glasses, gloves, etc.
Job Task #3:	**Hazards**	**Preventative Measures**
Use of utility knives to cut open cooler and seals.	Cuts.	Use proper safety with auto retracting blade and proper cutting techniques. Always cut away from body.
Job Task #4:	**Hazards**	**Preventative Measures**
Unpacking coolers and searching for sample within the coolers.	Possible cuts from broken sample containers.	Wear proper protective equipment such as Kevlar kit gloves and use of broken glass containers.
Job Task #5:	**Hazards**	**Preventative Measures**
Glassware Washing.	Possible cuts from broken glassware.	Wear proper protective equipment such as Kevlar kit gloves.
Job Task #6:	**Hazards**	**Preventative Measures**
Sample Testing and/or standard and reagent/solvent use.	Exposure to possible hazardous chemicals.	Wear gloves, safety glasses and lab coat. Work in fume hood and avoid skin contact with solvents/acids/reagents. Know location of safety shower, first aid kits, spill kits and fire extinguisher when handling flammable material.

5) Cautions

5.1 Routine preventative maintenance must be performed and documented to assure optimum instrument performance. Refer to the current revision of SOP HS-EQ004 for preventative maintenance schedules.

6) Interferences

6.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Since commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, very high ion currents at adjacent masses can also contribute to ion signals at the mass of interest. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require resolution improvement, matrix separation, or analysis using another verified and documented isotope, or use of another method.

6.2 Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Examples include $ArCl^+$ ions on the ^{75}As signal and MoO^+ ions on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below the natural isotope abundances from the literature, the most precise coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 %) counting statistics. Because the ^{35}Cl natural abundance of 75.77 % is 3.13 times the ^{37}Cl abundance of 24.23 %, the chloride correction for arsenic can be calculated (approximately) as follows (where the $^{38}Ar^{37}Cl^+$ contribution at m/z 75 is a negligible 0.06 % of the $^{40}Ar^{35}Cl^+$ signal):

6.2.1 Corrected arsenic signal (using natural isotopes abundances for coefficient approximations) = (m/z 75 signal) - (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal)

6.2.2 Where the final term adjusts for any selenium contribution at 77 m/z.

6.3 NOTE: Arsenic values can be biased high when the net signal at m/z 82 is caused by ions other than $^{82}Se^+$, (e.g., $^{81}BrH^+$ from bromine wastes). Similarly,

6.3.1 Corrected cadmium signal (using natural isotopes abundances for coefficient approximations) = (m/z 114 signal) - (0.027) (m/z 118 signal) - (1.63) (m/z 108 signal)

6.3.2 Where last 2 terms adjust for any Sn or MoO^+ contributions at m/z 114.

6.4 NOTE: Cadmium values will be biased low when $^{92}ZrO^+$ ions contribute at m/z 108, but use of m/z 111 for Cd is even subject to direct ($^{94}ZrOH^+$) and indirect ($^{90}ZrO^+$) additive interferences when Zr is present.

6.5 NOTE: As for the arsenic equation above, the coefficients in the Cd equation are ONLY illustrative. The most appropriate coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 %) counting precision.

6.6 The accuracy of these types of equations is based upon the constancy of the OBSERVED isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found to be reliable, e.g., oxide levels can vary. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by the use of an appropriate oxide IS previously demonstrated to form a similar level of oxide as the interferent. This type of correction has been reported for oxide-ion corrections using ThO^+/Th^+ for the determination of rare earth

elements. Techniques, such as the use of aerosol desolvation and/or mixed plasmas have been shown to greatly reduce molecular interferences. These techniques can be used provided that method detection limits, accuracy, and precision requirements for analysis of the samples can be met.

6.7 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) have been recommended to minimize solid deposition. An IS can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes. When the intensity level of any IS is less than 70%, the sample must be reanalyzed after a five-fold (1+4) or greater dilution has been performed.

6.8 Memory interferences can occur when there are large concentration differences between samples or standards that are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of the memory interferences that are observed. The rinse period between samples must be long enough to eliminate significant memory interference.

6.9 The total recoverable sample digestion procedure given in 200.8 is suitable for the determination of silver in aqueous samples containing concentrations up to 100 ppb. For the analysis of wastewater samples, containing higher concentrations of silver, succeeding smaller volume, well mixed sample aliquots must be prepare until the analysis solution contains <100ppb silver. The extraction of solid samples containing concentrations of silver >50 ppm should be treated in a similar manner.

7) Personnel Qualifications and Responsibilities

7.1 General Responsibilities - This method is restricted to use by or under the supervision of analysts experienced in the method.

7.2 Analyst - It is the responsibility of the analyst(s) to:

- 7.2.1 Each must read and understand this SOP and follow it as written. Any deviations or non-conformances must be documented and submitted to the QA Manager for approval.
- 7.2.2 Produce method compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP (HS-QS-009).
- 7.2.3 Complete the required initial demonstration of proficiency before performing this procedure without supervision.
- 7.2.4 Complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 7.2.5 The analysts must submit data for peer or supervisor review.

7.3 Section Supervisor - It is the responsibility of the section supervisor to:

- 7.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.
- 7.3.2 Ensure analysts have completed the required initial demonstration of proficiency before performing this procedure without supervision.

7.3.3 Ensure analysts complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.

7.3.4 Ensure analysts produce method compliant data that meet all quality requirements using this procedure and the Data Reduction, Review and Validation SOP.

7.4 Project Manager - It is the responsibility of the Project Manager to ensure that all method requirements for a client requesting this procedure are understood by the laboratory prior to initiating this procedure for a given set of samples.

7.5 QA Manager: The QA Manager is responsible for

7.5.1 Approving deviations and non-conformances

7.5.2 Ensuring that this procedure is compliant with method and regulatory requirements,

7.5.3 Ensuring that the analytical method and SOP are followed as written through internal method and system audits.

8) Sample Collection, Handling, and Preservation

8.1 Aqueous samples are collected in 500 mL plastic containers and preserved to a pH of <2 with HNO_3. Refrigerated storage is not required.

8.2 Soil samples are collected in 4 oz wide-mouth glass containers. Refrigerated storage is not required unless mercury is also required.

8.3 The holding time is six months for waters and soils.

9) Equipment and Supplies

9.1 Agilent 7500c and Agilent 7500ce with HMI (High Matrix Introduction) capability, 7700x (with HMI/Dilution Gon), 7700x ISIS-DS (Integrated Sample Introduction System – Discrete Sampling). These systems are capable of providing resolution, better than or equal to 1.0 amu at 5% peak height. The systems must have a mass range from at least 6 to 240 amu and data systems that allow corrections for isobaric interferences and the application of the IS technique. All use a mass-flow controller for the nebulizer argon and a peristaltic pump for the sample delivery.

9.2 Argon gas supply: high-purity grade (99.99%), and on-site bulk tank supply is used.

9.3 Various Class A volumetric flasks: Various sizes (must meet calibration standards stated in HS-EQ003, current version).

9.4 Fixed and Variable volume pipets: Various sizes (must meet calibration standards stated in HS-EQ003, current version).

10) Standards and Reagent

10.1 Note: Store all purchased standards according to manufacturer specifications. Store standard solutions (remaining stock, composite, calibration and surrogate) in glass

containers with Teflon™ lined lids or in accord with the manufacturer's recommended conditions. All purchased stock standard solutions must be replaced after reaching the manufacturer's expiration date assigned to the standard. All laboratory prepared standard solutions must be replaced after six months or sooner if routine QC indicates a problem or if required by reference method. An assigned expiration date of a lab prepared standard cannot exceed the manufacturer's expiration date for any component used in the standard formulation. When analyzing all standards, lot numbers must be associated with the run batch or prep batch. All standard container must be labeled for content and lot numbers. Internal prepared container must also include the GHS safety labeling info. All standards, reagents and supplies must be check for purity and concentration in accordance with corporate SOP CE-GEN-CE007 and HS-QS001 (HS-QS001 is equivalent to GEN-CE007.

10.2 DI Water: Deionized (DI) water produced from ion exchange purification resulting in water having and inline resistance > 17 megohm-cm (anion -cation free water).

10.3 Nitric Acid, HNO_3, Concentrated, trace-metal grade or better.

10.4 Hydrochloric Acid, HCL, Concentrated, trace-metal grade or better.

10.5 Instrument calibration standards: Instrument calibration standards are purchased from an approved vendor. Adhere to the manufacturer established expiration date. Stock standards required to perform an instrument calibration are:

- 10.5.1 Calibration Standard #1A, 20 mg/L: Elements included in this standard are Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Th, Tl, U, V, Zn, Mo, Sb. This standard is purchased commercially from an approved vendor (Inorganic Venture 2008CAL-2 and 2008CAL-1 or equivalent).
- 10.5.2 Calibration Standard #2, 500 mg/L: Elements included in this standard are Fe, K, Ca, Na, Mg. This standard is purchased commercially from an approved vendor (Inorganic Venture IV-Stock-33, or equivalent).
- 10.5.3 Strontium Standard, Sr, 1000 mg/L. This standard is purchased commercially from an approved vendor (SPEX Cat# CLSR2-2Y, or equivalent).
- 10.5.4 Titanium Standard, Ti, 1000 mg/L. This standard is purchased commercially from an approved vendor (SPEX Cat# CLTI9-2Y, or equivalent).
- 10.5.5 Tin Standard, Sn, 1000 mg/L. This standard is purchased commercially from an approved vendor (RICCA Cat# ASN1KH-100, or equivalent).

10.6 Daily multi-level calibration standards: These standards are prepared daily using the stock solutions listed in §10.5.

- 10.6.1 Sr/Ti/Sn Intermediate standard, 10 mg/L: Add 1 mL each of the elements listed in 10.5.3, 10.5.4 and §10.5.5 to a 100 mL flask containing 50 mL DI water and 5 mL HNO_3. Dilute to volume with DI water.
- 10.6.2 Intermediate daily calibration mix, 500/50,000 µg/L: This calibration mix contains the elements listed in 10.5.1 and §10.6.1 at a concentration of 500 µg/L, and the elements listed in § 10.5.2 at 50,000 µg/L.
  - 10.6.2.1 Add 1.25 mL of Cal Std #1 (§10.5.1), 2.5 mL of Cal Std#2 (§10.5.2), and 2.5 mL of Sr/Ti/Sn mix (§10.6.1) to a 50 mL volumetric flask containing 20 mL DI water, 2.5 mL HNO_3, and 0.5 mL HCl. Dilute to volume with DI water.
- 10.6.3 Working daily Calibration Standards: Prepare daily according to Table 10.6.3.
- 10.6.4 Working Calibration Standard for Lithium, Li: Prepare daily by first preparing an Intermediate Mix as described in 10.6.2 using 10.13 followed by diluting to different concentrations as shown in table 10.6.3.

Table 0.6.3 Calibration Standard Preparation Table

Table 10.6.3 Calibration Standard Preparation Table						
	Calibration Level	Daily Cal Mix		HNO_3 Added (mL)	HCL Added (mL)	Final Volume (mL)
Cal Blk	0	0 mL	--	2.5	0.5	50
Cal 5	200 / 20,000	20 mL	10.6.2	2.5	0.5	50
Cal 4	100 / 10,000	10 mL	10.6.2	2.5	0.5	50
Cal 3	10 / 1,000	5 mL	Cal 4	2.5	0.5	50
Cal 2	5 / 500	2.5 mL	Cal 4	2.5	0.5	50
Cal 1	2 / 200	1 mL	Cal 4	2.5	0.5	50

10.7 Initial Calibration Verification (ICV) Solution – The ICV solution is prepared as a second source for initial calibration verification. This standard is analyzed at the same concentration as the CCV (Table 10.11). The following stock standards must be obtained from a second source (different vendor, or if from the same vendor, obtain a different lot). Adhere to the manufacturer established expiration:

10.7.1 Instrument Check Standard #1, 10 mg/L: Elements included in this standard are Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Sb, Tl, U, V, Zn. This standard is purchased commercially from an approved vendor (SPEX Cat#CL-ICS-1, or equivalent).

10.7.2 Instrument Check Standard #2, 200 mg/L: Elements included in this standard are Fe, K, Ca, Na, Mg. This standard is purchased commercially from an approved vendor (SPEX Cat# CL-ICS-3, or equivalent).

10.7.3 Instrument Check Standard #3, 10 mg/L: Elements included in this standard are Sr, Ti, Sn, and Mo. This standard is purchased commercially from an approved vendor (SPEC Cat# CL-ICS-5, or equivalent).

10.7.4 Instrument Check Standard #4, 1000 mg/L: This is a dedicated standard for Uranium (U). Purchase commercially from an approved vendor (Ricca Cat #AU1KN-100 or equivalent).

10.7.4.1 Intermediate Check Standard, 10 mg/L "U": To a 50 mL volumetric Flask, fill half with DI Water. Add 2.5 mL HNO_3 and 0.5 mL of 10.7.4 "Li" Standard. Prepare to volume with DI Water.

10.7.5 Instrument Check Standard #5, 1000 mg/L: This is a dedicated standard for Lithium (Li). Purchased commercially from an approved vendor (Absolute Standard Cat #56003 or equivalent).

10.7.5.1 Intermediate Check Standard, 10 mg/L "Li": To a 50 mL volumetric Flask, fill half with DI Water. Add 2.5 mL HNO_3 and 0.5 mL of 10.7.5 "U" Standard. Prepare to volume with DI Water.

10.7.6 Working Instrument Check Standard (See Table 10.11 for concentrations):

10.7.6.1 Add 0.5 mL of Inst. Check Std #1 (§ 10.7.1), 2.5 mL of Inst. Check Std #2 (§10.7.2), 0.5 mL of Inst. Check Std #3 (§10.7.3), and 0.5 mL of Intermediate Check Standard #4. to a 50 mL volumetric flask containing 20 mL DI water, 2.5 mL HNO_3, and 0.5 mL HCl. Dilute to volume with DI water.

10.7.7 Working Instrument Check Standard (0.1 mg/L): Add 0.5 mL of instrument check standard 10.7.5.1 to a 50 mL volumetric flask containing 20 mL DI Water, 2.5 mL HNO_3 and 0.5 mL HCl. Dilute to volume with DI Water.

10.8 Initial Calibration Blank (ICB)/Rinse Blank/Continuing Calibration Blank (CCB): prepare fresh every day by adding 50 mL HNO_3 and 10 mL of HCL to a final volume of 1 liter with DI water.

10.9 Interference Check Solution #1: Table 10.9 outlines the concentrations of common

interferents used in this solution. The solution is purchased commercially from an approved vendor (SPEX Cat# CL-INT-A2, or equivalent). Adhere to the vendor's expiration date.

Table 10.9 Interference Check Solution Constituents

Table 10.9 Interference Check Solution Constituents	
Interferent	Concentration (ppm)
Cl^-	10,000
C	2,000
Al, Ca, Fe, K, Mg, Na, P, S	1,000
Mo, Ti	20

10.9.1 Interference Check Sample A (ICSA): The ICSA is prepared by diluting 5 mL of Interference Check Solution #1 (§10.9) to 50 mL volumetric flask containing 20 mL DI water, 2.5 mL HNO_3, and 0.5 mL HCL. Dilute to volume with DI water See Table 10.11 for ICSA metals concentrations. Prepare fresh daily.

10.9.2 Interference Check Sample AB (ICSAB): The purpose of this solution is to notice the impact of ICSA on common trace analytes of interest (Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, K, Se, Ag, Sr, Tl , Sn, V and Zn). To prepare this solution, add 0.5mL Instrument Check Standard #1 (§10.7.1) and 5 mL of the Interference Check Standard (§10.9) to a 50 mL volumetric flask with 20 mL DI water, 2.5 mL HNO3, and 0.5 mL HCL. Dilute to volume with DI water. See Table 10.11 for ICSAB concentrations. Prepare fresh daily.

10.10 Continuing Calibration Verification (CCV): see Table 10.6, Cal 4 (100/10,000 ppb std) and Table 10.11.

10.11 Linear Dynamic Range Check Sample (LDR), 2000/200,000 ppb solution – Add 1 mL of Cal Std #1 (§10.5.1), 2 mL of Cal Std #2 (§10.5.2) and 2 mL of Sr/Ti/Sn mix (§10.6.1) to a 10 mL volumetric flask and dilute to volume with DI water.

Table 0.11 ICV, CCV, ICSA, ICSAB and LDR Solutions

Table 10.11– ICV, CCV, ICSA, ICSAB and LDR Solutions				
	ICV / CCV	ICSA	ICSAB	LDR
Metal	µg/L	µg/L	µg/L	µg/L
Aluminum	100	100,000	100,100	2000
Antimony	100	0	100	2000
Arsenic	100	0	100	2000
Barium	100	0	100	2000
Beryllium	100	0	100	2000
Cadmium	100	0	100	2000
Calcium	10000	100,000	110,000	200000
Chromium	100	0	100	2000
Cobalt	100	0	100	2000
Copper	100	0	100	2000
Iron	10000	100,000	110000	200000
Lead	100	0	100	2000
Magnesium	10000	100,000	110000	200000

Table 10.11– ICV, CCV, ICSA, ICSAB and LDR Solutions				
	ICV / CCV	ICSA	ICSAB	LDR
Metal	µg/L	µg/L	µg/L	µg/L
Manganese	100	0	100	2000
Molybdenum	100	2000	2100	2000
Nickel	100	0	100	2000
Potassium	10000	100,000	110000	200000
Selenium	100	0	100	2000
Silver	100	0	100	500
Sodium	10000	100,000	110000	200000
Strontium	100	0	100	2000
Thallium	100	0	100	2000
Tin	100	0	100	2000
Titanium	100	2000	2100	2000
Vanadium	100	0	100	2000
Zinc	100	0	100	2000
Uranium	100	0	100	2000
Lithium	100	0	100	2000

10.12 Internal Standard Stock, 10 mg/L: This standard contains Li6, Ge72, In115, Bi209, Sc45, Y89, Ho165, and Tb159. Purchase from an approved vendor. Adhere to the vendor's expiration.

10.12.1 Internal Standard Mix (1 mg/L): Prepare this standard by diluting a 5 mL aliquot of the 10ppm IS Stock Standard to a final volume of 50 mL in DI water. Prepare fresh daily.

10.13 Tuning Stock Solution, 10-mg/L (SPEX Cat# CL-Tune-1, or equivalent): Containing the following metals – Barium (Ba), Beryllium (Be), Cerium (Ce), Cobalt (Co), Indium (In), Lithium (Li), Magnesium (Mg), Lead (Pb), Rhodium (Rh), Thallium (Tl), Uranium (U), Yttrium(Y). This solution is also used for calibration when needed for Li. Purchase from an approved vendor. Adhere to vendor's expiration.

10.13.1 Method Tune Solution (for 6020A and 200.8), 10-ppb: Dilute 1 mL of Tuning Stock Solution (§ 10.13) to a final volume of 1000 mL with DI water. Prepare fresh daily

10.14 Low-Level ICV/CCV Check Standard: See Cal 1 and Cal 2, from Table 10.6.

10.15 Instrument Check Standard (10ppm/1000ppm): Purchase from an approved vendor. Adhere to the manufacturer's expiration date.

11) Method Calibration

11.1 A Volumetric equipment calibration checks must be performed as required by SOP HS-EQ-003.

11.2 Start-up Procedure

11.2.1 Visual check of instrument:

11.2.1.1 Inspect auto sampler tubing; if the tubing has become flat, replace it with new tubing.

11.2.1.2 Inspect sampling cone and skimmer cone for deposit build up; if build up is noticed, either clean or replace cone.

11.2.1.3 Inspect Argon gas flow; Make sure there is 700 PKAG pressure in the dewer and 90 PSI coming through to the instrument. If not, check gas supplies or change dewer.

11.2.2 Turn plasma on and let the instrument stabilize for approximately 30-45 minutes.

11.3 Typical system parameters are:

11.3.1.1 RF power = 1500V

11.3.1.2 RF matching = 1.5 – 1.8V

11.3.1.3 Sample Depth = 10 mm

11.3.1.4 Carrier gas + Dilution gas = 0.9 – 1.1L/ min

11.3.1.5 Peripump = 0.1 rps

11.3.1.6 S/C Temp = 2˚C

11.3.1.7 Integration Time = 0.1s for all analytes except Internal Stds and As, Se, Cd, Sb = 0.3s

11.3.1.8 Number of Exposures = 3

11.3.2 Small adjustments with the EM voltage and/or maintenance are performed as needed to meet the HP criteria.

11.3.3 A P/A factor is performed as necessary by analyzing a 200-ppb standard (Cal 5) and a 2000 ppb LDR standard.

11.4 The tune requirements for both methods are evaluated by analysis of the same solution (§10.13.1)

11.4.1 EPA 200.8 Method Tune: Analyze the tune solution (§10.13.1) at least five integrations prior to the calibration. The 200.8 Method Tune Mass parameters are Beryllium (9), Magnesium (24), Cobalt (59), Indium (115), and Lead (208).

11.4.1.1 Acceptance Criteria: Achieve an RSD for the tune elements of ≤ 5 % with the mass calibrations for each being within 0.1 amu of the true value of each mass. The resolutions must be approximately 0.75 amu at 5 % peak height.

11.4.2 6020A Method Tune: Analyze the tune solution (§10.13.1) at least four integrations prior to the calibration. The 6020A Method Tune Mass parameters Lithium (7), Cobalt (59), Yttrium (89), Indium (115) and Thallium (205).

11.4.2.1 Acceptance Criteria: achieve an RSD for the tune elements of ≤5 % and the mass calibrations for each must be within 0.1 amu of the true value of each mass. The resolution must be less than 0.9 amu full width at 10 % peak height.

11.5 Single point calibrations are not employed for this procedure. Multipoint calibrations are performed by analyzing a blank and at least three standards.

11.5.1 Typical concentrations for trace element calibrations are 2.0, 5.0, 10.0, 100 and 200 ppb

11.5.2 Typical concentrations for the cation of Ca, Mg, Na, K, and Fe calibrations are 200, 500, 1000, 10000 and 20000 ppb

11.6 Initial Calibration Curve: A linear regression (first order fit) of the instrument response

versus the concentration of the standards is employed for quantitation. The instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). The regression will produce the slope and intercept terms for a linear equation in the form: $y = ax + b$

Where:

y = instrument response (peak area)
a = slope of the line (coefficient of x)
x = concentration of the calibration standard
b = intercept

11.6.1 NOTE: The analyst must not force the line through the origin, but have the intercept calculated from the four (or five) data points. The regression calculation will generate a correlation coefficient (r) that is a measure of the goodness of the fit of the regression line to the data. In order to be used for quantitative purposes, the correlation coefficient (r) must be greater than or equal to 0.998.

11.7 Initial Calibration Verification (ICV): The initial calibration verification standard is prepared at the mid-point calibration standard concentration (Table 10.6, Cal 4) using second source standards. The ICV is run after each new initial calibration curve. Analytes must fall within a ± 10 % range of the initial calibration for acceptance. See §10.7.

12) Sample Preparation/Analysis

12.1 Samples are prepared using a SW3010A, SW3050B digestion method See HS-MET001 or HS-MET002, current revision.

12.2 Samples are then transferred to 15 mL culture tubes (PPE) and placed in the rack in a sequential order. Samples are analyzed for dissolved metals may not require digestion, but digestion is typically performed to assure a uniform sample matrix and prevent potential IS failures. The auto sampler introduces the sample to the ICP via the peristaltic pump and adds an equal level of IS to all samples (calibration, client and QC samples). When a samples analyte response fall above the linear dynamic range, perform a dilution and reanalyze the diluted sample.

12.3 Typical Analytical Sequence (after the instrument has met tune requirements) :

12.3.1 Initial Calibration curve, five standards and a blank
12.3.2 Initial Calibration Verification standards
12.3.3 Initial Calibration Blank
12.3.4 Low Level Calibration Check Standard (or LLICV)
12.3.5 Interference Check Samples A/AB (ICSA/ICSAB)
12.3.6 Method blank
12.3.7 Laboratory Control Sample
12.3.8 Client sample
12.3.9 Duplicate
12.3.10 Matrix spike
12.3.11 Post-Dilution Spike (SW6020A only, one PDS per each batch of 20 or less)
12.3.12 Dilution Test (SW6020B only, one Dilution Test per each batch of 20 or less)
12.3.13 Continuing Calibration Checks (CCB/CCV) – every ten samples and at the end of the sequence.
12.3.14 Interference Check Samples A/AB (ICSA/ICSAB) – every 12 hours and at the

end of the sequence.

12.4 Post-Digestion Spike (PDS) Addition (SW6020A only): When MS or MSD results fall outside control limits. A Post-Digestion spike evaluation of the matrix must be performed. An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 80 – 120% of the known value or within the laboratory derived acceptance criteria. When performing the analysis of TCLP leachates, should the PDS test results fall outside the acceptance limits, the method of standard additions may be required, provided the analyte is detected at a level that potentially may exceed the RCRA TCLP regulatory limit for the metal.

12.4.1 Post Digestion Preparation (SW6020A only): To a 10 ml portion of sample digest, add a 0.1 ml volume of the check standard (§10.15), mix and analyze by the ICPMS. The theoretical spike is the 100 ppb for the trace metals and 10000 ppb for the minerals.

12.5 Dilution test (SW6020A only): For analyte concentrations within the instrument linear range and sufficiently high (e.g. a factor of at least 10 times greater than the MQL), an analysis of a fivefold (1+4) dilution must agree within ± 10% of the original determination. If not, an interference effect must be suspected. Provide a comment regarding the anomaly in the data review checklist.

12.6 When analyzing for Li, there are no associated Internal Standard since it will conflict with Li6. Run as a stand-alone analyte and report.

13) Troubleshooting

13.1 Prepare new standards, check instrument maintenance, prepare a new curve as needed, etc.

13.2 Proper use and maintenance of pipettes is important to achieve good technique and obtain consistent QC results. (See SOP HS-EQ003).

13.3 Daily Instrument Maintenance must be performed and documented according to SOP HS-EQ004.

14) Data Acquisition

14.1 Create a prep batch in LIMS. This information applies to final calculations.

14.2 The data acquired is transferred via Chemstation™ to LIMS electronically. Calculations are performed by Chemstation™ software. Analyst review of data is performed in LIMS prior to being validated. If results are above the highest the analyte linear range, appropriate dilutions are performed to generate reportable data.

14.3 All results are reported with three significant figures

15) Calculation, and Data Reduction Requirements

15.1 QC Calculations: LIMS calculates the percent recovery for various QC samples (LCS)

according to the following equations:

15.1.1 % Recovery, %R (for MS and MSD Samples)

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SR = Sample Result (unspiked).
SA = Spike Amount Added (mg/L or mg/kg).

15.1.2 % Recovery, %R (for standards and LCS)

$$\%R = \frac{SSR}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SA = Spike Amount Added (mg/L or mg/kg).

15.1.3 RPD (for precision or duplicate evaluation)

$$RPD = \frac{|SR_1 - SR_2|}{½(SR_1 + SR_2)} \times 100$$

Where:
SR_1 = Sample result for duplicate 1.
SR_2 = Sample result for duplicate 2.

15.2 Sample Concentration Calculation

15.2.1 Equation for water samples:

$$\text{Concentration (ug/L)} = \text{Sample Response (ug/L)} \times \text{Dilution Factor} \times \text{Prep Factor}$$

15.2.2 Equation for soil samples (external calibration):

$$\text{Concentration (ug/kg)} = \frac{\text{Sample Response (ug/L) x FV}}{\text{Weight of Sample (g)}} \text{ x Dil. Factor (If Applicable)}$$

Where:
FV = final volume of digestion, ml

If additional dilutions are used, the result must be multiplied by the total dilution factor. For example, if a 1:5 dilution is used - the raw concentration must be multiplied by 5 to obtain final result.

15.2.3 Hardness as CaCO3 by Calculation (SM 2340B)

Hardness, mg eqivalent $CaCO_3$/L = 2.497 [Ca, mg/L] + 4.118 [Mg, mg/L]

15.2.4 Reporting SiO2 from Si data, by Calculation (by request only)

SiO2, mg /L = Si, mg/L * 2.1394

15.2.5

16) Quality Control, Acceptance Criteria and Corrective Action

16.1 Initial Demonstration of Capability

16.1.1 Purpose: Verify the ability to produce data of acceptable precision and bias for a specific instrument type, matrix, method, and analyst.

16.1.2 Frequency: Initially during method development, and any time there is a significant change in instrument type, personnel, methodology, or matrix or a period greater than one year has lapsed since last performance of analysis.

16.1.3 Acceptance Criteria: Four consecutive LCS analysis meeting stated LCS criteria. The accuracy component must fall within 80-120% (SW6020A) or 85-115% (EPA 200.8) criteria. The precision component must be less than 20% (SW6020A, and 15% (EPA 200.8) for duplicate RPD data.

16.1.4 Corrective Action: Identify and correct the source of error. Reanalyze the demonstration.

16.2 Continuing Demonstration of Capability

16.2.1 Purpose: Verify the ability to produce data of acceptable precision and bias for a specific instrument type, matrix, method, and analyst.

16.2.2 Frequency: A. Annual to re-qualify analyst for analysts. If period greater than one year has lapse since the last performance of analysis than Initial Demonstration must be performed.

16.2.3 Acceptance Criteria: Four consecutive LCS analysis meeting stated LCS criteria or successful PT study.

16.3 Initial Calibration:

16.3.1 Purpose: Establishes the calibration curve for the quantification of the analytes of interest.

16.3.2 Frequency: A Calibration curve must be generated daily or when ICV or CCV are not met.

16.3.3 Acceptance Criteria:

16.3.3.1 Initial calibration is performed using a blank and at least three standards.

16.3.3.2 Linearity must be demonstrated with the regression, r ≥0.998.

16.3.4 Curve Failure Corrective Action:
Check standards and or perform maintenance as necessary to correct problem, then generate new curve.

16.4 Initial Calibration Verification, ICV (second source).

16.4.1 Purpose: Verifies the accuracy of the ICAL using a standard prepared from a source independent of the source of the standards for the ICAL and CCV.

16.4.2 Frequency: Perform daily after the initial daily curve is generated.

16.4.3 Acceptance criteria: agreement between the curve and the ICV results must be between 90 - 110 % of the ICV true values.

16.4.4 ICV Failure Corrective action - Rerun the ICV standard; observe the system for any tubing leaks or other issues. If the ICV standard fails again, prepare new standards and /or generate new calibration. Do not analyze samples until this

criterion has been me

16.5 Continuing Calibration Verification (CCV)

16.5.1 Purpose: Verifies that instrument response is reliable and has not changed significantly from the current ICAL.

16.5.2 Frequency: The calibration standard must be run after every 10 samples (including QC samples) and at the end of the analytical sequence.

16.5.3 Acceptance Criteria:

16.5.3.1 All analytes are 90 to 110 % of the expected value.

CCV failure Corrective Action: Identify and correct the problem. Re-analyze a second CCV and, if passing, continue the sequence. Samples before failing CCV must be run at a later time. If the second CCV fails, perform a new calibration curve

16.6 Low Level ICV (LLICV): This verifies the Method Quantitation Limit (MQL or Reporting Limit, RL) for trace metals at the beginning of a run.

16.6.1 Frequency: LLICV is analyzed daily to assess the accuracy reporting at the MQL.

16.6.2 Acceptance Criteria: Target trace metal analytes should be within 70 to 130% of the true value of the LLICV.

16.6.3 LLICV MQL assessment failure Corrective Action: If the MQL (LLICV) standard does not meet criteria for any required metals, discontinue the run, rinse the system and rerun the LLICV. If the second LLICV passes criteria, continue the run. If the second LLICV does not pass, discontinue the run, perform additional system corrective action (e.g. preparing fresh standards and generating a new ICAL) until a passing LLICV is achieved.

16.7 Initial and Continuing Calibration Blanks (ICB/CCB):

16.7.1 Frequency: The ICB is run after the ICV in the evaluation of each new initial calibration. The CCB must be run after every 10 samples (including QC samples) and at the end of the analytical sequence.

16.7.2 Acceptance Criteria:

16.7.2.1 All analytes must be less than the MQL. The CCB IS must fall within 80 to 120%.

16.7.2.2 ICB/CCB Corrective Action: If the ICB or CCB do not meet the detection level criteria, < MQL, identify the problem (i.e. system contamination, sample carryover, or instrument drifting). Re-analyze the CCB and any samples since the last passing CCB that have detections >MQL, once the problem has been addressed.

16.8 Linear Dynamic Range Determination (LDR) assessment

16.8.1 Frequency: Run initially and then least every six months thereafter at a minimum. The LDR sample is used to assess linearity of the daily calibration at points beyond the highest calibration point.

16.8.2 Acceptance Criteria: All analytes must be within 10% of the true value of the LDR standard.

16.8.3 LDR assessment failure Corrective Action: If the LDR does not meet criteria for a certain metal, no data for that element falling between the highest calibration standard and the LDR standard can be reported from the sequence. Dilution to a level below the highest standard is required. Preferably, dilute the analyte to between the mid-point standard and the highest standard. For metals with passing LDR criteria, metal concentrations

between the highest calibration standard and the LDR true value may be reported without "E" qualifiers.

16.9 Interference Check Solution (ICSA and ICSAB) evaluations:

16.9.1 Frequency: The ICSA and ICSAB solutions at the beginning of each daily run (after the daily LLICV and before the first CCV), every 12 hours during the course of analysis.

16.9.2 Acceptance Criteria:

16.9.2.1 All ICSA/ICSAB analytes are to be 80 to 120 % of their expected value.

16.9.3 ICSA/ICSAB Analyte failure Corrective Action: If the calibration does not meet the criteria, re-analyze the standard. It may be necessary to prepare a fresh standard. If the criteria are still not met, perform a new calibration curve.

16.10 Method Blank (MB)

16.10.1 Purpose: Assess background interference or contamination in the analytical system that may lead to high bias or false positive data.

16.10.2 Frequency: Analyze the method blank at a frequency of one per preparation batch of 20 or less samples.

16.10.3 Acceptance Criteria: All analytes of interest must be ≤ ½ MQL, except for certain common lab contaminants. Common lab contaminants (i.e., Sodium, Potassium, Calcium, Magnesium, Iron, Zinc and Aluminum) must be ≤ MQL, or, Analytes of interest must be less than 5% of the regulatory limit associated with an analyte or analytes of interest must be less than 5% of the sample result for the same analyte, whichever is greater.

16.10.4 Method Blank Contamination Corrective Action: Reanalyze the Method Blank to confirm failure. If the blank is still unacceptable, identify the source of the contamination. All samples in the associated preparation batch must be re-prepared and re-analyzed (including all appropriate QC samples).If samples cannot be re-run because of insufficient sample or other similar circumstances, an NCAR must be initiated and issued to project management and to the QAD. The NCAR must be detailed enough for preparation of the project narrative and all appropriate data flags are entered into LIMS for the final report preparation. Data reported with an associated contaminated method blank must be flagged with a "B", indicating the occurrence.

16.11 Laboratory Control Sample: The LCS is prepared from a calibration standard.

16.11.1 Purpose: Evaluates the performance of the entire analytical system, including all preparation and analysis steps. Assesses the ability of the laboratory/analyst to successfully recover the target analytes from a clean matrix. Contains all target analytes and surrogates.

16.11.2 LCS Frequency: The laboratory control sample is processed with each preparation batch of 20 or less samples for Method 6020A and laboratory control sample is processed with each preparation batch of 10 or less samples for Method 200.8.

16.11.3 Acceptance Criteria: For 6020A, acceptance range is between 80-120%; for 200.8, acceptance range is between 85-115 % recoveries.

16.11.4 LCS failure Corrective Action: If the LCS recoveries for the compounds of interest do not meet with the criteria, re-analyze the LCS to confirm failure. If it is still unacceptable, identify and correct the source of error. All samples in the associated preparation batch must be re-prepared and re-analyzed. If reprocessing is not possible due to lack of sample or expired hold time,

report (narrate) the variance to the client and flag the associated data as estimated.

16.12 Matrix Spike (If field sample is not available to perform both an MS and MSD, then perform an LCS and LCSD.

16.12.1 Purpose: Assesses the performance of the method on a particular matrix.

16.12.2 Frequency: For 6020A, the MS frequency must be at least one MS per 20 samples per matrix. For 200.8, the MS frequency must be at least one MS per 10 samples per matrix.

16.12.3 Acceptance Criteria: For 6020A, spike recovery criteria are 75 to 125%. For 200.8, spike recovery criteria are 70 – 130%. When the MS native concentration is four times or more the spiking level, evaluation of recovery is not practical because of the background analyte level weighing effect.

16.12.4 MS % Recovery Criteria Failure Corrective Action: If the MS has recoveries which are outside the target range, the poor recoveries in the MS may be due to matrix effects. The LCS, surrogate recoveries must all be evaluated in order to determine if matrix interference is present or if method performance is poor. Note that the MS are used to evaluate the matrix effect, not to control the analytical process. If the Matrix Spike is found to be out of control for the same analyte, a matrix effect is likely confirmed (assuming the LCS passes). If recovery of the MS is suspicious (laboratory error, etc) a PDS is performed (SW6020A only). For instance, if the matrix spike exhibit low recovery but good precision then it can be assumed that matrix interference is present. However, if precision between the MS is poor, technique error must be eliminated as a possible source of error before the data can be accepted. If matrix interference is highly suspected corrective action is not necessary unless a Quality Assurance Project Plan stipulates controlling based on MS recovery (USACE, CLP, etc.).

16.13 Duplicate Samples

16.13.1 Purpose: Provides information on the heterogeneity of the sample matrix. Also determines the precision of the analytical process for that matrix.

16.13.2 Frequency: For 6020A, the duplicate frequency must be at least one duplicate per 20 samples per matrix. For 200.8, the duplicate frequency must be at least one duplicate per 10 samples per matrix.

16.13.3 Acceptance Criteria: For SW6020A, the duplicate recovery criterion is ≤ 25% RPD. For 200.8 the duplicate recovery criteria is ≤ 30% RPD

16.13.4 Corrective Action: If the RPD fails, the data must be reevaluated for error and possible matrix effects and sample homogeneity. Perform a PDS for SW6020A only.

16.14 Internal Standards (IS) for Samples and QC samples (see Table 22.3

16.14.1 Frequency: Add IS to all samples and QC samples.

16.14.2 Acceptance Criteria: 6020A (non DoD) – field sample IS results must fall above 70 % of the IS result of the Cal Blk. 6020A (DoD) sample IS results must recover within 30-120% of the IS result of the Cal Blk. The processing software compares all 6020A data to a 70-120% acceptance range in order to meet the strictest requirement for both programs.

16.14.3 Acceptance Criteria - 200.8 – field sample IS results must fall between 60 and 125 % of the IS result of the Cal Blk.

16.14.4 IS failure corrective action: If sample criteria are not met due to interference

then samples are diluted (successive 5x dilutions as necessary, etc.) until the criteria is met.

16.15 Post Digestion spike (PDS), 6020A only
- 16.15.1 Frequency: Perform as needed for MS/MSD QC criteria failures.
- 16.15.2 Acceptance Criteria: Results should fall 80 to 120 % if the true value
- 16.15.3 PDS corrective action: Unacceptable results indicate a possible matrix effect. Perform Dilution Test.

16.16 Dilution Test Check (6020A only):
- 16.16.1 Frequency: Perform as needed for unacceptable PDS results.
- 16.16.2 Acceptance Criteria: 1+4 dilution must agree within ±10% of the original determination for analytes present at concentrations >10x concentration of the MQL.
- 16.16.3 Dilution test corrective action: Results indicate a possible matrix effect. Describe in the Lab Review Checklist

16.17 Method Detection Limits (MDLs) must be determined on each instrument on an annual basis (at minimum) or whenever major modifications are performed on instrumentation (ex: change detector, auto-sampler, etc.).
- 16.17.1 All compound must achieve the required 1-10 times spike ratio as noted in 40 CFR part 136.
- 16.17.2 Corrective Action: For ratio less than 1 ratio the pike amount for ratio greater than 10 decrease the spike amount.

16.18 Limit of Detection Determination and Verification:
- 16.18.1 Purpose: Validates the established Detection Limit.
- 16.18.2 Frequency: Prior to sample analysis and verified quarterly. Verification must is performed on each instrument. The LOD is spiked at 2-3 times the detection limit for single compound analyses and 1-4 times the detection limit for multi-analyte standards.
- 16.18.3 Acceptance Criteria: The apparent signal to noise ratio at the LOD must be at least three and the results must meet all method requirements for analyte identification (e.g., ion abundance, second-column confirmation, or pattern recognition.) For data systems that do not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least three standard deviations greater than the mean method blank concentrations.
- 16.18.4 Corrective Action: Repeat the Detection Limit Determination and LOD Verification at a higher concentration or perform and pass two consecutive LOD verifications at a higher concentration and set the LOD at the higher concentration.

16.19 Limit of Quantitation Establishment and Verification:
- 16.19.1 Purpose: Validates the lower quantitation limit of the analysis.
- 16.19.2 Frequency: Prior to sample analysis and verified quarterly.
- 16.19.3 Acceptance Criteria: Data must empirically demonstrate precision and bias at the LOQ.
- 16.19.4 Corrective Action: Identify and correct the source of error, reanalyze the LOQ. If failure persists re-evaluate the appropriateness of the LOQ.
  Initial Demonstration of Proficiency – The laboratory must demonstrate initial proficiency with each sample preparation and determinative method

combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operation annually and whenever new staff members are trained or significant changes in instrumentation are made.

16.20 Deviations and non-conforming events must be documented using a Nonconformance Corrective Action Report (NCAR) form or as an Exception Report item on the laboratory review checklist. For mandatory QC failures (e.g. LCS), the NCAR must be submitted to the QA Manager.

17) Data Records Management

17.1 All data is stored electronically and/or hard copy for 5 years or longer, depending on client's request or regulatory requirements.

17.2 All analytical sequence IDs and standard preparation information must be recorded in the Run logbook. Hardcopy computer printouts of analytical sequences and raw data must be retained and initialed by the analyst (electronic initials are acceptable). To simplify standard and reagent tracking, analyst must attempt to use single lots of reagents and standards.

17.3 Complete all pertinent sections in the respective logbooks. If not-applicable then line out the section and "Z" out or "X" out all large sections of the worksheet that are not used. Make all corrections with single line through, date and initial. Make NO obliterations when manually recording data.

17.4 Logbooks are controlled. Never remove a page from a logbook. Completed logbooks are returned to the QA department when filled and no longer needed in the work area.

18) Contingencies for Handling Out of Control Data

18.1 When method required QC exceedances occur, in every case where sample data quality are affected, the source of the QC exceedance must be determined, corrected and sample reanalysis carried out when possible.

18.2 When affected sample analysis cannot be repeated due to limitations (i.e. sample availability, or if reanalysis can only be performed after expiration of a sample hold time), the reporting of data associated with exceeded QC data must be appropriately flagged and narrated. This documentation is necessary to define for the data user the effect of the error has upon the data quality of the results reported (e.g. E flag data indicate the result to be only an estimate).

18.3 All analysts must report sufficient comments in laboratory data review checklist for exceeded QC associated with sample results so that project management can further narrate and ensure data qualifiers (flags) are properly assigned to the reported data.

18.4 NCARs must be issued for QC system exceedances. Matrix interferences are reported using the analyte reporting comment section in LIMS or using the Laboratory Data

review checklist.

19) Method Performance

19.1 Refer Method SW-846 Method 6020A and EPA 200.8.

20) Summary of Changes

Table 0.1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
8.5 Sec 10.6	03/05/2020	E. Marinez	Removed blank section 10.16 which had no text in any prior revisions.
8.4	10/15/2018	G. Moulton	Update to new cover, added new QA Manager
8.4 sec 21.1 and sec 21.2	10/15/2018	G. Moulton	Modified reference
8.4 Sec 17.1	10/15/2018	G. Moulton	Modified data storage time.
8.4	10/15/2018	G. Moulton	Sec 16.14.2 DoD requirements for 6020A IS
08.2	05/01/2013	T. Yen	Signature Page – New QA Manager and Lab Director.
08.2	05/01/2013	T. Yen	Document Footer – "A Campbell Brothers Limited Company" changed to "An ALS Limited Company" to reflect parent company name change.
08.2 – Section 17.2	05/01/2013	T. Yen	To simplify standard tracking, analyst must attempt to use single lots in sequence or batch.
08.2 - Section 17.5	05/01/2013	T. Yen	SOP effective date defined.
08.1	03/20/2012	J. Cady	Added U and Li procedures.
08.0	08/01/2011	I. Williams	Major document format revision.

21) References and Related Documents

21.1 Current TNI Standards.

21.2 Current Department of Defense Quality Systems Manual.

21.3 Referenced Documents

21.3.1 Method 6020A, "Inductively Coupled Plasma Mass Spectrometry", Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), U.S. Environmental Protection Agency, OSWER, Method Revision 1, February 2007

21.3.2 Method 200.8, "Inductively Coupled Plasma – Mass Spectrometry," Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, EPA-600/4-79-020, Revision 5.4, 1994.

21.3.3 Method 2340 B, Hardness by Calculation, Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005.

21.3.4 Current version DOD/DoE Quality Systems Manual.

21.4 Related Documents

21.4.1 HS-MET001, Hot Block Digestion of Soils for Metals Analysis, current revision

21.4.2 HS-MET002, Hot Block Digestion of Aqueous Samples for Metals Analysis, current revision.

22) Appendix.

Table 22.1 Metals Analysis

Table 22.1 - Metals Analysis by ICP/MS – SW 6020A – EPA 200.8 LODs and MQLs, current at time of SOP revision. LODs are determined annually at a minimum, and are subject to change.							
Analyte – Water Matrix	Isotope	LOD* µg/L	MQL* µg/L	Analyte - Soil Matrix	Isotope	LOD* mg/Kg	MQL* mg/Kg
Al	27	3.7	10	Al	27	0.2	1
Sb	121	0.5	5	Sb	121	0.25	0.5
As	75	0.9	5	As	75	0.06	0.5
Ba	135	0.7	5	Ba	135	0.08	0.5
Be	9	0.3	5	Be	9	0.05	0.5
B	11	15	20	B	11	1.5	2.5
Cd	111	0.6	2	Cd	111	0.04	0.5
Ca	44	50	500	Ca	44	10	50
Cr	52	0.6	5	Cr	52	0.05	0.5
Co	59	0.5	5	Co	59	0.03	0.5
Cu	65	0.5	5	Cu	65	0.14	0.5
Fe	56	36	200	Fe	56	4	50
Pb	208	0.4	5	Pb	205	0.05	0.5
Mg	24	39	500	Mg	24	3.3	50
Mn	55	0.8	5	Mn	55	0.07	0.5
Mo	95	0.6	5	Mo	95	0.05	0.5
Ni	60	1.4	5	Ni	60	0.06	0.5
K	39	100	500	K	39	3.6	50
Se	78	2.5	5	Se	78	0.25	0.5
Ag	109	0.7	2	Ag	109	0.04	0.5
Na	23	100	500	Na	23	4	50
Sr	88	0.5	5	Sr	88	0.06	0.5
Tl	203	0.8	2	Tl	203	0.07	0.5
Sn	118	0.6	5	Sn	118	0.14	2.5
Ti	47	1.2	5	Ti	47	0.13	0.5
V	51	0.7	5	V	51	0.07	0.5
Zn	66	2.5	5	Zn	66	0.25	0.5
U	238			U	238		
Li	7			Li	7		

*Limit of Detection (LOD) and Method Quantitation Level (MQL) are in effect at time of SOP creation and are subject to change with MDL study.

Table 22.2 Metals Analysis

Table 22.2 - Metals Analysis by ICP/MS – SW 6020A Internal Standard Criteria for CCV, CCB and samples; The reference IS amu should be within 50 amu of the analyte amu									
CCV & CCB	Isotope	Ref IS	Lower %	Upper %	Samples and QC	Isotope	Ref IS	Lower %	Upper %
Be	9	Li^{6}	70	n/a	Be	9	Ge^{72}	70	n/a
Na	23	Ge^{72}	70	n/a	Na	23	Ge^{72}	70	n/a
Mg	24	Ge^{72}	70	n/a	Mg	24	Ge^{72}	70	n/a
Al	27	Ge^{72}	70	n/a	Al	27	Ge^{72}	70	n/a
K	39	Ge^{72}	70	n/a	K	39	Ge^{72}	70	n/a
Ca	44	Ge^{72}	70	n/a	Ca	44	Ge^{72}	70	n/a
Ti	47	Ge^{72}	70	n/a	Ti	47	Ge^{72}	70	n/a
V	51	Ge^{72}	70	n/a	V	51	Ge^{72}	70	n/a
Cr	52	Ge^{72}	70	n/a	Cr	52	Ge^{72}	70	n/a
Mn	55	Ge^{72}	70	n/a	Mn	55	Ge^{72}	70	n/a
Fe	57	Ge^{72}	70	n/a	Fe	57	Ge^{72}	70	n/a
Co	59	Ge^{72}	70	n/a	Co	59	Ge^{72}	70	n/a
Ni	60	Ge^{72}	70	n/a	Ni	60	Ge^{72}	70	n/a
Cu	65	Ge^{72}	70	n/a	Cu	65	Ge^{72}	70	n/a
Zn	66	Ge^{72}	70	n/a	Zn	66	Ge^{72}	70	n/a
As	75	Ge^{72}	70	n/a	As	75	Ge^{72}	70	n/a
Se	78	Ge^{72}	70	n/a	Se	78	Ge^{72}	70	n/a
Sr	88	Ge^{72}	70	n/a	Sr	88	Ge^{72}	70	n/a
Mo	98	Ge^{72}	70	n/a	Mo	98	In^{115}	70	n/a
Ag	109	Ge^{72}	70	n/a	Ag	109	In^{115}	70	n/a
Cd	111	In^{115}	70	n/a	Cd	111	In^{115}	70	n/a
Sn	118	In^{115}	70	n/a	Sn	118	In^{115}	70	n/a
Sb	121	Ge^{72}	70	n/a	Sb	121	Ge^{72}	70	n/a
Ba	135	In^{115}	70	n/a	Ba	135	In^{115}	70	n/a
Tl	203	Bi^{209}	70	n/a	Tl	203	Bi^{209}	70	n/a
Pb	208	Bi^{209}	70	n/a	Pb	208	Bi^{209}	70	n/a
U	238	Bi^{209}	70	n/a	U	238	Bi^{209}	70	n/a
Li	7	n/a	n/a	n/a	Li	7	n/a	n/a	n/a

Table 22.3 Summary of Calibration and QC Procedures

Table 22.3 - Summary of Calibration and QC Procedures for Method SW6020A / 200.8			
QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
MS tuning sample.	Prior to initial calibration and calibration verification.	Meet criteria for both SW6020A and EPA 200.8 (see §11.4 of this SOP)	Retune instrument then reanalyze tuning solution.
Initial calibration (minimum 3 standards and a blank).	Daily initial calibration prior to sample analysis.	r > 0.998	Prepare a fresh standard and recalibrate the instrument
Initial Calibration verification (ICV - second source).	Daily, after initial calibration and after every recalibration	All analytes within ±10% of expected value.	Correct problem and repeat initial calibration.
LLICV.	Daily, after ICV	All analytes should be within ±30% of expected value.	Rinse system again , and repeat LLICV
Calibration blank (ICB and CCB).	Run the ICB after the ICV and run a CCB after every 10 samples and at the end of the analytical sequence	Assess analytes detected > MQL	If any >MQL, Correct problem then re-analyze the CCB and any affected previous samples having detections >MQL.
Interference check solutions (ICS-A and ICS-AB).	At the beginning of each daily analytical run and after every 12 hour period thereafter as the run continues	ICS-A: All non-spiked trace analytes < MQL and others ±20% of true value. ICS-AB: trace analytes within ±20% of true value.	Terminate analysis; locate and correct problem; reanalyze ICS; reanalyze all affected samples.
Calibration verification (CCV-Instrument Check Standard).	After every 10 samples and at the end of the analysis sequence.	All analyte(s) within ±10% of expected value.	Correct problem then repeat calibration and reanalyze all samples since last successful CCV.

Table 22.3 - Summary of Calibration and QC Procedures for Method SW6020A / 200.8			
QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
LLCCV.	After every calibration and at the end of each analytical batch	All analytes should be within ±30% of expected value.	Rinse the system, re-analyze the LLCCV. If reanalysis is unacceptable, any data at that level is questionable and must not be reported. Recalibrate the instrument and reanalyze affected samples
Demonstrate ability to generate acceptable accuracy and precision using four replicate LCS	Once per analyst initially and annually thereafter.	QC acceptance criteria, SW6020A: QC acceptance criteria, within 80-120%; 200.8: Recovery within 85-115% of expected results. .	Recalculate results; locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria.
Method blank.	One per preparation batch.	No analytes detected > ½ MQL, common lab contaminants > MQL (Na, K, Mg, Ca, Fe, Al, Zn)	Correct problem, re-digest and analyze method blank and all samples processed with the contaminated blank.
LCS for the analyte.	One LCS per preparation batch.	SW6020A: QC acceptance criteria, within 80-120%; 200.8: Recovery within 85-115% of expected results.	Correct problem, re-digest and reanalyze the LCS and all samples in the affected preparation batch.
MS	SW6020A:One MS per every 20 field samples per matrix; 200.8: One MS per every 10 field samples per matrix.	SW6020A: QC advisory criteria, recovery within 75-125%; 200.8: QC advisory criteria, recovery within 70-130% of expected results	Describe in Laboratory Review Checklist. Perform PDS for SW6020A

Table 22.3 - Summary of Calibration and QC Procedures for Method SW6020A / 200.8			
QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Post Digestion Spike (PDS) addition (6020A only).	One PDS per each preparatory batch. .	Recovery within 75-125% of expected results for 6020A, the step is not required for 200.8.	Describe in Laboratory Review Checklist. Perform Dilution Test for SW6020A
Dilution test (6020A only).	Each preparatory batch.	1+4 dilution must agree within ±10% of the original determination for analytes present at a concentration 50 times greater than MQL for 6020A; step is not required for 200.8.	Describe in Laboratory Review Checklist.
Duplicate	SW6020A: One duplicate per 20 samples. 200.8: One duplicate per 10 samples.	SW6020A: ≤ 25% RPD 200.8: ≤ 30% RPD	Evaluate for error or matrix effects and non-homogeneity. Perform the PDS for SW6020A only.
Internal Standards (IS).	Every sample.	For 6020A: See Table 22.2 – Sample IS intensity above 70% of intensity of IS in the ICAL standard. For 200.8: Sample IS intensity within 60-125% of intensity of IS in the ICAL blank.	Perform corrective action as described in Method SW6020A, §9.6.
MDL study.	Statistical MDL Study performed annually. Limits are checked quarterly through Detection Limit Check Study (DCS)	Detection limits established shall be ≤1/2 the LOQs.	None.
Linear Dynamic Range	Initially at instrument set-up and every 6 months thereafter.	All analytes must be within 10% of known value.	Do not report E-qualified data.

LOW-LEVEL SEMI-VOLATILE ORGANIC COMPOUNDS BY SW846-8270D/EPA 625/EPA 625.1

DOCUMENT ID: HS-MSSV003, REV 7.2

Approved By: _____ Date: 8/3/2020
Technical and Laboratory Director, Hoai Van

Prepared By: _____ Date: 08/03/2020
Quality Assurance Manager, Erica Marinez

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1) Identification of the Method, Applicable Matrices, Scope and Applicability

1.1 This method can be used to quantitate at low levels of a number neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic (GC) fused-silica capillary column coated with slightly polar silicone. Detection is by Mass Spectrometry (MS). Method 8270D is applicable to aqueous and non-aqueous liquid samples and solid samples. Method 625 and 625.1 are applicable to aqueous samples.

1.1 The compounds most commonly included in the procedure are the polynuclear aromatic hydrocarbons (PAH), but other base neutral and acid compounds may include when requested by a project. Table 2.1 contains a list of semivolatiles organics that have been analyzed using this low-level method.

1.2 The following compounds may require special treatment when being determined:

- 1.2.1 Benzidine can be subject to oxidative losses during solvent concentration. Also, care must be taken to minimize active sites in the chromatography system.
- 1.2.2 Hexachlorocyclopentadiene is subject to thermal decomposition in the GC inlet, chemical reaction in acetone solution, and photochemical decomposition.
- 1.2.3 N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine.
- 1.2.4 Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline and 4-chloroaniline are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.
- 1.2.5 Pyridine may perform poorly at the GC injection port temperatures listed in the method.

2) Summary of Procedure

2.1 Samples are extracted following the appropriate method/SOP for semivolatiles extraction for the sample matrix type. The extracts are then analyzed using the GC/MS instrument. The semivolatiles compounds that can be reported are those compounds listed in Table 2.1. The specific list reported is based upon client request through project management.

2.2 Typical Limit of Quantitation (LOQ) by this method for an individual compound is approximately 6.6 µg/kg (wet weight) for soil/sediment samples, 0.2 µg/L for water samples and 0.1 ug/L for the PAH compounds. LOQs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector or chromatographic system.

Table 2.1 Characteristic Ions for Semivolatiles Compounds and LOQ at time of SOP revision. Values are subject to change, see LIMS or QA for latest Limits.

Table 2.1 Compound	CAS No	Primary Ion	Secondary Ion(s)
1,1´-Biphenyl	92-52-4	154	153, 76
1,2,4,5-Tetrachlorobenzene	95-94-3	216	214, 179
1,2,4-Trichlorobenzene	120-82-1	180	182, 145
1,2-Dichlorobenzene	95-50-1	146	148, 111
1,2-Diphenylhydrazine	122-66-7	77	105, 182
1,3-Dichlorobenzene	541-73-1	146	148, 111
1,3-Dinitrobenzene	99-65-0	168	50, 63
1,4-Dichlorobenzene	106-46-7	146	148, 111
1,4-Dioxane	123-91-1	88	58, 43
1,4-Naphthoquinone	130-15-4	158	104, 102
1-Methyl-2-pyrrolidone	872-58-4	99	98
1-Methylnaphthalene	90-12-0	142	141
1-Naphthylamine	134-32-7	143	115, 89
2,3,4,6-Tetrachlorophenol	58-90-2	232	131, 230
2,4,5-Trichlorophenol	95-95-4	196	198, 97
2,4,6-Trichlorophenol	88-06-2	196	198, 200
2,4-Dichlorophenol	120-83-2	162	164, 98
2,4-Dimethylphenol	105-67-9	122	107, 121
2,4-Dinitrophenol	51-28-5	184	63, 154
2,4-Dinitrotoluene	121-14-2	165	63, 89
2,6-Dichlorophenol	87-65-0	162	164, 126
2,6-Dinitrotoluene	606-20-2	165	63, 89
2-Acetylaminofluorene	53-96-3	181	180, 223
2-Chloronaphthalene	91-58-7	162	127, 164
2-Chlorophenol	95-57-8	128	64, 130
2-Methylnaphthalene	91-57-6	142	141
2-Methylphenol	95-48-7	107	108, 77
2-Naphthylamine	91-59-8	143	115, 116
2-Nitroaniline	88-74-4	65	92, 138
2-Nitrophenol	88-75-5	139	109, 65
2-Picoline	109-06-8	93	66, 92
3&4-Methylphenol	106-44-5	108	107, 77
3,3'-Dichlorobenzidine	91-94-1	252	254, 126
3,3´-Dimethylbenzidine	119-93-7	212	106, 196
3-Chlorophenol	108-43-0	128	130, 65
3-Methylcholanthrene	56-49-5	268	252, 253

Table 2.1 Compound	CAS No	Primary Ion	Secondary Ion(s)
3-Nitroaniline	99-09-2	138	108, 92
4,4'-DDD	72-54-8	235	237, 165
4,4'-DDE	72-55-9	246	248, 176
4,4'-DDT	50-29-3	235	237, 185
4,6-Dinitro-2-methylphenol	534-52-1	198	51, 105
4-Bromophenyl phenyl ether	101-55-3	248	250, 141
4-Chloro-3-methylphenol	59-50-7	107	144, 142
4-Chloroaniline	106-47-8	127	129, 65
4-Chlorophenol	106-48-9	128	130, 65
4-Chlorophenyl phenyl ether	59-50-7	204	206, 141
4-Nitroaniline	100-01-6	138	108, 92
4-Nitrophenol	100-02-7	139	109, 65
4-Nitroquinoline-1-oxide	56-57-5	190	89, 160
5-Nitro-o-toluidine	99-55-8	152	77, 79
6-Methyl chrysene	1705-85-7	242	241, 119
7,12-Dimethylbenz(a)anthracene	57-97-6	256	241, 239
a,a-Dimethylphenethylamine	122-09-8	58	91, 65
Acenaphthene	83-32-9	153	154, 152
Acenaphthylene	208-96-8	152	151, 153
Acetophenone	98-86-2	105	77, 51
Alachlor	15972-60-8	160	188, 45
Aldrin	309-00-2	66	263, 220
Alpha-BHC	319-84-6	183	181, 109
alpha-Chlordane	5103-71-9	373	237, 272
Ametryn	834-12-8	227	212, 170
Aniline	62-53-3	93	66, 65
Anthracene	120-12-7	178	176, 179
Atraton	1610-17-9	211	196, 58
Atrazine	1912-24-9	200	173, 215
Azinphos-methyl (Guthion)	86-50-0	132	77, 160
Benz(a)anthracene	56-55-3	228	229, 226
Benzal Chloride	98-87-3	125	127, 89
Benzaldehyde	100-52-7	77	105, 106
Benzenethiol	108-98-5	110	66, 109
Benzidine	92-87-5	184	92, 185
Benzo(a)pyrene	50-32-8	252	253, 125
Benzo(b)fluoranthene	205-99-2	252	253, 125
Benzo(e) pyrene	192-97-2	252	125, 113
Benzo(g,h,i)perylene	191-24-2	276	138, 277
Benzo(k)fluoranthene	207-08-9	252	253, 125

Table 2.1 Compound	CAS No	Primary Ion	Secondary Ion(s)
Benzoic Acid	65-85-0	122	105, 77
Benzotrichloride	98-07-7	159	161, 89
Benzyl alcohol	100-51-6	108	79, 77
Beta-BHC	319-85-7	181	183, 109
Bis(2-chloroethoxy) methane	117-81-7	93	95, 123
Bis(2-chloroethyl) ether	111-44-4	93	63, 95
Bis(2-chloroisopropyl) ether	108-60-1	45	77, 121
Bis(2-ethylhexyl)phthalate	117-81-7	149	167, 279
Bis(chloromethyl)ether	542-88-1	79	81, 49
Bromacil	314-40-9	205	207, 162
Butachlor	23184-66-9	176	160, 57
Butyl benzyl phthalate	85-68-7	149	91, 206
Butylate	2008-41-5	146	57,89
Caprolactam	105-60-2	55	56, 113
Captan	133-06-2	79	149,117
Carbazole	86-74-8	167	166, 139
Carbophenothion	786-19-6	157	97, 121
Carboxin	5234-68-4	143	87, 235
Chlorpropham	101-21-3	127	43
Chlorpyrifos	2921-88-2	97	314
Chrysene	218-01-9	228	226, 229
Cyanazine	21725-46-2	225	172, 68
Cycloate	1134-23-2	83	154
Delta-BHC	319-86-8	183	181, 109
Demeton-O	298-03-3	88	60, 171
Demeton-S	126-75-0	88	60, 143
Demeton, Total	8065-48-3	88	60,143,171
Diallate	2303-16-4	86	234, 43
Diazinon	333-41-5	137	152, 79
Dibenz(a,h)acridine	226-36-8	279	139, 278
Dibenz(a,h)anthracene	53-70-3	278	139, 279
Dibenz(a,j)acridine	224-42-0	279	280, 277
Dibenzofuran	132-64-9	168	139
Dichlorvos	62-73-7	109	185, 79
Dicofol	115-32-2	139	111, 251
Dieldrin	60-57-1	79	263, 279
Diethylphthalate	84-66-2	149	177, 150
Dimethoate	60-51-5	87	93, 125
Dimethylphthalate	131-11-3	163	194, 164
Dinoseb	88-85-7	211	163, 147

Table 2.1 Compound	CAS No	Primary Ion	Secondary Ion(s)
Di-n-butylphthalate	84-74-2	149	150, 104
Di-n-octylphthalate	117-84-0	149	167, 43
Dioxathion	78-34-2	270	125, 97
Diphenamide	957-51-7	72	167, 165
Diphenylamine	122-39-4	169	168, 167
Diphenyl ether	101-84-8	170	141, 77
Disulfoton	298-04-4	88	97, 89
Disulfoton sulfone	2497-06-5	213	153, 97
Diuron	330-54-1	72	232, 234
Endosulfan I	959-98-8	195	339, 341
Endosulfan II	33213-65-9	337	339, 341
Endosulfan sulfate	1031-07-8	272	387, 422
Endrin	72-20-8	263	82, 81
Endrin Aldehyde	7421-93-4	67	345, 250
Endrin ketone	53494-70-5	317	67, 319
EPTC	759-94-4	128	43, 86
Ethion	563-12-2	231	97, 153
Ethoprophos	13194-48-4	58	97, 126
Etridiazole	2593-15-9	183	211, 140
Ethyl methanesulfonate	62-50-0	79	109. 97
Ethyl parathion	56-38-2	109	97, 291
Famphur	52-85-7	218	125, 93
Fenamiphos	22224-92-6	303	154, 80
Fenarimol	60168-88-9	139	107, 249
Fluoranthene	206-44-0	202	101, 203
Fluorene	86-73-7	166	165, 167
Fluridon	59756-60-4	328	329
Fonofos	944-22-9	109	137, 246
Gamma-BHC	58-89-9	183	181, 109
gamma-Chlordane	5103-74-2	373	237, 272
Heptachlor	76-44-8	100	272, 274
Heptachlor epoxide	1024-57-3	353	355, 351
Hexachlorobenzene	118-74-1	283	142, 249
Hexachlorobutadiene	87-68-3	225	223, 227
Hexachlorocyclopentadiene	77-47-4	237	235, 272
Hexachloroethane	67-72-1	117	201, 199
Hexazinone	51235-04-2	171	83
Indeno(1,2,3-cd)pyrene	193-39-5	276	138, 227
Isodrin	465-73-6	193	66, 195
Isophorone	78-59-1	82	95, 138

Table 2.1 Compound	CAS No	Primary Ion	Secondary Ion(s)
Isosafrole	120-58-1	162	131, 104
Kepone	143-50-0	272	274, 237
Malathion	121-75-5	125	173, 93
Merphos	150-50-5	209	57, 153
Methapyrilene	91-80-5	97	58, 191
Methoxychlor	72-43-5	227	228, 152
Methyl chrysene	1705-85-7	242	241, 119
Methyl methanesulfonate	66-27-3	80	79, 65
Methyl paraoxon	950-35-6	109	96, 230
Methyl parathion	298-00-0	109	125, 263
Metolachlor	51218-45-2	162	238, 45
Metribuzin	21087-64-9	198	68, 170
Mevinphos	7786-34-7	127	109, 192
MGK-264	113-48-4	164	66
Mirex	2385-85-5	272	237, 274
Molinate	2212-67-1	126	55, 83
Naphthalene	91-20-3	128	129, 127
Napropamide	15299-99-7	72	128, 100
Nitrobenzene	98-95-3	77	123, 65
N-Nitroso-di-n-butylamine	924-16-3	84	57, 41
N-Nitrosodiethylamine	55-18-5	102	42, 57
N-Nitrosodimethylamine	62-75-9	74	42, 44
N-Nitrosodi-n-propylamine	621-64-7	70	43, 101
N-Nitrosodiphenylamine	86-30-6	169	168, 167
N-Nitrosomethylethylamine	10595-95-6	88	42, 43
N-Nitrosomorpholine	59-89-2	56	86, 116
N-Nitrosopiperidine	100-75-4	114	42, 55
N-Nitrosopyrrolidine	93-55-2	100	41, 42
Norflurazon	27314-13-2	145	102, 303
O,O,O-Triethylphosphorothioate	126-68-1	121	198, 97
o-Toluidine	95-53-4	106	107, 77
p-Dimethylaminoazobenzene	60-11-7	225	120, 77
p-Phenylenediamine	106-50-3	108	80, 53
Pebulate	1114-71-2	128	57, 72
Pentachlorobenzene	608-93-5	250	252, 108
Pentachloronitrobenzene	82-68-8	237	142, 214
Pentachlorophenol	87-86-5	266	264, 268
Phenacetin	62-44-2	108	80, 179
Phenanthrene	85-01-8	178	179, 176
Phenol	108-95-2	94	65, 66

Table 2.1 Compound	CAS No	Primary Ion	Secondary Ion(s)
Phorate	298-02-2	75	121, 97
Phosmet	732-11-6	160	158, 77
Prometon	1610-18-0	210	225, 168
Prometryne	7287-19-6	184	241, 226
Pronamide	23950-58-5	173	175, 145
Propachlor	1918-16-7	120	77, 93
Propazine	139-40-2	214	229, 58
Pyrene	129-00-0	202	200, 203
Pyridine	110-86-1	79	52
Quinoline	91-22-5	129	128, 102
Ronnel	299-84-3	285	287, 125
Safrole	94-59-7	162	104, 77
Simazine	122-34-9	201	186, 158
Simetryne	1014-70-6	213	68, 170
Stirofos (Tetrachlorvinphos)	22248-79-9	109	153, 329
Sulfolane	126-33-0	120	55, 56
Tebuthiuron	34014-18-1	226	185, 170
Tris(2,3-dibromopropyl) phosphate	126-72-7	201	137, 119
Sym-Trinitrobenzene	99-35-4	75	74, 213
Terbacil	5902-51-2	161	117, 160
Terbufos	13071-79-9	231	57, 153
Terbutryn	886-50-0	226	185, 170
Triadimefon	43121-43-3	57	208
Tricyclazole	41814-78-2	189	162, 161
Trifluralin	1582-09-8	306	264, 43
Vernolate	1929-77-7	128	43, 186
Acenaphthene-d10 (I.S.)	15067-26-2	164	162, 160
Chrysene-d12 (I.S.)	1719-03-5	240	120, 236
1,4-Dichlorobenzene-d4 (I.S.)	2199-69-1	152	150, 115
Napthalene-d8 (I.S.)	1146-65-2	136	68
Phenanthrene-d10 (I.S.)	1517-22-2	188	94, 80
Perylene-d12 (I.S.)	1520-96-3	264	260, 265
Nitrobenzene-d5 (surr.)	4165-60-0	82	128, 54
Phenol-d6 (surr.)	4165-62-2	99	42, 71
2,4,6-Tribromophenol (surr.)	118-79-6	330	332, 141
2-Fluorobiphenyl (surr.)	321-60-8	172	171
2-Fluorophenol (surr.)	367-12-4	112	64
Terphenyl-d14 (surr.)	1718-51-0	244	122, 212
Notes : I.S. = Internal Standard ; surr. = Surrogate			

3) Definitions

3.1 Batch: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** is composed of one (1) to twenty (20) environmental sample of the same quality systems matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be twenty-four (24) hours. An **analytical batch** is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.

3.2 Coefficient of Determination (COD): The Coefficient of Determination, r^2, is used to determine quadratic (non-linear) calibration curve fit.

3.3 Demonstration of Capability: The analysis of QC samples in series to verify the ability to produce data of acceptable precision and bias.

3.4 Exception Report: Appropriate comments reported with the associated sample batch that addresses sample anomalies such as demonstrated sample matrix effects.

3.5 Extracted Ion Current Profile (EICP): a plot of ion abundance versus time or scan number.

3.6 GC/MS = Gas Chromatograph/Mass Spectrometer

3.7 Initial Calibration Verification (ICV): Second source stock standards are prepared and analyzed to verify the calibration. ICV is analyzed after the ICAL and before any customer samples.

3.8 Laboratory Control Sample (LCS): A sample matrix, free from the analytes of interest, spiked with known amounts of analytes or a material containing known and verified amounts of analytes.

3.9 Limit of Detection (LOD): an estimate of the minimum amount of a substance that an analytical process can reliably detect. The LOD is determined annually through the execution of a Method Detection Limit Study, and verified quarterly through the analysis of a Detectability Check Sample (DCS).

3.10 Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met.

3.11 Matrix Spike (MS): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available.

3.12 Matrix Spike Duplicate (MSD): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of recovery for each analyte.

3.13 Matrix: The substrate (e.g., water, soil, etc.) which may contain the analyte of interest.

3.14 Method Blank (MBLK): A sample of a matrix similar to the batch of associated samples

(when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analysis.

3.15 Method Detection Limit (MDL) study: a procedure described in 40CFR Part 136, Appendix B, that describes how to produce an MDL, a reporting element of certain EPA methods. The MDL study is one approach to determine the LOD.

3.16 NCAR: Nonconformance Corrective Action Report (refer to SOP HS-QS003, current revision).

3.17 Preparation Batch: A defined set of one to 20 client samples of the same matrix, meeting the batch definition criteria, and prepared for analysis within 24 hours. The preparation batch must also contain the required determinative method defined batch QC samples (e.g. method blank, laboratory control samples, matrix spikes, duplicates, etc.).

3.18 Reagent Water: Deionized (DI) reagent purified by filtration thru mix resin and carbon beds. For additional purification, the DI water is passed through an activated carbon filter.

3.19 Retention Time Window: The length of time between sample injection and the appearance of a peak at the detector. The window of time is established for each analyte or group of analytes and is set for complete elution of analyte peaks. It is based upon a series of analyses and statistical calculations that establish the measured band on the chromatogram that can be associated with a specific analyte or group of analytes.

3.20 Second Source Stock Standard: A standard obtained or prepared from a source independent of the source of standards that was used to prepare the instrument calibration (different vendor or if necessary, a different lot number from the same vendor). The prepared concentration should be at or near the middle of the calibration range. It is performed after the ICAL.

3.21 Surrogate: An analyte added to a sample, which is unlikely to be found in any sample at significant concentration, and which is added directly to a sample aliquot in known amounts before any sample processing procedures are conducted. It is measured with the same procedures used to measure other sample components. The purpose of the surrogate analyte is to monitor method performance with each sample.

3.22 Surrogate Spike: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environmental samples and is added to them for quality control purposes.

3.23 Tuning: The analysis of a standard compound to verify the mass spectrometer meets standard mass spectra abundance criteria prior to sample analysis (DoD QSM).

3.24 DoD – United States Department of Defense.

3.25 DoD QSM – DoD Quality Systems Manual.

4) Safety

4.1 Lab Safety: Due to various hazards in the laboratory, safety glasses and laboratory

coats or aprons must be worn at all times while in the laboratory. In addition, gloves and a face shield should be worn when dealing with toxic, caustic, and/or flammable chemicals.

4.2 Chemical Hygiene: The toxicity or carcinogenicity of each reagent used has not been precisely defined; however, each chemical used should be treated as a potential health hazard. Exposure to laboratory reagents should be reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets (MSDS) is available to all personnel involved in these analyses.

4.2.1 All standards and sample extracts are in methylene chloride and therefore should be treated with caution. Care should be taken to avoid contact with liquid or vapors of all samples and standards which may contain compounds which are known or suspected human carcinogens or mutagens

4.3 Waste Management: The principal wastes generated by this procedure are the method-required chemicals and standards. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required. Laboratory procedures in SOP SHWDF001, Waste Disposal Procedures, must be followed.

4.3.1 Extracts generated for the performance of this procedure are collected and combined with other solvent waste. The waste is then disposed of with a permitted hazardous waste disposal company.

4.4 Pollution Prevention: The materials used in this method pose little threat to the environment when recycled and managed properly. The quantities of chemicals purchased should be based on the expected usage during its shelf life. Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards or reagents to be disposed.

4.5 Job Safety Assessment

HAZARD ASSESSMENT		
Job Task #1:	**Hazards**	**Preventative Measures**
Cooler and sample handling.	Injury due to lifting heavy coolers and placing/removing samples to/from storage locations.	Use proper lift technique and cart to move coolers and stools/stepladder when working reaching above shoulder height in sample storage cooler.
Job Task #2:	**Hazards**	**Preventative Measures**
Sample container handling and preservation checks.	Exposure to possible hazardous chemicals.	Use of proper PPE, i.e. Lab coats, safety glasses, gloves, etc.
Job Task #3:	**Hazards**	**Preventative Measures**
Use of utility knives to cut open cooler and seals.	Cuts.	Use proper safety with auto retracting blade and proper cutting techniques. Always cut away from body.

Job Task #4:	**Hazards**	**Preventative Measures**
Unpacking coolers and searching for sample within the coolers.	Possible cuts from broken sample containers.	Wear proper protective equipment such as Kevlar kit gloves and use of broken glass containers.
Job Task #5:	**Hazards**	**Preventative Measures**
Glassware Washing.	Possible cuts from broken glassware.	Wear proper protective equipment such as Kevlar kit gloves.
Job Task #6:	**Hazards**	**Preventative Measures**
Sample Testing and/or standard and reagent/solvent use.	Exposure to possible hazardous chemicals & puncture wound with syringe.	Wear gloves, safety glasses and lab coat. Work in fume hood and avoid skin contact with solvents/acids/reagents. Know location of safety shower, first aid kits, spill kits and fire extinguisher when handling flammable material.
Job Task #7:	**Hazards**	**Preventative Measures**
Heated surface such as injector and detector.	Burn potential.	Allow surfaces time to cool down before handling. Wear gloves, safety glasses and lab coat.

5) Maintenance

5.1 Routine preventative maintenance must be performed and documented to assure optimum instrument performance. Refer to the current revision of SOP HS-EQ004 for preventative maintenance schedules.

5.2 Extracts requiring longer storage (> 5 days) before testing should have portions stored in screw cap vials as opposed to crimp cap vials, to prevent possible solvent leakage.

6) Interferences

6.1 Organic compounds present in extraction solvents and glassware contamination in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory method and instrument blanks.

6.2 Raw GC/MS data from all blank samples and spikes must be evaluated for interferences. Determine whether a source of interference is from a sample preparation and/or cleanup step, and perform required corrective action.

6.3 Contamination by carry-over can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between sample injections. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross-contamination.

6.4 Matrix interferences may be caused by contaminants that are co-extracted from a sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled.

7) Personnel Qualifications and Responsibilities

7.1 General Responsibilities - This method is restricted to use by or under the supervision of analysts experienced in the method.

7.2 Analyst - It is the responsibility of the analyst(s) to:

- 7.2.1 Each must read and understand this SOP and follow it as written. Any deviations or non-conformances must be documented and submitted to the QA Manager for approval.
- 7.2.2 Produce method compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP (HS-QS009).
- 7.2.3 Complete the required initial demonstration of proficiency before performing this procedure without supervision.
- 7.2.4 Complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 7.2.5 The analysts must submit data for peer or supervisor review.

7.3 Section Supervisor - It is the responsibility of the section supervisor to:

- 7.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.
- 7.3.2 Ensure analysts have completed the required initial demonstration of proficiency before performing this procedure without supervision.
- 7.3.3 Ensure analysts complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 7.3.4 Ensure analysts produce method compliant data that meet all quality requirements using this procedure and the Data Reduction, Review and Validation SOP.

7.4 Project Manager - It is the responsibility of the Project Manager to ensure that all method requirements for a client requesting this procedure are understood by the laboratory prior to initiating this procedure for a given set of samples.

7.5 QA Manager: The QA Manager is responsible for

- 7.5.1 Approving deviations and non-conformances
- 7.5.2 Ensuring that this procedure is compliant with method and regulatory requirements,
- 7.5.3 Ensuring that the analytical method and SOP are followed as written through internal method and system audits.

8) Sample Collection, Handling, and Preservation

8.1 Water samples are collected in 1 liter glass jars with Teflon lined lids. Samples are stored >0 to 6°C until extraction and extracted within 7 days of collection.

- 8.1.1 Note: Water samples with target compound lists eligible for microextraction by EPA Method 3511 (SOP HS-EXT007) may be collected in 40 mL glass VOA vials with PTFE lined septum screw tops and stored at >0 to 6°C until

extraction. Samples should be extracted as soon after collection as possible, but no longer than 14 days from the date of collection for sulfuric or hydrochloric acid preserved samples. If samples are not acidified, the extraction should be performed within 7 days from date of collection.

8.2 Soil samples are collected in glass jars with Teflon lined lids. Soil samples are stored >0 to 6°C until extraction and extracted within 14 days of sample collection.

8.3 Store sample extracts tightly capped at less than 6 °C. Extracts must be analyzed within 40 days of the extraction date.

8.4 Water samples are prepared by separatory funnel extraction (method SW3510C, SOP-HS-EXT001). The samples is first extracted at pH <2 and then extracted at a pH >11.

8.4.1 Note: Water samples with target compound lists eligible for microextraction are extracted using method SW3511 (SOP HS-EXT007). Samples are prepared by liquid liquid extraction with organic solvent in field sampling containers.

8.5 Soil samples are extracted by method SW3541, automated soxhlet extraction (SOP HS-EXT002).

9) Equipment and Supplies

9.1 Syringes: 10, 25, 50, 100, 500, 1000, 5000 uL, Hamilton Gastight 1000, 1700 or 1800 series, certified accuracy ±1% (or lab verified accuracy ±2%). Verification must be performed upon first use and semiannually afterward.

9.2 Volumetric Flasks, Class A: 10 mL, 25 mL, 50 mL and 100mL.

9.3 Certified weights – verified every two years.

9.4 Analytical Balance: capable of measuring to nearest 0.0001 gram (0.1 milligram). Serviced annually and verified every day prior to use

9.5 Vials-glass with Teflon™-lined screw caps and/or crimp tops.

9.6 Semi-Volatile computer hardware Unit #4 and #5 (SV4, & SV5) = Agilent 6890 GC, Agilent 5973 MSD or equivalent. Semi-Volatile Unit #6 and #7 (SV6 & SV7) = Agilent 7890A GC, Agilent 5975C MSD or equivalent

9.7 GC Columns – Capable of resolving the compounds listed in Table 2.1 of this SOP. Silicone coated fused-silica capillary column - 30 meters long by 0.25 mm ID with a 0.25 µm film thickness (Rtx-5 SIL MS, or equivalent).

9.8 Data System:

9.8.1 Data Acquisition using Agilent ChemStation Computer Software: Allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The software is interfaced to the mass spectrometer. This software provides the sequence log of run order for the data to be collected. The software does allow for searching any GC/MS data file for ions of a specified mass and plotting such ion abundance versus time or scan number. After data acquisition, collected data is automatically transferred into the Target Server for data processing.

9.8.2 Target DB Data Processing software: Target software is used for

chromatographic data processing, data review and reporting where data and results can reside across multiple computers. Target complies with GALP using audit trails, validation checks, method and data locking, user security and data versioning, ensuring data integrity. The software allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundance versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Version NBS75K of the EPA/NIST Mass Spectral Library is used for data processing. The SV units employ the same data systems.

9.9 Mass Spectrometer: HP system or equivalent, capable of producing a mass spectrum that meets method tune criteria when 50ng of DFTPP (Sec 10.8) is injected. SV4, SV5, SV6 & SV7 meet the criteria.

9.10 Agilent GC/MS Operating Conditions (SV4, SV5, SV6, and SV7): The MS units are set at 70 electron volts and a scan range of 35-500 m/e. GC System Typical Conditions for analysis are included in Table 9.1. The typical conditions may vary slightly between units due to small improvements made by the manufacture of each model.

Table 9.10 Typical GC/MS System Conditions

System/Condition:	SV4, SV5, SV6 & SV7
Injector:	Pulsed Splitless @ 250ºC, 1µl Injection volume
MS Source Temp:	230ºC
MS Quad Temp:	150ºC
Transfer line Temp	280ºC
Carrier gas parameters:	Helium @ 1.4 mL/min constant flow
GC Oven Temp Program :	--
Initial GC Oven	55ºC, for 0.5 min.
Oven Temp Rate 1:	Ramp to 265ºC @25oC /min.
Oven Temp Rate 2:	Ramp to 320ºC @6oC /min.
Final temperature:	320ºC

10) Standards and Reagents

10.1 Note: Store all purchased standards according to manufacturer recommended specifications. Store prepared standard solutions (remaining stock, composite, calibration and surrogate) below 6 °C in glass containers having Teflon™ lined lids or in accord with the manufacturer's recommended conditions. All purchased stock standard solutions must be replaced after reaching the manufacturer's expiration date assigned to the standard. All laboratory prepared standard solutions must be replaced after six months or sooner if routine QC indicates a problem. An assigned expiration date of a lab prepared standard cannot exceed the manufacturer's expiration date for any component used in the standard formulation. When analyzing or preparing samples, all standards, lot numbers must be associated with the run batch or prep batch.

10.2 Methylene Chloride - Pesticide grade or equivalent.

10.3 Methanol (MeOH) - Pesticide quality or equivalent.

10.4 Stock solutions for analytes, internal and surrogate standards are purchased as certified standards from approved (NVLAP/NIST) vendors (Restek, Absolute Standards, AccuStandard, Supelco, etc.). Once opened for use, the stock standards are transferred to a 1.0 or 2.0 mL amber glass vials with Teflon™-lined caps. Store all stock and prepared standards in refrigerator below 6˚C.

10.4.1 Stock Semivolatiles (SV) Internal Standards, 4000 µg/ml: Restek SV Internal Standard mix, #31006 or equivalent.

10.4.1.1 Internal Standard Mix, 200 µg/ml: 1,4-dichlorobenzene-d5, naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chry-sene-d12 and perylene-d12. Prepare 200 µg/ml from stock (10.4.1).

10.4.2 Stock SV Acid Surrogates, 10,000 µg/ml: Restek SV Acid Surrogate Standard mix, #31087 or equivalent.

10.4.3 Stock SV Base/Neutral Surrogates, 5000 µg/ml: Restek SV Base/Neutral Surrogate Standard mix, #31086 or equivalent.

10.4.4 Stock Tuning Standard: DFTPP/Pentachlorophenol /Benzidine/4,4'-DDT-1000 ug/mL (1000 ppm): ChemService CLP-T51M or equivalent.

10.4.4.1 Intermediate Tuning Standard, 25 µg/ml solution in methylene chloride: ~ 9.5 ml of methylene chloride is added to a 10 ml volumetric flask, then using a uL syringe, add 250-µl of the 1000 ppm Stock Tuning Standard. Fill the flask to the mark with methylene chloride and mix the solution. Transfer into the appropriate storage vials. Prepare fresh every six months.

10.4.5 Stock SV Analyte certified standards are purchased at concentrations of 2000 µg/ml. Stock standards used to prepare calibration intermediates standards are prepared from several multi-component mixes that are purchased from a same vender. When certain calibration compounds co-elute to a point that mass resolutions cannot be adequately made, these compounds shall be separated during preparation and analysis during calibration procedures. The following is an example preparation of the Intermediate Calibration Standard for SV analytes.

10.4.5.1 8270 MegaMix, Restek, Inc., Cat # 31850, 1000 ppm in Methylene Chloride, 76 Base/Neutral/Acid SVOCs; store -10-20 ºC

10.4.5.2 Organochlorine Pesticide Mix AB, Restek, Inc. Cat#32415

10.4.5.3 Nitrogen / Phosphorus Pesticide Mix 2, Restek, Inc. Cat#33423

10.4.5.4 Organonitrogen Pesticide Mix 1, Restek, Inc. Cat#33012

10.4.5.5 Organophosphorus Pesticide Mix AB, Restek, Inc. Cat#33013

10.4.5.6 Miscellaneous single components, as 1000-ppm: Quinoline, store at or below 6˚C.

10.4.6 Typical SV Intermediate Calibration Standard @ 200 ppm, in methanol - This standard is used the list of compounds noted in Table 10.1. Use Calibrated syringes for volume measurements. Prepare a new intermediate standard every six months.

Table 10.4.6 STD Intermediate ICAL Standard @ 200 ppm

Table 10.4.6 Stock Name	Analyte Conc., ppm	Amt Added, ml	Final Vol, ml	Final Conc. ppm
8270 Mega Mix	1000	1.0	5-ml	200
Quinoline	1000	1.0		200
Organochlorine Pest Mix AB	1000	1.0		200
Nitrogen/Phosphorus Pest Mix 2	1000	1.0		200
Organonitrogen Pest Mix 1	1000	1.0		200
Organophosphorus Pest Mix 1	1000	1.0		200
8270 BN Surr	5000	0.20		200
8270 Acid Surr	10000	0.10		200

10.4.7 Low Level SV Intermediate Calibration Standard @ 100 ppm - prepare in methanol – Dilute 0.50 ml of 200 ppm SV Intermediate Calibration Standard (10.4.6) to final volume of 1.0 ml.

10.4.7.1 Initial and Continuing Calibration Standards: These standards are prepared at minimally eight levels as follows using the Intermediate prepared in 10.4.6. Prepare fresh every six months. A second source ICV is made using the same approach as the 2.5-ppm standard "SLSTD2.5" listed below.

Table 10.4.7.1 SV Working Calibration Standards

Table 10.4.7.1 Standard Name	Int. Stdn Conc., ppm	Amt Added, µL	Final Volume , ml	Final Conc. ppm
SLSTD0.1*	100	1.0	1.0	0.1
SLSTD0.2	100	2.0		0.2
SLSTD0.5	100	5.0		0.5
SLSTD1.0	100	10.0		1.0
SLSTD2.5**	100	25.0		2.5
SLSTD5.0	100	50.0		5.0
SLSTD7.5	100	75.0		7.5
SLSTD10.0	100	100.0		10.0

SLSD0.1* - only for select PAH compounds.
SLSTD2.5** -CCV

10.4.8 LCS Spike Stock Standards (samples processed by extraction lab): Stock SV Analyte certified standards are purchased at typical concentrations of 2000 µg/ml. Stock standards used to prepare intermediate spike standards are typically prepared from several multi-component mixes. The following is an example of Stocks used to prepare an SV Intermediate Spike Standard

10.4.8.1 8270 MegaMix, Restek, Inc., Cat # 31850, 1000 ppm in Methylene Chloride, 76 Base/Neutral/Acid SVOCs; store -10-20 ºC

10.4.8.2 Miscellaneous single components, 1000-ppm: Quinoline, store at or below 6˚C.

10.4.9 Typical SV Low Level LCS/MS Spike Standard @ 5 ppm - prepared in methanol

- This type of standard covers the routine SV LCS / MS Spike for the list noted in Table 21.2. Calibrated µL syringes shall be used for volume measurements.

Table 10.4.9 SV PAH / Pentachlorophenol LCS Intermediate Spike Standard

Table 10.4.9 SV PAHs and Phenols @ 5.0 ppm				
Stock Name	Stock Conc., ppm	Amt Added, µL	Final Volume, mL	Final Conc. ppm
8270 MegaMix	1000	250	50.0	5.0
Misc. Analyte #1	1000	250		5.0

10.4.10 SV Surrogate Spiking Solution, @ 100 ppm: prepare using mL syringes and a 100 ml volumetric flask

Table 10.1.10 SV Surrogate Spike Standard @ 100 ppm

Table 10.4.10 Stock Name	Stock Conc., ppm	Amt Added, µL	Final Volume, mL	Final Conc. ppm
BN Surr Restek 31087	5000	100	100.0	5.0
Acid Surr Restek 31086	10000	50		5.0

10.5 Reagent Storage - Transfer the mixtures to multiple amber glass vials with Teflon™-lined caps and store in the refrigerator below 6 ºC. Working standards should be prepared as needed from stocks. Stock standards should be replaced after 1 year or sooner if a manufacturer expiration date has been reached. Prepared intermediate standards should be replaced every 6 months or sooner if a component expires sooner.

10.6 Reagent Preparation Records: Record Stock Standards in the Chemical Inventory Log-book and record all standards prepared in the Standard Preparation Logbook according to SOP HS-QS001 (latest revision thereof). Label standards appropriately so that they can be easily cross-referenced to other records.

11) Method Calibration

11.1 GC/MS Tuning: Tune the GC/MS to meet the criteria specified in Table 11.1 when DFTPP is injected. Inject 50 ng of Tuning Mix (Section 10.4.4, DFTPP, etc.). The tuning criteria in Table 11.1 must be met to allow performance of an initial or continuing calibration and further analysis. This criterion must be demonstrated for every twelve-hours of operation for method 8270D and 24 hours for method 625.

11.2 Tune Criteria

11.2.1 8270D

Table 11.2.1 DFTPP tuning Criteria, from Method 8270D

Mass	Table 11.2.1 – 8270D M/z Abundance Criteria
51	10-80% of mass 198
68	Less than 2% of mass 69 present
70	Less than 2% of mass 69 present

Mass	Table 11.2.1 – 8270D M/z Abundance Criteria
127	10-80 % of mass 198
197	Less than 2% of mass 198
198	Base peak, 100% relative abundance or >50% of mass 442
199	5-9% of mass 198
275	10-60% of mass 198 (Base Peak)
365	Greater than 1.0 % of mass 198
441	Present but less than 24% of mass 442
442	Greater than 50 percent of mass 198
443	15-24 percent of mass 442

11.2.2 EPA 625/EPA 625.1 Tune Criteria

Table 11.2.2 DFTPP tuning Criteria, from Method 625

Mass	Table 11.2.2 – 625 M/z Abundance Criteria
51	30-60% of mass 198
68	Less than 2% of mass 69 present
70	Less than 2% of mass 69 present
127	40-60 % of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198 (Base Peak)
365	Greater than 1.0 % of mass 198
441	Present but less than mass 443
442	Greater than 40 percent of mass 198
443	17-23 percent of mass 442

11.3 When performing the above tune, the mass spectrum of DFTPP is acquired using the following approach: three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP.

11.4 Besides the DFTPP solution, the Tuning Mix also contains pentachlorophenol, benzidine, and DDT. Benzidine and pentachlorophenol are used to evaluate peak tailing. DDT is used to evaluate whether degradation to DDD and DDE is occurring.

11.4.1 Tailing standard evaluation for benzidine /pentachlorophenol: no peak tailing should be visible, the Benzidine / pentachlorophenol tailing factors must be calculated and less than 2. Perform column maintenance if the tailing factor criteria cannot be achieved.

11.4.2 Breakdown standard evaluation for DDT: degradation of DDT to DDE and DDD should not exceed 20%. If degradation is excessive, poor chromatography is noted, the injection port may require cleaning. After performing maintenance,

retune as required to meet the specified criteria. Whenever maintenance or service is performed on the instrument which may change or affect the tune, (i.e., source cleaning or repair, etc.) the tune will be verified irrespective of the twelve-hour requirements. Record all maintenance performed.

11.4.3 When the tune criteria have been met, make a graphics electronic copy of the chromatogram and spectrum, a mass listing normalized to 198 = 100% and a copy of the tune form and save on the processing computer. These files are automatically backed up nightly.

11.5 Initial Calibration - Eight concentrations (nominally 0.1(PAHs only), 0.2, 0.5, 1.0, 2.5, 5.0, 7.5, 10 ng/ul) of target compound standards are analyzed to initially calibrate the GC/MS and determine linearity of response. The initial calibration is verified every twelve hours at the 2.5-ng/ul level. For Standard Preparations, see Sect.10.

11.5.1 Internal Calibration: Internal standards (2 ng/ul) are added to each calibration standard for quantitation and QA/QC purposes.

11.5.2 Response Factors (RF) and %RSD for each target compound at each calibration level are tabulated to assess them against method criteria. Refer to Section 15.1.1 for calculation of the RFs and the RSDs.

11.5.3 Percent Relative Standard Deviation (% RSD): The RSD should be less than or equal to 20% for each target analyte. Each target analyte should meet the minimum response factor noted in Table 21.1 (the most common target analytes identified by method 8270D). These are to be demonstrated for each individual calibration level as a means to ensure that these compounds are behaving as expected. In addition, meeting the minimum response factor criteria for the lowest calibration standard is critical in establishing and demonstrating the desired sensitivity. Due to the large number of compounds that may be analyzed by this method, some compounds may fail to meet the criteria. For these occasions, it is acknowledged that the failing compounds may not be critical (if not required target analytes) for the specific project. If required, their reporting would require use of data qualifier flags to indicate the data as estimated values (e.g. useable for screening purposes if acceptable in a client project plan). **Note** DoD QSM requires 15% RSD for average response, see Table 24.5.

11.5.4 If more than 10% of the required target compounds included with the initial calibration exceed the 20% RSD limit and do not meet the minimum Coefficient of Determination (COD) of >0.99 for alternate curve fits, then the chromatographic system is considered too reactive for analysis to begin. System maintenance must then be performed (e.g. clean or replace the injector liner and/or capillary column, then repeat the calibration procedure).

11.5.5 Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. The resolution is verified on the mid-point concentration of the initial calibrations well as the laboratory designated continuing calibration verification level if closely eluting isomers are to be reported (e.g., benzo(b)fluoranthene and benzo(k)fluoranthene).

11.6 Linearity of target analytes: If the RSD of any target analyte is 20% or less, then the relative response factor is assumed to be constant over the calibration range, and the

average relative response factor may be used for quantitation. If the RSD of any target analyte is greater than 20%, the linear or non-linear calibration options may be evaluated and applied.

11.6.1 When the RSD exceeds 20%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc. **Note** DoD QSM requires 15% RSD for average response, see Table 24.5.

11.6.1.1 Analyst has two options (1) Create single calibration on with 15% RDS criteria or (2) create two curve from calibration with one using 20% method criteria and on with 15% DoD QSM criteria.

11.6.2 Due to the large number of compounds that may be analyzed, some compounds may fail to meet either the 20% RSD, minimum correlation coefficient criteria (0.99), or the acceptance criteria for alternative calibration procedures in Method 8000C. Either the linear or non-linear calibration models described in Method 8000C may be used, but they should be used consistently. It is considered inappropriate once the calibration analyses are completed to select an alternative calibration procedure in order to pass the recommended criteria on a case by case basis. In order to report non-detects, it must be demonstrated that there is adequate sensitivity to detect the failed compounds at the applicable lower quantitation limit. NOTE: The option for non-linear calibration may be necessary but it may not be used to compensate for detector saturation or to avoid proper instrument maintenance. The calibration model must be continuous and monotonic. Linear fits require five levels minimally and non-linear (quadratic) fits require six levels minimally.

11.6.3 The method of linear regression analysis has the potential for a significant bias to the lower portion of a calibration curve, while the relative percent difference and quadratic methods of calibration do not have this potential bias. When calculating the calibration curves using the linear regression model, a minimum quantitation check on the viability of the lowest calibration point should be performed by re-fitting the response from the low concentration calibration standard back into the curve (See Method 8000C for additional details). It is not necessary to re-analyze a low concentration standard, rather the data system can recalculate the concentrations as if it were an unknown sample. The recalculated concentration of the low calibration point should be within ± 30% of the standard's true concentration. Should any recalculated analyte be greater than 30% at the MQL, the analyst should review the results (proper identification, area counts, calibration or response factors, and RSD). For those analytes affected, ensure that the problem is not associated with just one of the initial calibration standard. If the problem appears to be associated with a single standard, then that one standard may be reanalyzed once, to rule out problems due to a random chance, and the RSD or correlation recalculated. Replacing the standard may be necessary in some cases. All reanalysis of any calibration standard must be performed within the same tuning period for a GC/MS method. This reanalysis must also commence before any samples are analyzed. If this criterion cannot be met then repeat the entire initial calibration.

11.6.3.1 NOTE: Reanalyzing or replacing a single standard must NOT be

confused with the practice of discarding individual calibration results for specific target compounds in order to pick and choose a set of results that will meet the RSD or correlation criteria for the linear model. The practice of discarding individual calibration results is addressed as a fourth alternative option and is very specific as to how a set of results are chosen to be discarded. If a standard is reanalyzed or a new standard is analyzed, then ALL of the results from the original analysis of the standard in question must be discarded. Further, the practice of running additional standards at other concentrations and then picking only those results that meet the calibration acceptance criteria is EXPRESSLY PROHIBITED, since the analyst has generated data that demonstrate that the linear model does not apply to all of the data.

11.6.3.2 Another alternative is to narrow the calibration range by replacing one or more of the calibration standards with standards that cover a narrower range. If linearity can be achieved using a narrower calibration range, document the calibration linearity, and proceed with analyses. The changes to the upper end of the calibration range will affect the need to dilute samples above the range, while changes to the lower end will affect the reliable quantitation of the method at low concentration levels.

11.6.3.3 Corrective action may be required if the criteria for %RSD, r, or COD (r^2) are not met. The calibration may not be used for quantitative analyses of that analyte when %RSD, r or COD are not met.

11.6.4 Initial Calibration using Linear Regression (First Order Fit Determinations): When the average response factor RSD is greater than 20% over the calibration range, linearity through the origin cannot be assumed. A linear regression (first order fit) of the response versus the concentration of the standards is evaluated. The instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). The regression produces the slope and intercept terms for a linear equation in the following form:

$$y = a + bx$$

Where,

y = instrument response in peak area or height
x = concentration of the calibration standard
a = Slope of the line (also called the coefficient of x)
b = The intercept

11.6.4.1 Linear Fit Criteria: The analyst must not force the line through the origin, but have the intercept calculated from the five data points minimally. The origin (0,0) is NOT included as a sixth calibration point. The regression calculation will generate a correlation coefficient (r) that is a measure of the "goodness of the fit" of the regression line to the data. The linear fit correlation coefficient (r) must be 0.995 or better.

11.6.5 Quadratic (second order non-linear) Fits: to use a quadratic fit, six data points minimally are required. The regression curve uses the following equation:

$$y = a + bx + cx^2$$

Where a, b, and c are constants defined by the curve.

11.6.5.1 The quadratic (non-linear) fit must generate a coefficient of determination (COD) greater than or equal to 0.99. Response must increase with increasing concentration.

11.7 Initial Calibration Verification (ICV): Using a second source standard, each new initial calibration must be verified once. Typical verification will be at the midpoint of the curve or at 2.5 ng/ul. The percent recoveries of the verification standard must fall within 80-120% for all target analytes. **Note** DoD QSM requires ICV recoveries to be within 80-120 for all target analytes, to ensure DoD limits are achieved analysts must use the DoD codes in LIMS.

11.7.1 Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. The resolution is verified on the mid-point concentration of the initial calibrations well as the laboratory designated continuing calibration verification level if closely eluting isomers are to be reported (e.g., benzo(b)fluoranthene andbenzo(k)fluoranthene).

11.8 Continuing Calibration Verification (CCV): Every twelve-hour time period the validity of the initial calibration is checked. A 2.5-ng/ul-calibration standard (see section 10) is analyzed and the RFs for the CCV are compared to the average RFs of the initial calibration and evaluated against the minimum RFs in Table 21.1.

11.8.1 CCV Internal Standard Retention Time and Area criteria - The CCV retention times and areas of the internal standards in the CCV are checked against the mid-point of the initial calibration. If the retention times change more than 30 seconds or the area changes by a factor of two (-50% to +100%), the GC/MS must be inspected and appropriate maintenance and/or corrections made. The CCV relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units. Late-eluting target analytes usually have much better agreement.

11.8.2 The CCV %Drift or %D for all reported target compounds must <20%. Corrective action must be initiated when %D exceeds 20%.

11.8.3 Isomeric Separation – See Section 11.4.5.

11.8.4 DoD projects will require closing CCV for each analytical batches, with %Drift or %D for all reported target compounds must <50%. Corrective action must be initiated when %D exceeds 50%. DoD samples must be logged with DoD testcode to ensure DoD recovery limits are applies to QC and field samples.

12) Sample Preparation/Analysis

12.1 Sample Preparations:

12.1.1 For aqueous samples, refer to separatory funnel liquid –liquid extraction (method 3510 C, SOP HS-EXT001).

12.1.2 For solid/soil samples, refer to automated soxhlet extraction (method 3541), SOP HS-EXT002. Sample cleanup steps are not routinely performed.

12.1.3 GPC Cleanup can be performed should a project require it or if sample matrix issues suggest its use and Project Management acquires client approval for the use.

12.2 Daily Instrument Maintenance

12.2.1 Prior to tune and analysis the following maintenance must be performed daily:

- Replace Liner and o-ring
- Replace Septum
- Clean injection port
- Clean gold seal or replace if worn.
- Clip approximately two to six inches of the column.

12.3 Sample Extract Analysis

12.3.1 Analysis of sample extracts may begin once all the calibration, tune and continuing calibration criteria must be met, see Sections 11.1-11.3 if no initial calibration followed by 11.6-11.7. IF initial calibration is needed, then all steps in Section 11 must be performed.

12.3.2 Sample Extracts - Allow sample extracts to warm to room temperature, add 10 µL of 200 µg/ml internal standard (see section 10), cap the extract vial and invert the sample vial several times to mix. The extract vial is ready for analysis.

12.3.3 When the analysis is complete, verify that the internal standards, surrogates, and compounds of interest are properly identified and quantified, and that the surrogate recoveries are within the acceptable range for the sample type. DoD sample must be logged and analyzed using the DoD LIMS codes ensure limits from DoD QSM QC limits are applied to samples.

12.3.4 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place. Additional internal standard is added to the diluted extract to maintain the required 2 ng/uL of each internal standard in the extracted volume.

12.3.5 When ions from a compound in the sample saturate the detector, this analysis should be followed by the analysis of an instrument blank consisting of clean solvent. If the blank analysis is not free of interferences, then the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences. Contamination from one sample to the next on the instrument usually takes place in the syringe. If adequate syringe washes are employed, then carryover from high concentration samples can usually be avoided.

12.3.6 When a compound has been identified, the compound quantitation is based on the integrated abundance from the EICP of the primary characteristic ion.

12.3.6.1 Secondary ion quantitation should be used only when there are sample interferences with the primary ion. NOTE: It may be a useful diagnostic tool to monitor internal standard retention times in all samples, spikes, blanks, and standards to effectively check drifting, method performance, poor injection execution, and anticipate the need for system inspection and/or maintenance. Internal standard responses (area counts) must be monitored in all samples, spikes, blanks for similar reasons. If the EICP area for any of the internal standards in samples, spikes and blanks changes by a factor of two (-50% to +100%) from the areas determined in the continuing calibration analyzed that day, corrective action must be taken. The samples, spikes or blanks should be reanalyzed or the data should be qualified.

12.4 Qualitative Analysis (including Tentatively Identified Compounds or TICs)

12.4.1 Analyte identification is performed by comparing the spectrum of the suspected compound with that of a standard reference spectrum. The sample component RRT must be within±0.06 RRT units of the RRT of the current CCV. For mass spectra comparisons, all ions in the standard spectrum at an intensity of >10% relative to the most abundant ion must be present in the sample spectrum. In addition, the above qualifying ions must agree within ±20% unless in the judgement of the mass spectral interpreter, an identification is possible.

12.4.2 When requested, a library search will be performed on each sample to identify any components not matched to calibration standard spectra. This search is performed using the Data General data system in conjunction with the Wiley Mass Spectral Library or the Chemstation NIST library. The analyst will report the 20 largest of the unknown peaks. The interpretation specialist determines tentative identification of the results. Ions with relative intensities of >10% in the reference spectrum must be in the sample spectrum and agree within ±20%. The molecular ions present in the reference spectrum should be in the sample spectrum. Check for background contamination when ions that are not in the reference spectrum are in the sample spectrum. The analyst reviewing the library search results makes final identification and if no adequate match can be determined, the compound is reported as an UNKNOWN.

12.5 Quantitative Analysis:

12.5.1 The internal standard method is used for quantitation of target compounds identified. The area of the characteristic ions (extracted ion) of analytes and internal standards are used. If the %RSD of a compound's relative response factor is 20% or less over the calibration range, then linearity through the origin may be assumed, and then the concentration in the extract is be determined using the average response factor (Ave. RF) from the Initial Calibration (ICAL) data.

13) Troubleshooting

13.1 Check instrument maintenance; prepare a new curve as needed.

13.2 Possible problems could be standard mixture degradation, column contamination, or active sites in the column or chromatography system.

14) Data Acquisition

14.1 Data is collected with "Chemstation" data acquisition software. This software provides the sequence log of run order for the data to be collected.

14.2 "Target DB" data processing software converts the acquired signal information from "Chemstation" into final presentation results. Target processes the calibration curve and all associated sample and QC data.

14.3 LIMS receives the processed "Target" data in its data entry module and links the data to the samples in a specific work order. The QC batch data is also linked to the data.

15) Calculation, and Data Reduction Requirements

15.1 Quantification Calculations

15.1.1 Initial Calibration (ICAL) Calculations (RRF and RSD): Calculate the average relative response factor (Ave. RRF or Ave.RF) for each compound across the five or more calibration concentrations using the below equations (The Target Software performs the calculation):

$$RF = \frac{A_X \times C_{is}}{A_{is} \times C_x}$$

Where:
A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard.
C_x = Concentration of the compound being measured.

15.1.2 ICAL Percent Relative Standard Deviation (% RSD): Calculate the %RSD(s) for each compound as follows:

$$\%RSD = \frac{SD}{Avg(X)} \text{ x } 100$$

where:
RSD = relative standard deviation.
Avg(X) = mean of 7 initial Response factors (RFs) for a compound.
SD = standard deviation of average RFs for a compound.

15.2 Continuing Calibration

15.2.1 Calculation of % drift (regression model curve fits) by using the following formula:

$$\%Drift = \frac{Conc_{calc'd} - Conc_{Theor}}{Conc_{Theor}} \times 100$$

15.2.2 Percent difference (response factor calibration fit) is calculated as follows:

$$\text{Percent Difference} = \frac{\overline{RF_I} - RF_C}{\overline{RF_I}} \; x\,100$$

Where:
RF_i = average relative response factor from the initial calibration
RF_C = response factor from current verification check standard

15.3 Analyte Calculations, aqueous samples:

$$\text{Conc. (ug/l)} = \frac{(A_x)(I_s)(V_t)}{(V_i)(A_{is})(\overline{RFi})(V_o)}$$

Where:
A_x = Area of characteristic ion for compound being measured.
I_s = Amount of internal standard injected (ng).
V_t = Volume of total extract, taking into account dilutions (i.e., a 1 to 10 dilution of a ml extract will mean Vt = 10,000-µl. If half the base/neutral extract and half the acid extract are combined, Vt = 2,000).
A_{is} = Area of the characteristic ion for the specific internal standard.

RF_i = average relative response factor from the initial calibration
V_o = Volume of water extracted (ml).
V_i = Volume of extract injected (µl).

15.4 Analyte Calculations, soil or solid waste samples:

$$\text{Concentration (ug/kg)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(\overline{RFi})(V_i)(W_s)(D)}$$

Where
RF_i, A_x, I_s, A_{is}, V_i = same as for water.
W_s = weight of sample extracted (g). The wet weight or dry weight may be used, depending upon the specific applications of the data.
D = (percent moisture in sample)/100, or 1 for a wet-weight basis.

15.4.1 The analyst must know how to use the above equations. The equations are necessary tools for troubleshooting calibration files, ID files, and acquired data files. The sample concentration is quantified and a report generated utilizing computer software.

15.4.2 The equations used for calculating concentrations of TICs are the same as those used for target compounds with the following modifications: peak areas are derived from the total ion instead of the extracted ion, and a RRF of 1 is assumed. TIC concentrations are always reported as estimated values and have an associated data qualifier reported.

15.5 QC Calculations: LIMS calculates the percent recovery for various QC samples (LCS) according to the following equations:

15.5.1 % Recovery, %R (for MS and MSD Samples)

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SR = Sample Result (unspiked).
SA = Spike Amount Added (mg/L or mg/kg).

15.5.2 % Recovery, %R (for standards and LCS)

$$\%R = \frac{(SSR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SA = Spike Amount Added (mg/L or mg/kg).

15.5.3 RPD (for precision or duplicate evaluation)

$$RPD = \frac{|SR_1 - SR_2|}{½(SR_1 + SR_2)} \times 100$$

Where:
SR_1 = Sample result for duplicate 1.
SR_2 = Sample result for duplicate 2.

16) Quality Control, Acceptance Criteria and Corrective Action

16.1 Instrument Tuning, DDT breakdown and Benzidine / PCP tailing factors:

16.1.1 Frequency: perform at the beginning of each 12 hours shift

16.1.2 Acceptance Criteria: refer to section 11.1 (table 11.1, section 11.1.1, etc); all criteria must be met

16.1.3 Tuning Criteria Failure Corrective action: discontinue operation, perform instrument maintenance; a passing tune must be achieved prior to resumption of operation/sample analysis; any samples run after a failing tune must be reanalyzed after corrective action has been performed.

16.2 Initial Calibration:

16.2.1 Frequency: A new curve must be generated when CCV criteria are not met, or after major instrument maintenance such as column replacement or changes in operating conditions

16.2.2 Acceptance Criteria:

16.2.2.1 Initial calibration curve must have 5-points minimally for all analytes; six points are required for second order curve fits.

16.2.2.2 RFs for each analyte at each level and the respective average RF must meet minimum analyte designated RF values in Table 24.1 and each analyte % RSD must be ≤ 20% (15% for DoD).

16.2.2.3 Perform the linear curve fit where r >0.995 for analytes where RSD is >20 % or perform the non-linear curve fit where the COD, r^2 >0.990 for analytes where RSD is >20 %.

16.2.2.4 When calculating the calibration curves using the linear regression model or non-linear curves, a minimum quantitation check on the viability of all calibration points should be performed by re-fitting the response from the low concentration calibration standard back into the curve (See Method 8000D for additional details). This check is the refitting of the calibration data back to the model or the comparison of the calculated amount of each of the standards against the expected amount. If any analyte for any calibration standard has a percent error > ±30% as described in Section11.5.4.1 of Method 8000D, corrective action may be needed.

16.2.3 Curve Failure Corrective Action:

16.2.3.1 Check standards and or perform maintenance as necessary to correct problem, then generate new curve.

16.3 Initial Calibration Verification (ICV) using a second source standard:

16.3.1 Frequency: Perform this evaluation each time a new curve is generated.

16.3.2 Acceptance criteria: agreement between the curve and ICV results must be between 80 – 120 % of the ICV true values.

16.3.3 ICV Failure Corrective action: evaluate condition and age of standards being used and/or perform any needed system maintenance. Do not analyze samples until the criteria can be met or prepare new standards and /or generate new curve if criteria cannot be met.

16.4 Continuing Calibration Verification (CCV):

16.4.1 Frequency: The calibration standard must be run at the beginning of every 12

hour analytical sequence for 8270D/625.1 and 24 hours for EPA 625.

16.4.2 Acceptance Criteria: CCV acceptance criteria for each compound must be ≤ 20% of the true value. Blank must have not compounds greater than ½ LOS and surrogate within 20% of true value.

16.4.3 Corrective Action: If the CCV does not meet the criteria, correct the problem and re-analyze the CCV. If the CCV is still out, prepare a new calibration curve. Samples associated with marginal exceedance target analyte can be reported when the result is "not detected". Corrective action must still be carried out to address the exceedance.

16.4.4 DoD samples require closing CCV with each compound within 50% of the true value. This CCV must be analyzed within the 12 or 24 hour tune period. DoD samples must be bracketed by successful CCV or samples re-analzyed. :

16.5 CCV/CCB Internal Standard Area Requirements:

16.5.1 Frequency: every CCV/CCB is spiked with internal standards.

16.5.2 CCV IS Acceptance Criteria: Review the quantitation report for each sample and check the CCV IS retention time windows and the CCV IS areas.

16.5.2.1 The CCV IS retention time widow must be ± 30 seconds from the RT established in the ICAL.

16.5.2.2 The CCV IS areas must not differ from the areas established in the ICAL by more than a factor of two (-50 % to +100 %)

16.5.3 CCV Internal Standard RT window or Area Failure Corrective Action**:** If the CCV internal standard areas do not fall within CCV IS criteria for RT or areas, the system problem must be corrected prior to running any samples. If any samples were run after failing IS in a CCV, all those samples must be reanalyzed.

16.6 CCV Internal Standard RT window or Area Failure Corrective Action**:** If the CCV internal standard areas do not fall within CCV IS criteria for RT or areas, the system problem must be corrected prior to running any samples. If any samples were run after failing IS in a CCV, all those samples must be reanalyzed.

16.7 Method Blank:

16.7.1 Frequency: Analyze the method blank at a frequency of one per preparation batch of 20 or less samples by 8270D/625.1 and one per preparation batch of 10 or less samples for 625. The method blank should be analyzed after the calibration standard, or at any other time during the analytical shift, to ensure that the total system is free of contaminants. If the method blank indicates contamination, it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples.

16.7.2 Acceptance Criteria: All target analytes must be < ½ LOQ in Table 21.4 .

16.7.2.1 Other approved QA program requirements must be followed when the acceptable blank contamination specified in the approved quality assurance project plan differs from the above.

16.7.2.2 Analytes of interest must be less than 5% of the regulatory limit associated with an analyte or analytes of interest must be less than 5% of the sample result for the same analyte, whichever is greater.

16.7.3 Method Blank Contamination Corrective Action: If the method blank results do not meet the acceptance criteria above, then the laboratory must take corrective action to locate and reduce the source of the contamination and to

re-extract and reanalyze any samples associated with the contaminated method blank. If samples cannot be re-run because of insufficient sample or other similar circumstances, a corrective action report must be initiated and issued to project management and to the QAD. The NCAR must be detailed enough for preparation of the project narrative and all appropriate data flags are entered into LIMS for the final report preparation. Data reported with an associated contaminated method blank must be flagged with a "B", indicating the occurrence.

16.8 Laboratory Control Sample (LCS):

16.8.1 LCS Frequency: For LCS frequency of at least one LCS per 20 samples or 8270D/625.1 and one LCS per 10 samples for 625. All samples in the batch must be processed on the same 24 hour period.

16.8.2 Acceptance Criteria: refer to Table 24.3 for criteria. Acceptance allowances provided for sporadic marginal exceedances according to Table 24.4, where water and soil matrix allowances are expanded to be between the control limit (three standard deviation) and four standard deviations from the statistical mean. See SOP HS-QS018, Sporadic Marginal Exceedance. For DoD samples, DoD QSM control limits must be used. To ensure application of DoD QSM control limits DoD LIMS codes and spec must be used. DoD control limits can be found LIMS or DoD QSM. For latest control limits see Testcode Specs in LIMS.

16.8.3 LCS failure Corrective Action: If the LCS recovery for the compounds of interest does not meet with the criteria, the sample batch must be re-analyzed. If reprocessing it is not possible due to lack of sample or expired hold time, report (narrate) the variance to the client and flag the associated data as estimated.

16.9 Matrix Spike (MS) and Matrix Spike Duplicate (MSD)

16.9.1 Frequency: Perform MS and MSD at a frequency of at least one MS and MSD per 20 samples or 8270D/625.1 and. one MS and MSD per 10 samples for 625. If an MSD cannot be processed due to insufficient sample, a duplicate LCS shall be processed to assess the duplicate RPD criteria.

16.9.2 Acceptance Criteria: Spike recovery criteria are specified in the Table 24.3. For DoD samples, DoD QSM control limits must be used. To ensure application of DoD QSM control limits DoD LIMS codes and spec must be used. DoD control limits can be found LIMS or DoD QSM.

16.9.3 Corrective Action:

16.9.3.1 If the MS/MSD native concentration is four times or more the spiking level, calculated recoveries or RPD values may be difficult to evaluate. Professional judgment must be used to assess QC results in this situation.

16.9.4 MS/MSD % Recovery Criteria Exceedance Corrective Action: If the MS and MSD have recoveries which are outside the target range, the poor recoveries in the MS and MSD may be due to matrix effects. The LCS, surrogate recoveries and calibration results must all be evaluated in order to determine if matrix interference is present or if method performance is poor. Note that the MS and MSD are used to evaluate the matrix effect, not to control the analytical process. If both the Matrix Spike and Matrix Spike Duplicate are found to be out of control for the same analyte, a matrix effect is likely confirmed

(assuming the LCS passes). If recoveries of the MS/MSD pair are suspicious (laboratory error, etc.) another set of MS/MSD must be re-extracted with the sample batch. For instance, if both matrix spikes exhibit low recovery but good precision then it can be assumed that matrix interference is present. However, if precision between the MS and the MSD is poor, technique error must be eliminated as a possible source of error before the data can be accepted. If matrix interference is highly suspected corrective action is not necessary.

16.9.5 MS/MSD RPD Criteria Exceedance Corrective Action: If the RPD fails, the data must be evaluated for error. Perform sample/batch QC reprocessing as necessary.

16.10 Surrogates (Surr)

16.10.1 Frequency: Surrogates are spiked into each sample and QC sample. The recoveries must be evaluated for all samples and QC samples.

16.10.2 Criteria: Acceptance limits for each matrix are specified in the Table 24.3. All base-neutral (BN) and acid (A) surrogates should meet the acceptance range. Any surrogate below 10% recovery requires re-extraction and re-analysis. If anyone acid or BN surrogate (or one of each) exceed criteria, they must be re-analyzed to confirm. Any two of either acid or BN exceed criteria, sample re-extraction and analysis must be performed. For DoD samples, DoD QSM control limits must be used. To ensure application of DoD QSM control limits DoD LIMS codes and spec must be used. DoD control limits can be found LIMS or DoD QSM.

16.10.3 Surrogate Exceedance Corrective Action: If the surrogate recoveries do not meet the criteria in Table 24.2:

16.10.3.1 Check for possible errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly.

16.10.3.2 Examine chromatograms for interfering peaks and integrated peak areas.

16.10.3.3 If no calculation or integration errors are found, and the surrogate recovery remains outside the limit and the prep blank is acceptable, re-analyze the sample extract to confirm analysis. If any surrogate recovery is below 10%, the sample must be re-extracted and re-analyzed.

16.10.3.4 If the exceedances repeat, re-extract and reanalyze sample, if possible. (It may not be possible to re-extract water samples). If re-extraction and re-analysis yields a recovery that is again outside limits, matrix interference likely.

16.10.3.5 Additionally, check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract. Some samples may require dilution in order to bring one or more target analytes within the calibration range or to overcome significant interferences with some analytes. This may result in the dilution of the surrogate responses to the point that the recoveries cannot be measured. If the surrogate recoveries are available from a less-diluted or undiluted aliquot of the sample or sample extract, those recoveries may be used to demonstrate that the surrogates were within the QC limits, and no further action is

required. However, the results of both the diluted and undiluted (or less-diluted) analyses should be reported.

16.10.3.6 If no instrument problem is found, the sample should be re-extracted and re-analyzed. If, upon re-analysis, the recovery is again not within limits, report the data and document the failing results as confirmed by reanalysis. If the recovery is within the limits in the re-analysis, report the re-analysis data.

16.10.3.7 If the holding time for the method has expired prior to the re-analysis, provide both the original and re-analysis results to the data user, and note the holding time problem.

16.11 Internal Standard Retention Time Windows and Area Requirements:

16.11.1 Frequency: All samples and QC samples are spiked with internal standards.

16.11.2 IS Acceptance Criteria: Review the quantitation report for each sample and check the IS retention time windows and the IS areas.

16.11.2.1 The IS retention time widow must be ± 30 seconds from the associated twelve (12) hour daily CCV

16.11.2.2 The IS areas should not differ from the associated twelve (12) hour daily CCV by more than a factor of two (-50 % to +100 %)

16.11.3 Internal Standard RT window or Area Exceedance Corrective Action: If the internal standard areas do not fall within IS criteria for RT or areas, the sample(s) must be re-run as confirmation of matrix effect. Confirmed matrix effects will be reported to project management for sample narrative comments. If the rerun internal standards do not confirm a matrix effect, review the calculations and check for instrument error. If no errors are found, an NCAR must be issued to project management and to the QAD. The NCAR detailed enough for preparation of the project narrative and all appropriate data flags must be entered into the LIMS for final reporting.

16.11.4 NOTE: Several sample types exhibit matrix effects that make recovery of the internal standards and surrogates very difficult. These samples must be run at a dilution to achieve acceptable criteria. However, if target compounds are present in undiluted runs with failing QC (surrogates or internal standards) and are diluted out to achieve passing QC, it may be necessary to report the undiluted analyses with data qualifier flags and an appropriate discussion within the case narrative by project management.

16.12 The Data Assessment Checklist must be used for data review documentation (SOP HS-QS009, current revision) unless an alternative approved QA program document is required. The completed checklist is filed with the associated batch data.

16.13 Manual Integration: ALS procedures for Manual Integration, HS-QS016, must be followed.

16.14 Initial Demonstration of Capability (IDOC)

16.14.1 Purpose: Verify the ability to produce data of acceptable precision and bias for a specific instrument type, matrix, method, and analyst.

16.14.2 Frequency: Initially during method development, and any time there is a significant change in instrument type, personnel, methodology, or matrix

16.14.3 Acceptance Criteria: Four aliquots at one (1) to four (4) time the limit of quantitation and analyzed according to the method either concurrently or

over a period of day. Calculate mean recovery and standard deviation for each analyte of interest. Compare recovery and standard deviation to the corresponding acceptance criteria for precision and accuracy in the method (if applicable) or to lab-generated acceptance limits. If anyone compound does not achieve acceptance criteria, the performance is unacceptable for

16.14.4 Corrective Action: Identify and correct the source of error. Reanalyze the demonstration.

16.15 Continuing Demonstration of Capability (DOC)

16.15.1 Purpose: Verify the ability to produce data of acceptable precision and bias for a specific instrument type, matrix, method, and analyst.

16.15.2 Frequency: Annual to re-qualify analyst for analysts. If period of greater than one year lapse between DOCs, then analyst must repeat IDOC.

16.15.3 Acceptance Criteria: Four consecutive LCS analysis meeting stated LCS criteria or successful PT study.

16.16 Method Detection Level (MDL) or Detection Limit Procedure

16.16.1 Purpose: To establish the method detection limit, see SOP HS-QS006 for detail on MDL, LOD and LOQ procedures.

16.16.2 Frequency: Establish the initial MDL of an instrument by process a minimum of 7 spiked aliquots at the appropriate matrix spike level and 7 method blank samples through all steps of the method. The samples used for the MDL must be prepared in at least three batches on three separate calendar dates and analyzed on three separate calendar dates. After analysis determine the MDLs (spiked MDL) and MDLb (blank MDL). Select the highest MDL as the initial MDL. MDL must be determined for each analyte per matrix per method.

16.16.3 Ongoing Data Collection: On a quarterly basis, two MDL spikes must be prepared at the MDL spiking level and analyzed. Ensure minimum of seven spiked samples and seven method blanks are completed for the annual verification. If only one instrument is in use, a minimum of seven spikes are still required.

16.16.3.1 If new instrument is added to group of instruments, analyze a minimum of two spike replicates and two method blanks. If both blank MDL and are below the MDL then instrument is considered valid. Combine new spied samples with existing MDL and recalculate the MDL. If the recalculated MDL does not vary by the specified factor then existing MDL is validated. If either one of these conditions are not met, then than the MDL must be regenerated.

16.16.4 Annual Verification

16.16.4.1 Recalculate the MDLs and MDLb from the spike samples and method blank from the last twenty four months, but only data with the same spiking level. Include initial MDL if data was within 24 months.

16.16.4.2 If the verified MDL is the greater of MDLs or MDLb. If the verified MDL is within 0.5 to 2.0 times the existing MDL and fewer than 3% of the method blank have numerical results above the existing

MDL, then the existing MDL may be left unchanged. Otherwise adjust the MDL to the new verified MDL.

16.10.5 Current MDLs may be found in the Limits tab of each testcode in LIMS.

16.17 Limit of Detection (LOD) Verification

16.17.1 Purpose: Validates the established Detection Limit.

16.17.2 Frequency: Prior to sample analysis and verified quarterly Verification must is performed on each instrument. The LOD is spiked at 2-3 times the detection limit for single compound analyses and 1-4 times the detection limit for multi-analyte standards. Sample must be taken through all preparatory steps such as digestion, extraction clean-up, etc.

16.17.2.1 With each MDL study, all compound must be confirmed at a concentration equal to 1-2 time the calculated MDL. To achieve this confirmation multiple concentration may need to be analyzed. Remaining quarterly checks may be performed at 2-3 times the MDL until the next MDL study.

16.17.3 Acceptance Criteria: The apparent signal to noise ratio at the LOD must be at least three and the results must meet all method requirements for analyte identification (e.g., ion abundance, second-column confirmation, or pattern recognition.) For data systems that do not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least three standard deviations greater than the mean method blank concentrations.

16.17.4 Corrective Action: Repeat the Detection Limit Determination and LOD Verification at a higher concentration or perform and pass two consecutive LOD verifications at a higher concentration and set the LOD at the higher concentration.

16.17.5 Current LOD values may be found in LIMS under the QA Section in the Limit Manager feature.

16.18 Limit of Quantitation (LOQ) Establishment and Verification:

16.18.1 Purpose: Validates the lower quantitation limit of the analysis. Can be performed at 1-2 X the LOQ. Sample must be taken through all preparatory steps such as digestion, extraction clean-up, etc.

16.18.2 Frequency: Prior to sample analysis and verified quarterly.

16.18.3 Acceptance Criteria: Data must empirically demonstrate precision and bias at the LOQ using LCS control limits.

16.18.4 Corrective Action: Identify and correct the source of error, reanalyze the LOQ. If failure persists re-evaluate the appropriateness of the LOQ.
Initial Demonstration of Proficiency – The laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operation annually and whenever new staff members are trained or significant changes in instrumentation are made.

16.18.5 LOQ at time of SOP creation is found in Table 24.1 of this SOP. For latest LOQ confirmation values, see Limit Manager feature in LIMS under the QA Section.

17) Data Records Management

17.1 All data is stored electronically and/or hard copy for five years or ten (10) years in the state of Louisiana. Operational software is maintained for the same duration.

17.1.1 Hard copy documentation is maintained via logbooks for standard and chemical tracking, extraction procedures, instrument maintenance and run logs.

17.2 All samples are recorded in the instrumental analysis log, along with the data file name, sample matrix, dilution factor, and analysis type. Raw data is reviewed after analysis, with each sample data print-out containing notations as to the likely presence or absence of any analyte quantifying above the LOQ. Additionally, each report must be initialed and dated by the primary reviewing analyst.

17.3 Instrument hardcopies are turned-in for review by batch ID. Each batch contains data from only one instrument performed on one day and/or analytical sequence. The batch must also contain a copy of the applicable logbook pages with reportable runs clearly marked, a completed review checklist, and the data segregated by channel and in chronological order.

17.4 Once the data has been reviewed and verified in the LIMS system, it is stored in designated file boxes located in the Organic Data Review section of the laboratory. After approximately four months from analysis date, data is moved to the GC/MS Semi-volatiles section of the permanent storage.

17.5 All signals produced by the detector(s) during analysis are collected via analog to digital converter and stored on the designated drive of the network server by GC/MS – SV personnel. The data from each analysis is stored in a separate file whose name corresponds to a run number recorded in an instrument specific logbook. Data is transferred to the LIMS.

17.6 As data is collected, the electronic files are stored on the network server. All electronic data which has been stored on the designated drive of the network server is backed up daily by the IT Manager on a tape drive.

17.7 Nomenclature for Analysis Raw Data Naming: The data from each analysis is stored in a separate file whose name corresponds to the run number that is recorded in the sample run log as described below.

17.7.1 Example: 1106040-01A

17.7.1.1 11 – last 2 digits of current year

17.7.1.2 06 – the month sample received

17.7.1.3 040 – sequentially assigned project #

17.7.1.4 01 – sample #.

17.7.1.5 A – sample fraction (bottle container ID)

17.8 All data is stored both electronically and hard copy for 10 years.

17.9 All analytical sequence IDs and standard preparation information must be recorded in the analytical run logbook or similar record. Hardcopy computer printouts of analytical sequences and raw data must be retained and initialed by the analyst (electronic initials are acceptable). To simplify standard and reagent tracking, analyst must attempt to use single lots of reagents and standards.

17.10 Complete all pertinent sections in the respective logbooks. If not-applicable then line out the section. “Z” out or “X” out all large sections of the worksheet that are not used. Make all corrections with single line through, date and initial. Make NO obliterations

when manually recording data.

17.11 Logbooks are controlled. Never remove a page from a logbook. Completed logbooks are returned to the QA department when filled and no longer needed in the work area.

17.12 SOP effective date is the date noted in the header or last signature date, whichever is most recent.

18) Contingencies for Handling Out of Control Data

18.1 When method required QC exceedances occur, in every case where sample data quality are affected, the source of the QC exceedance must be determined, corrected and sample reanalysis carried out when possible.

18.2 When data is generated that is associated with a high failing CCV, it can only be reported provided the result is "not detected". The situation must be narrated in the report. Data associated with a low failing CCV cannot be reported.

18.3 When affected sample analysis cannot be repeated due to limitations (i.e. sample availability, or if reanalysis can only be performed after expiration of a sample hold time), the reporting of data associated with exceeded QC data must be appropriately flagged and narrated. This documentation is necessary to define for the data user the effect of the error has upon the data quality of the results reported (e.g. E flag data indicate the result to be only an estimate).

18.4 All analysts must report sufficient comments in laboratory data review checklist for exceeded QC associated with sample results so that project management can further narrate and ensure data qualifiers (flags) are properly assigned to the reported data.

18.5 NCARs must be issued for QC system exceedances. Matrix interferences are reported using the analyte reporting comment section in LIMS or using the Laboratory Data review checklist.

19) Method Performance

19.1 Method performance is determined by passing surrogates, internal standards PTs also by the performance of MDLs and other quality control standards.

19.2 The method detection limit (MDL) is established using the procedure described in the SOP *Performing and Documenting Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (CE-QA011). Method Reporting Limits are established for this method based on the low calibration point and the MDL study results.

20) Pollution Prevention and Waste Management

20.1 It is the laboratory's practice to minimize the amount of solvents, acids, and reagents used to perform this method wherever feasibly possible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine

laboratory use is kept on site. The threat to the environment from solvents and/or reagents used in this method can be minimized when recycled or disposed of properly.

20.2 The laboratory will comply with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Chemical Hygiene Plan and Lab Waste Management Plan.

20.3 Laboratory procedures in SOP SHWD-001, Waste Disposal Procedures, must be followed.

21) Training

21.1 Training outline

21.1.1 Review literature (see references section). Read and understand this SOP. Also review the applicable SDS for all reagents and standards used. Following the reviews, observe the procedure as performed by an experienced analyst at least three times.

21.1.2 The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

21.1.3 Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

21.2 Training is documented following *SOP CE-QA003*).

21.3 When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

22) Summary of Changes

Table 22.1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
7.2	8/03/2020	G. Moulton	Sec 1: added scope and applicability, and Identification of the method.
7.2	8/03/2020	G. Moulton	Sec 12.4.1: added last statement about analyst judgement.
7.2	8/03/2020	G. Moulton	Sec 19: Added method performance

7.2	8/03/2020	G. Moulton	Sec 20: Added Pollution prevention and waste management.
7.2	8/03/2020	G. Moulton	Sec 21: Added a training section.
7.2	8/03/2020	G. Moulton	Sec 24:Updated table numbers due to added sections.
7.1 Sec 3	07/26/2019	E. Howard	Alphabetized Definitions section Added Coefficient of Determination (COD) to Definitions section Clarified Retention Time Window definition
7.1 Sections 8.1.1, 8.4.1	07/26/2019	E. Howard	Added information for samples eligible for microextraction by SW3511.
7.1 Sec 9.5, 9.9, 9.10, Table 9.10	07/26/2019	E. Howard	Removed References to SV2 and SV3 (permanently retired instruments)
7.1 Table 9.10	07/26/2019	E. Howard	Corrected: 1uL is injected, flow is 1.4 mL/min, and flow is constant
7.1 Sec 10.4.1.1	07/26/2019	E. Howard	Reference corrected to section 10.4.1
7.1 Sec 11.4.3	07/26/2019	E. Howard	Specified electronic files stored for tune.
7.1 Sec 11.5	07/26/2019	E. Howard	Specified eight levels.
7.1 Sec 16.2.2.3	07/26/2019	E. Howard	Corrected linear curve (r) and specified COD is r^2
7.1 Sec 16.7.2	07/26/2019	E. Howard	Specified blank detections must be <1/2 LOQ.
7.0	07/19/2019	G. Moulton	Updated to the newest company cover, updated new QA manager signature.
7.0	07/19/2019	G. Moulton	Updated header to add method identification
7.0	07/19/2019	G. Moulton	Modified 21.1.3 and 21.1.4 References.
7.0	07/19/2019	G. Moulton	Modified storage time of data
07	10/15/2018	T. Yen	New Lab Director and Organic Manager added 625.1 criteria.
07- Section 11.1	10/15/2018	T. Yen	Applicable matrices.
07- Section 11.2	10/15/2018	T. Yen	Tune tables for EPA 625, EPA 625.1 and SW8270D. Table 11.2.1-8270D, Table 11.2.2 – 625 and 625.1.

07 – Section 4.5	10/15/2018	T. Yen	Job Safety Assessment added.
07- Table 2.2	10/15/2018	T. Yen	Table 2.2 update for low level PAH LOQ.
07- Table 10.4.7.1	10/15/2018	T. Yen	Table 10.4.7.1 update for low level PAH calibration standard prep.
07- Section 11.2	10/15/2018	T. Yen	Tune Tables for 8270D, 625, and 625.1.
07- Sections 11.4.3, 11.7.4 & 12.3.3	10/15/2018	T. Yen	Use of DoD LIMS testcodes to ensure use of DoD recovery limits in QC and field samples.
07- Section 11.4.3, 11.5.1, 11.6.1, 16.2.2.3 & Table 22.5	10/15/2018	T. Yen	DoD ICAL %RSD of 15%
07- Sections 11.6 & 16.3.2.	10/15/2018	T. Yen	DoD ICV acceptance limits of ±20% from true value.
07- Section 16.2.2.4	10/15/2018	T. Yen	Linear and non linear calibration refit of all levels on the calibration curve.
07- Section 16.3	10/15/2018	T. Yen	ICAL RF & ICAL RF
07- Section 16.4	10/15/2018	T. Yen	CCV/ICV update
07- Section 16.5	10/15/2018	T. Yen	Internal Standard update
07- Sections 16.7, 16.8 & 16.9	10/15/2018	T. Yen	Use of DoD LIMS codes to ensure DoD QSM control limits are applied to sample and QC.
07- Section 16.7	10/15/2018	T. Yen	MB limits and criteria to <1/2 LOQ update.
07- Sections	10/15/2018	T. Yen	LCS/LCSD & MS/MSD Limits update.

16.8 & 16.9			
07- Sections 16.14 & 16.15	10/15/2018	T. Yen	IDOC/DOC criteria added.
07- Section 16.16	10/15/2018	T. Yen	MDL/DL criteria added.
07- Section 16.17	10/15/2018	T. Yen	LOD criteria added.
07- Section 16.18	10/15/2018	T. Yen	LOQ criteria added.
07- Section 21	10/15/2018	T. Yen	Reference update – DoD QSM, 625.1 and 8000D
07- Table 22.3	10/15/2018	T. Yen	Table 22.3 update.
06.0	09/08/2014	T. Yen	SOP Format Change and New Lab Director and QA Manager.
06.0 – Section 17.9	09/08/2014	T. Yen	Use of single lots of standard/reagent to simplify standard tracking.
06.0 – Section 12.2	09/08/2014	T. Yen	Daily maintenance defined.
06.0 – Section 17.12	09/08/2014	T. Yen	SOP effective date defined.
06.0 – Section 21.	09/08/2014	T. Yen	References updated.
05.2	08/01/2012	J. Cady	Minor revision. Format/font change.
05.1	08/23/2012	D. Pangrazio	Added Compounds to analyte tables

23) References and Related Documents

23.1 Referenced Documents

23.1.1 U.S. Environmental Protection Agency, "Method 8270D, Semivolatiles Organic Compounds by Gas Chromatography/Mass Spectrometry", Test Methods for Evaluating Solid Waste Physical/Chemical Methods, Method Revision 4, February 2006.

23.1.2 U.S. Environmental Protection Agency, "Method 8000D Determinative

Chromatographic Separations", Test Methods for Evaluating Solid Waste Physical/Chemical Methods, Revision 4, July 2014.

23.1.3 Current TNI Standards.

23.1.4 Current Department of Defense Manual.

23.1.5 U.S. Environmental Protection Agency, "Method 625, Semivolatiles Organic Compounds by Gas Chromatography/Mass Spectrometry", 40 CFR Part 136.

23.1.6 U.S. Environmental Protection Agency, "Method 625.1 - Base. Neutrals and Acid by GCMS", EPA-821-R14-015

24) Tables, Diagrams, Flowcharts and Validation Data

Table 24.1 Recommended RF Limits for SW8270D/625

Table 24.1 Analyte - 8270 Low	RF minimum	Recommended Internal Standard
1,1´-Biphenyl	0.010	Not method defined, default to use closest IS
1,2,4,5-Tetrachlorobenzene	0.010	Not method defined, default to use closest IS
1,2,4-Trichlorobenzene	0.010	Napthalene-d8
1,2-Dichlorobenzene	0.010	1,4-Dichlorobenzene-d4
1,2-Diphenylhydrazine	0.010	Not method defined, default to use closest IS
1,3-Dichlorobenzene	0.010	1,4-Dichlorobenzene-d4
1,3-Dinitrobenzene	0.010	Not method defined, default to use closest IS
1,4-Dichlorobenzene	0.010	1,4-Dichlorobenzene-d4
1,4-Dioxane	0.010	Not method defined, default to use closest IS
1,4-Naphthoquinone	0.010	Not method defined, default to use closest IS
1-Methyl-2-pyrrolidone	0.010	Not method defined, default to use closest IS
1-Methylnaphthalene	0.010	Not method defined, default to use closest IS
1-Naphthylamine	0.010	Not method defined, default to use closest IS
2,3,4,6-Tetrachlorophenol	0.010	Not method defined, default to use closest IS
2,4,5-Trichlorophenol	0.200	Acenaphthene-d10
2,4,6-Trichlorophenol	0.200	Acenaphthene-d10
2,4-Dichlorophenol	0.200	Napthalene-d8
2,4-Dimethylphenol	0.200	Napthalene-d8
2,4-Dinitrophenol	0.010	Acenaphthene-d10
2,4-Dinitrotoluene	0.200	Acenaphthene-d10
2,6-Dichlorophenol	0.010	Not method defined, default to use closest IS
2,6-Dinitrotoluene	0.200	Acenaphthene-d10
2-Acetylaminofluorene	0.010	Not method defined, default to use closest IS
2-Chloronaphthalene	0.010	Not method defined, default to use closest IS
2-Chlorophenol	0.800	1,4-Dichlorobenzene-d4
2-Methylnaphthalene	0.400	Napthalene-d8
2-Methylphenol	0.700	1,4-Dichlorobenzene-d4
2-Naphthylamine	0.010	Not method defined, default to use closest IS
2-Nitroaniline	0.010	Perylene-d12
2-Nitrophenol	0.100	Napthalene-d8
2-Picoline	0.010	Not method defined, default to use closest IS

Table 24.1 Analyte - 8270 Low	RF minimum	Recommended Internal Standard
3&4-Methylphenol	0.600	1,4-Dichlorobenzene-d4
3,3´-Dichlorobenzidine	0.010	Chrysene-d12
3,3´-Dimethylbenzidine	0.010	Not method defined, default to use closest IS
3-Chlorophenol	0.010	Not method defined, default to use closest IS
3-Methylcholanthrene	0.010	Not method defined, default to use closest IS
3-Nitroaniline	0.010	Acenaphthene-d10
4,4'-DDD	0.010	Not method defined, default to use closest IS
4,4'-DDE	0.010	Not method defined, default to use closest IS
4,4'-DDT	0.010	Not method defined, default to use closest IS
4,6-Dinitro-2-methylphenol	0.010	Phenanthrene-d10
4-Bromophenyl phenyl ether	0.100	Phenanthrene-Fd10
4-Chloro-3-methylphenol	0.200	Napthalene-d8
4-Chloroaniline	0.010	Napthalene-d8
4-Chlorophenol	0.010	Not method defined, default to use closest IS
4-Chlorophenyl phenyl ether	0.400	Acenaphthene-d10
4-Nitroaniline	0.010	Acenaphthene-d10
4-Nitrophenol	0.010	Perylene-d12
4-Nitroquinoline-1-oxide	0.010	Not method defined, default to use closest IS
5-Chloro-o-toluidine	0.010	Not method defined, default to use closest IS
6-Methyl chrysene	0.010	Not method defined, default to use closest IS
7,12-Dimethylbenz(a)anthracene	0.010	Not method defined, default to use closest IS
a,a-Dimethylphenethylamine	0.010	Not method defined, default to use closest IS
Acenaphthene	0.900	Acenaphthene-d10
Acenaphthylene	0.900	Acenaphthene-d10
Acetophenone	0.010	Not method defined, default to use closest IS
Alachlor	0.010	Not method defined, default to use closest IS
Aldrin	0.010	Not method defined, default to use closest IS
Alpha-BHC	0.010	Not method defined, default to use closest IS
alpha-Chlordane	0.010	Not method defined, default to use closest IS
Ametryn	0.010	Not method defined, default to use closest IS
Aniline	0.010	Not method defined, default to use closest IS
Anthracene	0.700	Phenanthrene-d10
Atraton	0.010	Not method defined, default to use closest IS
Atrazine	0.010	Not method defined, default to use closest IS
Azinphos-methyl	0.010	Not method defined, default to use closest IS
Benz(a)anthracene	0.800	Chrysene-d12
Benzal Chloride	0.010	Not method defined, default to use closest IS
Benzaldehyde	0.010	Not method defined, default to use closest IS
Benzenethiol	0.010	Not method defined, default to use closest IS
Benzidine	0.010	Not method defined, default to use closest IS
Benzo(a)pyrene	0.700	Perylene-d12
Benzo(b)fluoranthene	0.700	Perylene-d12
Benzo(e)pyrene	0.010	Not method defined, default to use closest IS
Benzo(g,h,i)perylene	0.500	Perylene-d12
Benzo(k)fluoranthene	0.700	Perylene-d12
Benzoic acid	0.010	Not method defined, default to use closest IS

Table 24.1 Analyte - 8270 Low	RF minimum	Recommended Internal Standard
Benzotrichloride	0.010	Not method defined, default to use closest IS
Benzyl alcohol	0.010	Not method defined, default to use closest IS
Beta-BHC	0.010	Not method defined, default to use closest IS
Bis(2-chloroethoxy)methane	0.300	Napthalene-d8
Bis(2-chloroethyl)ether	0.700	1,4-Dichlorobenzene-d4
Bis(2-chloroisopropyl)ether	0.010	1,4-Dichlorobenzene-d4
Bis(2-ethylhexyl)phthalate	0.010	Chrysene-d12
Bis(chloromethyl)ether	0.010	Not method defined, default to use closest IS
Bromacil	0.010	Not method defined, default to use closest IS
Butachlor	0.010	Not method defined, default to use closest IS
Butyl benzyl phthalate	0.010	Chrysene-d12
butylate	0.010	Not method defined, default to use closest IS
Caprolactam	0.010	Not method defined, default to use closest IS
Carbazole	0.010	Not method defined, default to use closest IS
Captan	0.010	Not method defined, default to use closest IS
Carboxin	0.010	Not method defined, default to use closest IS
Carbophenothion	0.010	Not method defined, default to use closest IS
Chlorfenvinphos	0.010	Not method defined, default to use closest IS
Chlorpropham	0.010	Not method defined, default to use closest IS
Chlorpyrifos	0.010	Not method defined, default to use closest IS
Chrysene	0.700	Chrysene-d12
Coumaphos	0.010	Not method defined, default to use closest IS
Cyanazine	0.010	Not method defined, default to use closest IS
Cycloate	0.010	Not method defined, default to use closest IS
Delta-BHC	0.010	Not method defined, default to use closest IS
Demeton-O	0.010	Not method defined, default to use closest IS
Demeton-S	0.010	Not method defined, default to use closest IS
Diallate	0.010	Not method defined, default to use closest IS
Dioxathion	0.010	Not method defined, default to use closest IS
Diazinon	0.010	Not method defined, default to use closest IS
Dibenz(a,h)acridine	0.010	Not method defined, default to use closest IS
Dibenz(a,h)anthracene	0.400	Perylene-d12
Dibenz(a,j)acridine	0.010	Not method defined, default to use closest IS
Dibenzofuran	0.800	Acenaphthene-d10
Dichlorvos	0.010	Not method defined, default to use closest IS
Dicofol	0.010	Not method defined, default to use closest IS
Dieldrin	0.010	Not method defined, default to use closest IS
Diethyl phthalate	0.010	Acenaphthene-d10
Dimethoate	0.010	Not method defined, default to use closest IS
Dimethyl phthalate	0.010	Acenaphthene-d10
Dinoseb	0.010	Not method defined, default to use closest IS
Di-n-butyl phthalate	0.010	Phenanthrene-d10
Di-n-octyl phthalate	0.010	Perylene-d12
Diphenamide	0.010	Not method defined, default to use closest IS
Diphenylamine	0.010	Phenanthrene-d10
Diphenyl ether	0.010	Not method defined, default to use closest IS

Table 24.1 Analyte - 8270 Low	RF minimum	Recommended Internal Standard
Disulfoton	0.010	Not method defined, default to use closest IS
Disulfoton sulfone	0.010	Not method defined, default to use closest IS
Diuron	0.010	Not method defined, default to use closest IS
Endosulfan I	0.010	Not method defined, default to use closest IS
Endosulfan II	0.010	Not method defined, default to use closest IS
Endosulfan sulfate	0.010	Not method defined, default to use closest IS
Endrin	0.010	Not method defined, default to use closest IS
Endrin Aldehyde	0.010	Not method defined, default to use closest IS
Endrin ketone	0.010	Not method defined, default to use closest IS
EPTC	0.010	Not method defined, default to use closest IS
Ethion	0.010	Not method defined, default to use closest IS
Ethoprophos	0.010	Not method defined, default to use closest IS
Etridiazole	0.010	Not method defined, default to use closest IS
Ethyl methanesulfonate	0.010	Not method defined, default to use closest IS
Ethyl parathion	0.010	Not method defined, default to use closest IS
Famphur	0.010	Not method defined, default to use closest IS
Fenamiphos	0.010	Not method defined, default to use closest IS
Fenarimol	0.010	Not method defined, default to use closest IS
Fensulfothion	0.010	Not method defined, default to use closest IS
Fenthion	0.010	Not method defined, default to use closest IS
Fluoranthene	0.600	Phenanthrene-d10
Fluorene	0.900	Acenaphthene-d10
Fluridon	0.010	Not method defined, default to use closest IS
Fonofos	0.010	Not method defined, default to use closest IS
Gamma-BHC	0.010	Not method defined, default to use closest IS
gamma-Chlordane	0.010	Not method defined, default to use closest IS
Heptachlor	0.010	Not method defined, default to use closest IS
Heptachlor epoxide	0.010	Not method defined, default to use closest IS
Hexachlorobenzene	0.100	Phenanthrene-d10
Hexachlorobutadiene	0.010	Napthalene-d8
Hexachlorocyclopentadiene	0.050	Acenaphthene-d10
Hexachloroethane	0.300	1,4-Dichlorobenzene-d4
Hexazinone	0.010	Not method defined, default to use closest IS
Indeno(1,2,3-cd)pyrene	0.500	Perylene-d12
Isodrin	0.010	Not method defined, default to use closest IS
Isophorone	0.400	Napthalene-d8
Isosafrole	0.010	Not method defined, default to use closest IS
Kepone	0.010	Not method defined, default to use closest IS
Malathion	0.010	Not method defined, default to use closest IS
Merphos	0.010	Not method defined, default to use closest IS
Methapyrilene	0.010	Not method defined, default to use closest IS
Methoxychlor	0.010	Not method defined, default to use closest IS
Methyl chrysene	0.010	Not method defined, default to use closest IS
Methyl methanesulfonate	0.010	Not method defined, default to use closest IS
Methyl paraoxon	0.010	Not method defined, default to use closest IS
Methyl parathion	0.010	Not method defined, default to use closest IS

Table 24.1 Analyte - 8270 Low	RF minimum	Recommended Internal Standard
Metolachlor	0.010	Not method defined, default to use closest IS
Metribuzin	0.010	Not method defined, default to use closest IS
Mevinphos	0.010	Not method defined, default to use closest IS
MGK-264	0.010	Not method defined, default to use closest IS
MGK-264(1)	0.010	Not method defined, default to use closest IS
MGK-264(2)	0.010	Not method defined, default to use closest IS
Mirex	0.010	Not method defined, default to use closest IS
Molinate	0.010	Not method defined, default to use closest IS
Naphthalene	0.700	Napthalene-d8
Napropamide	0.010	Not method defined, default to use closest IS
Nitrobenzene	0.200	Napthalene-d8
N-Nitroso-di-n-butylamine	0.010	Not method defined, default to use closest IS
N-Nitrosodiethylamine	0.010	Not method defined, default to use closest IS
N-Nitrosodimethylamine	0.010	1,4-Dichlorobenzene-d4
N-Nitrosodi-n-propylamine	0.500	1,4-Dichlorobenzene-d4
N-Nitrosodiphenylamine	0.010	Phenanthrene-d10
N-Nitrosomethylethylamine	0.010	Not method defined, default to use closest IS
N-Nitrosomorpholine	0.010	Not method defined, default to use closest IS
N-Nitrosopiperidine	0.010	Not method defined, default to use closest IS
N-Nitrosopyrrolidine	0.010	Not method defined, default to use closest IS
Norflurazon	0.010	Not method defined, default to use closest IS
O,O,O-Triethylphosphorothioate	0.010	Not method defined, default to use closest IS
o-Toluidine	0.010	Not method defined, default to use closest IS
p-Dimethylaminoazobenzene	0.010	Not method defined, default to use closest IS
p-Phenylenediamine	0.010	Not method defined, default to use closest IS
Pebulate	0.010	Not method defined, default to use closest IS
Pentachlorobenzene	0.010	Not method defined, default to use closest IS
Pentachloronitrobenzene	0.010	Not method defined, default to use closest IS
Pentachlorophenol	0.050	Phenanthrene-d10
Phenacetin	0.010	Not method defined, default to use closest IS
Phenanthrene	0.700	Phenanthrene-d10
Phenol	0.800	1,4-Dichlorobenzene-d4
Phorate	0.010	Not method defined, default to use closest IS
Phosmet	0.010	Not method defined, default to use closest IS
Prometon	0.010	Not method defined, default to use closest IS
Prometryne	0.010	Not method defined, default to use closest IS
Pronamide	0.010	Not method defined, default to use closest IS
Propachlor	0.010	Not method defined, default to use closest IS
Propazine	0.010	Not method defined, default to use closest IS
Pyrene	0.600	Chrysene-d12
Pyridine	0.010	1,4-Dichlorobenzene-d4
Quinoline	0.010	Napthalene-d8
Ronnel	0.010	Not method defined, default to use closest IS
Simazine	0.010	Not method defined, default to use closest IS
Simetryne	0.010	Not method defined, default to use closest IS
Stirofos	0.010	Not method defined, default to use closest IS

Table 24.1 Analyte - 8270 Low	RF minimum	Recommended Internal Standard
Sulfolane	0.010	Not method defined, default to use closest IS
Sym-Trinitrobenzene	0.010	Not method defined, default to use closest IS
Tebuthiuron	0.010	Not method defined, default to use closest IS
Terbacil	0.010	Not method defined, default to use closest IS
Terbufos	0.010	Not method defined, default to use closest IS
Terbutryn	0.010	Not method defined, default to use closest IS
Triadimefon	0.010	Not method defined, default to use closest IS
Tricyclazole	0.010	Not method defined, default to use closest IS
Trifluralin	0.010	Not method defined, default to use closest IS
Tris(2,3-dibromopropyl) phosphat	.010	Not method defined, default to use closest IS
Vernolate	0.010	Not method defined, default to use closest IS
Nitrobenzene-d5 (surr.)	0.200	Napthalene-d8
Phenol-d6 (surr.)	0.800	1,4-Dichlorobenzene-d4
2,4,6-Tribromophenol (surr.)	0.800	Acenaphthene-d10
2-Fluorobiphenyl (surr.)	0.010	Acenaphthene-d10
2-Fluorophenol (surr.)	0.010	1,4-Dichlorobenzene-d4
Terphenyl-d14 (surr.)	0.010	Chrysene-d12

Table 24.2 LOQ for Low-Level Semivolatiles by SW8270D/EPA 625/ EPA 625.1 at time of SOP generation and are subject to change, see LIMS or QA for latest LOQ.

Table 24.2 – LOQ Analyte – water matrix	MQL µg/L	Analyte - solid/soil matrix	MQL µg/Kg
1,1´-Biphenyl	0.2	1,1'-Biphenyl	6.6
1,2,4,5-Tetrachlorobenzene	0.2	1,2,4,5-Tetrachlorobenzene	6.6
1,2,4-Trichlorobenzene	0.2	1,2,4-Trichlorobenzene	6.6
1,2-Dichlorobenzene	0.2	1,2-Dichlorobenzene	6.6
1,2-Diphenylhydrazine	0.2	1,2-Diphenylhydrazine	6.6
1,3-Dichlorobenzene	0.2	1,3-Dichlorobenzene	6.6
1,3-Dinitrobenzene	0.2	1,3-Dinitrobenzene	6.6
1,4-Dichlorobenzene	0.2	1,4-Dichlorobenzene	6.6
1,4-Dioxane	0.2	1,4-Dioxane	6.6
1,4-Naphthoquinone	0.2	1,4-Naphthoquinone	6.6
1-Methylnaphthalene	0.1	1-Methylnaphthalene	3.3
1-Naphthylamine	0.2	1-Naphthylamine	6.6
2,3,4,6-Tetrachlorophenol	0.2	2,3,4,6-Tetrachlorophenol	6.6
2,4,5-Trichlorophenol	0.2	2,4,5-Trichlorophenol	6.6
2,4,6-Trichlorophenol	0.2	2,4,6-Trichlorophenol	6.6
2,4-Dichlorophenol	0.2	2,4-Dichlorophenol	6.6
2,4-Dimethylphenol	0.2	2,4-Dimethylphenol	6.6
2,4-Dinitrophenol	1	2,4-Dinitrophenol	33
2,4-Dinitrotoluene	0.2	2,4-Dinitrotoluene	6.6
2,6-Dichlorophenol	0.2	2,6-Dichlorophenol	6.6
2,6-Dinitrotoluene	0.2	2,6-Dinitrotoluene	6.6
2-Acetylaminofluorene	0.2	2-Acetylaminofluorene	6.6
2-Chloronaphthalene	0.2	2-Chloronaphthalene	6.6

Table 24.2 – LOQ Analyte – water matrix	MQL µg/L	Analyte - solid/soil matrix	MQL µg/Kg
2-Chlorophenol	0.2	2-Chlorophenol	6.6
2-Methylnaphthalene	0.1	2-Methylnaphthalene	3.3
2-Methylphenol	0.2	2-Methylphenol	6.6
2-Naphthylamine	0.2	2-Naphthylamine	6.6
2-Nitroaniline	0.2	2-Nitroaniline	6.6
2-Nitrophenol	0.2	2-Nitrophenol	6.6
2-Picoline	0.2	2-Picoline	6.6
3&4-Methylphenol	0.2	3 & 4-Methylphenol	6.6
3,3´-Dimethylbenzidine	0.2	3,3´-Dimethylbenzidine	33
3,3'-Dichlorobenzidine	1.0	3,3´-Dichlorobenzidine	6.6
3-Chlorophenol	0.2	3-Chlorophenol	6.6
3-Methylcholanthrene	0.2	3-Methylcholanthrene	6.6
3-Nitroaniline	0.2	3-Nitroaniline	6.6
4,4'-DDD	0.2	4,4'-DDD	6.6
4,4'-DDE	0.2	4,4'-DDE	6.6
4,4'-DDT	0.2	4,4'-DDT	6.6
4,6-Dinitro-2-methylphenol	0.2	4,6-Dinitro-2-methylphenol	6.6
4-Aminobiphenyl	0.2	4-Aminobiphenyl	6.6
4-Bromophenyl phenyl ether	0.2	4-Bromophenyl phenyl ether	6.6
4-Chloro-3-methylphenol	0.2	4-Chloro-3-methylphenol	6.6
4-Chloroaniline	0.2	4-Chloroaniline	6.6
4-Chlorophenol	0.2	4-Chlorophenol	6.6
4-Chlorophenyl phenyl ether	0.2	4-Chlorophenyl phenyl ether	6.6
4-Nitroaniline	0.2	4-Nitroaniline	6.6
4-Nitrophenol	1	4-Nitrophenol	6.6
4-Nitroquinoline-1-oxide	0.2	4-Nitroquinoline-1-oxide	6.6
5-Nitro-o-toluidine	0.2	5-Nitro-o-toluidine	6.6
7,12-Dimethylbenz(a)anthracene	0.1	7,12-Dimethylbenz(a)anthracene	3.3
a,a-Dimethylphenethylamine	0.2	a,a-Dimethylphenethylamine	6.6
Acenaphthene	0.1	Acenaphthene	3.3
Acenaphthylene	0.1	Acenaphthylene	3.3
Acetophenone	0.2	Acetophenone	6.6
Alachlor	0.2	Alachlor	6.6
Aldrin	0.2	Aldrin	6.6
Alpha-BHC	0.2	Alpha-BHC	6.6
alpha-Chlordane	0.2	alpha-Chlordane	6.6
Ametryn	0.2	Ametryn	6.6
Aniline	0.2	Aniline	6.6
Anthracene	0.1	Anthracene	3.3
Atraton	0.2	Atraton	6.6
Atrazine	0.2	Atrazine	6.6
Azinphos-methyl	0.2	Azinphos-methyl	6.6
Benz(a)anthracene	0.1	Benz(a)anthracene	3.3
Benzal Chloride	0.2	Benzal Chloride	6.6
Benzaldehyde	0.2	Benzaldehyde	6.6

Table 24.2 – LOQ Analyte – water matrix	MQL µg/L	Analyte - solid/soil matrix	MQL µg/Kg
Benzenethiol	0.2	Benzenethiol	6.6
Benzidine	0.2	Benzidine	6.6
Benzo(a)pyrene	0.1	Benzo(a)pyrene	3.3
Benzo(b)fluoranthene	0.1	Benzo(b)fluoranthene	3.3
Benzo(e) pyrene	0.2	Benzo(e) pyrene	6.6
Benzo(g,h,i)perylene	0.1	Benzo(g,h,i)perylene	3.3
Benzo(k)fluoranthene	0.1	Benzo(k)fluoranthene	3.3
Benzoic acid	0.2	Benzoic acid	6.6
Benzotrichloride	0.2	Benzotrichloride	6.6
Benzyl alcohol	0.2	Benzyl alcohol	6.6
Beta-BHC	0.2	Beta-BHC	6.6
Bis(2-chloroethoxy) methane	0.2	Bis(2-chloroethoxy)methane	6.6
Bis(2-chloroethyl) ether	0.2	Bis(2-chloroethyl)ether	6.6
Bis(2-chloroisopropyl) ether	0.2	Bis(2-chloroisopropyl)ether	6.6
Bis(2-ethylhexyl)phthalate	0.2	Bis(2-ethylhexyl)phthalate	6.6
Bis(chloromethyl)ether	0.2	Bis(chloromethyl)ether	6.6
Bromacil	0.2	Bromacil	6.6
Butachlor	0.2	Butachlor	6.6
Butyl benzyl phthalate	0.2	Butyl benzyl phthalate	6.6
butylate	0.2	butylate	6.6
Caprolactam	0.2	Caprolactam	6.6
Captan	0.2	Captan	6.6
Carbazole	0.2	Carbazole	6.6
Carbophenothion	0.2	Carbophenothion	6.6
Carboxin	0.2	Carboxin	6.6
Chlorfenvinphos	0.2	Chlorfenvinphos	6.6
Chlorobenzilate	0.2	Chlorobenzilate	6.6
Chlorpropham	0.2	Chlorpropham	6.6
Chlorpyrifos	0.2	Chlorpyrifos	6.6
Chrysene	0.1	Chrysene	3.3
Coumaphos	0.2	Coumaphos	6.6
Cyanazine	0.2	Cyanazine	6.6
Cycloate	0.2	Cycloate	6.6
Delta-BHC	0.2	Delta-BHC	6.6
Demeton-O	0.2	Demeton-O	6.6
Demeton-S	0.2	Demeton-S	6.6
Diallate	0.2	Diallate	6.6
Diazinon	0.2	Diazinon	6.6
Dibenz(a,h)acridine	0.2	Dibenz(a,h)acridine	6.6
Dibenz(a,j)acridine	0.2	Dibenz(a,j)acridine	6.6
Dibenz(a,h)anthracene	0.1	Dibenz(a,h)anthracene	3.3
Dibenzofuran	0.2	Dibenzofuran	6.6
Dichlorvos	0.2	Dichlorvos	6.6
Dicofol	0.2	Dicofol	6.6
Dieldrin	0.2	Dieldrin	6.6

Table 24.2 – LOQ Analyte – water matrix	MQL µg/L	Analyte - solid/soil matrix	MQL µg/Kg
Diethylphthalate	0.2	Diethyl phthalate	6.6
Dimethoate	0.2	Dimethoate	6.6
Dimethylphthalate	0.2	Dimethyl phthalate	6.6
Di-n-butylphthalate	0.2	Di-n-butyl phthalate	6.6
Di-n-octylphthalate	0.2	Di-n-octyl phthalate	6.6
Dinoseb	0.2	Dinoseb	6.6
Dioxathion	0.2	Dioxathion	6.6
Diphenamide	0.2	Diphenamide	6.6
Diphenylamine	0.2	Diphenylamine	6.6
Diphenyl ether	0.2	Diphenyl ether	6.6
Disulfoton	0.2	Disulfoton	6.6
Disulfoton sulfone	0.2	Disulfoton sulfone	6.6
Diuron	0.2	Diuron	6.6
Endosulfan I	0.2	Endosulfan I	6.6
Endosulfan II	0.2	Endosulfan II	6.6
Endosulfan sulfate	0.2	Endosulfan sulfate	6.6
Endrin	0.2	Endrin	6.6
Endrin Aldehyde	0.2	Endrin Aldehyde	6.6
Endrin ketone	0.2	Endrin ketone	6.6
EPTC	0.2	EPTC	6.6
Ethion	0.2	Ethion	6.6
Ethoprophos	0.2	Ethoprophos	6.6
Ethyl methanesulfonate	0.2	Ethyl methanesulfonate	6.6
Ethyl parathion	0.2	Ethyl parathion	6.6
Etridiazole	0.2	Etridiazole	6.6
Famphur	0.2	Famphur	6.6
Fenamiphos	0.2	Fenamiphos	6.6
Fenarimol	0.2	Fenarimol	6.6
Fensulfothion	0.2	Fensulfothion	6.6
Fenthion	0.2	Fenthion	6.6
Fluoranthene	0.1	Fluoranthene	3.3
Fluorene	0.1	Fluorene	3.3
Fluridon	0.2	Fluridon	6.6
Fonofos	0.2	Fonofos	6.6
Gamma-BHC	0.2	Gamma-BHC	6.6
gamma-Chlordane	0.2	Gamma-Chlordane	6.6
Heptachlor	0.2	Heptachlor	6.6
Heptachlor epoxide	0.2	Heptachlor epoxide	6.6
Hexachlorobenzene	0.2	Hexachlorobenzene	6.6
Hexachlorobutadiene	0.2	Hexachlorobutadiene	6.6
Hexachlorocyclopentadiene	0.2	Hexachlorocyclopentadiene	6.6
Hexachloroethane	0.2	Hexachloroethane	6.6
Hexazinone	0.2	Hexazinone	6.6
Indeno(1,2,3-cd)pyrene	0.1	Indeno(1,2,3-cd)pyrene	3.3
Isodrin	0.2	Isodrin	6.6

Table 24.2 – LOQ Analyte – water matrix	MQL µg/L	Analyte - solid/soil matrix	MQL µg/Kg
Isophorone	0.2	Isophorone	6.6
Isosafrole	0.2	Isosafrole	6.6
Kepone	0.2	Kepone	6.6
Malathion	0.2	Malathion	6.6
Maleic anhydride	0.2	Maleic anhydride	6.6
Merphos	0.2	Merphos	6.6
Methapyrilene	0.2	Methapyrilene	6.6
Methoxychlor	0.2	Methoxychlor	6.6
Methyl chrysene	0.2	Methyl chrysene	6.6
Methyl chrysene	0.2	Methyl chrysene	6.6
Methyl methanesulfonate	0.2	Methyl methanesulfonate	6.6
Methyl paraoxon	0.2	Methyl paraoxon	6.6
Methyl parathion	0.2	Methyl parathion	6.6
Metolachlor	0.2	Metolachlor	6.6
Metribuzin	0.2	Metribuzin	6.6
Mevinphos	0.2	Mevinphos	6.6
MGK-264	0.2	MGK-264	6.6
MGK-264(1)	0.2	MGK-264(1)	6.6
MGK-264(2)	0.2	MGK-264(2)	6.6
Mirex	0.2	Mirex	6.6
Molinate	0.2	Molinate	6.6
Naphthalene	0.1	Naphthalene	3.3
Napropamide	0.2	Napropamide	6.6
Nitrobenzene	0.2	Nitrobenzene	6.6
N-Nitrosodiethylamine	0.2	N-Nitrosodiethylamine	6.6
N-Nitrosodimethylamine	0.2	N-Nitrosodimethylamine	6.6
N-Nitroso-di-n-butylamine	0.2	N-Nitroso-di-n-butylamine	6.6
N-Nitrosodi-n-propylamine	0.2	N-Nitrosodi-n-propylamine	6.6
N-Nitrosodiphenylamine	0.2	N-Nitrosodiphenylamine	6.6
N-Nitrosomethylethylamine	0.2	N-Nitrosomethylethylamine	6.6
N-Nitrosomorpholine	0.2	N-Nitrosomorpholine	6.6
N-Nitrosopiperidine	0.2	N-Nitrosopiperidine	6.6
N-Nitrosopyrrolidine	0.2	N-Nitrosopyrrolidine	6.6
Norflurazon	0.2	Norflurazon	6.6
O,O,O-Triethylphosphorothioate	0.2	O,O,O-Triethylphosphorothioate	6.6
o-Toluidine	0.2	o-Toluidine	6.6
Pebulate	0.2	Pebulate	6.6
p-Dimethylaminoazobenzene	0.2	p-Dimethylaminoazobenzene	6.6
Pentachlorobenzene	0.2	Pentachlorobenzene	6.6
Pentachloronitrobenzene	0.2	Pentachloronitrobenzene	6.6
Pentachlorophenol	0.2	Pentachlorophenol	6.6
Phenacetin	0.2	Phenacetin	6.6
Phenanthrene	0.1	Phenanthrene	3.3
Phenol	0.2	Phenol	6.6
p-Phenylenediamine	0.2	p-Phenylenediamine	6.6

Table 24.2 – LOQ Analyte – water matrix	MQL µg/L	Analyte - solid/soil matrix	MQL µg/Kg
Phorate	0.2	Phorate	6.6
Phosmet	0.2	Phosmet	6.6
Prometon	0.2	Prometon	6.6
Prometryne	0.2	Prometryne	6.6
Pronamide	0.2	Pronamide	6.6
Propachlor	0.2	Propachlor	6.6
Propazine	0.2	Propazine	6.6
Pyrene	0.1	Pyrene	3.3
Pyridine	1	Pyridine	6.6
Quinoline	0.2	Quinoline	6.6
Ronnel	0.2	Ronnel	6.6
Safrole	0.2	Safrole	6.6
Simazine	0.2	Simazine	6.6
Simetryne	0.2	Simetryne	6.6
Stirofos	0.2	Stirofos	6.6
Sulfolane	0.2	Sulfolane	6.6
Sym-Trinitrobenzene	0.2	Sym-Trinitrobenzene	6.6
Tetraethyldithiopyrophosphate	0.2	Tetraethyldithiopyrophosphate	6.6
Thionazin	0.2	Thionazin	6.6
Tebuthiuron	0.2	Tebuthiuron	6.6
Terbacil	0.2	Terbacil	6.6
Terbufos	0.2	Terbufos	6.6
Terbutryn	0.2	Terbutryn	6.6
Triadimefon	0.2	Triadimefon	6.6
Tricyclazole	0.2	Tricyclazole	6.6
Trifluralin	0.2	Trifluralin	6.6
Tris(2,3-dibromopropyl) phosphate	0.2	Tris(2,3-dibromopropyl) phosphat	6.6
Vernolate	0.2	Vernolate	6.6

Table 24.3 LCS/MS Recovery Limits - Low Level Semivolatiles by 8270D/625/625.1 at time of SOP creation and/or are subject to change, see LIMS for current limits. Note DoD LIMS codes and specs must be used for DoD project/sample to ensure DoD QSM limits are used, for compounds not listed in DoD QSM (current version), internal lab limits will apply.

Table 24.3	Water Matrix (SW8270D/EPA 625/EPA 625.1)				Soil Matrix (SW-8270D)			
Analyte	SPK µg/L	Low %	High %	RPD %	SPK µg/Kg	Low %	High %	RPD %
1,1´-Biphenyl	5	45	125	20	166.7	50	120	30
1,2,4,5-Tetrachlorobenzene	5	40	140	20	166.7	40	120	30
1,2,4-Trichlorobenzene	5	45	120	20	166.7	50	120	30
1,2-Dichlorobenzene	5	45	120	20	166.7	50	120	30
1,2-Diphenylhydrazine	5	39	127	20	166.7	50	132	30

Table 24.3	Water Matrix (SW8270D/EPA 625/EPA 625.1)				Soil Matrix (SW-8270D)			
Analyte	SPK µg/L	Low %	High %	RPD %	SPK µg/Kg	Low %	High %	RPD %
1,3-Dichlorobenzene	5	45	120	20	166.7	50	120	30
1,3-Dinitrobenzene	5	40	130	20	166.7	50	120	30
1,4-Dichlorobenzene	5	40	120	20	166.7	50	120	30
1,4-Dioxane	5	30	140	20	166.7	40	140	30
1,4-Naphthoquinone	5	40	140	20	166.7	40	140	30
1-Methylnaphthalene	5	45	120	20	166.7	50	120	30
1-Naphthylamine	5	40	140	20	166.7	40	140	30
2,3,4,6-Tetrachlorophenol	5	30	140	20	166.7	40	140	30
2,4,5-Trichlorophenol	5	46	120	20	166.7	45	127	30
2,4,6-Tribromophenol (surr)	5	40	125	20	166.7	36	126	30
2,4,6-Trichlorophenol	5	42	120	20	166.7	45	130	30
2,4-Dichlorophenol	5	49	120	20	166.7	45	125	30
2,4-Dimethylphenol	5	35	120	20	166.7	45	120	30
2,4-Dinitrophenol	5	15	120	20	166.7	10	126	30
2,4-Dinitrotoluene	5	50	122	20	166.7	50	130	30
2,6-Dichlorophenol	5	40	120	20	166.7	40	140	30
2,6-Dinitrotoluene	5	50	120	20	166.7	50	125	30
2-Acetylaminofluorene	5	40	120	20	166.7	10	120	30
2-Chloronaphthalene	5	50	130	20	166.7	50	145	30
2-Chlorophenol	5	40	120	20	166.7	45	120	30
2-Fluorobiphenyl (surr)	5	45	120	20	166.7	43	125	30
2-Fluorophenol (surr)	5	20	120	20	166.7	37	125	30
2-Methylnaphthalene	5	50	120	20	166.7	50	120	30
2-Methylphenol	5	45	120	20	166.7	50	120	30
2-Naphthylamine	5	40	120	20	166.7	40	140	30
2-Nitroaniline	5	28	139	20	166.7	50	138	30
2-Nitrophenol	5	40	120	20	166.7	45	125	30
2-Picoline	5	40	140	20	166.7	30	130	30
3&4-Methylphenol	5	35	120	20	166.7	45	120	30
3,3´-Dichlorobenzidine	5	15	120	20	166.7	15	120	30
3,3´-Dimethylbenzidine	5	20	120	20	166.7	30	140	30
3-Chlorophenol	5	40	120	20	166.7	45	120	30
3-Methylcholanthrene	5	40	120	20	166.7	40	140	30
3-Nitroaniline	5	30	120	20	166.7	40	120	30
4,4'-DDD	5	40	140	20	166.7	40	140	20
4,4'-DDE	5	40	140	20	166.7	40	140	20
4,4'-DDT	5	40	140	20	166.7	40	140	20
4,6-Dinitro-2-methylphenol	5	25	121	20	166.7	15	135	30

Table 24.3	Water Matrix (SW8270D/EPA 625/EPA 625.1)				Soil Matrix (SW-8270D)			
Analyte	SPK µg/L	Low %	High %	RPD %	SPK µg/Kg	Low %	High %	RPD %
4-Aminobiphenyl	5	40	120	20	166.7	30	140	30
4-Bromophenyl phenyl ether	5	45	120	20	166.7	50	125	30
4-Chloro-3-methylphenol	5	47	120	20	166.7	45	130	30
4-Chloroaniline	5	20	120	20	166.7	20	120	30
4-Chlorophenol	5	40	120	20	166.7	45	120	30
4-Chlorophenyl phenyl ether	5	50	120	20	166.7	50	120	30
4-Nitroaniline	5	30	133	20	166.7	50	127	30
4-Nitrophenol	5	30	130	20	166.7	40	149	30
4-Nitroquinoline-1-oxide	5	40	120	20	166.7	40	140	30
4-Terphenyl-d14 (surr)	5	40	135	20	166.7	32	125	30
5-Nitro-o-toluidine	5	40	120	20	166.7	30	140	30
7,12-Dimethylbenz(a)anthracene	5	30	140	20	166.7	20	120	30
a,a-Dimethylphenethylamine	5	40	120	20	166.7	30	140	30
Acenaphthene	5	45	120	20	166.7	50	120	30
Acenaphthylene	5	47	120	20	166.7	50	120	30
Acetophenone	5	40	120	20	166.7	50	120	30
Alachlor	5	40	140	20	166.7	40	140	30
Aldrin	5	40	140	20	166.7	40	140	30
Alpha-BHC	5	40	140	20	166.7	40	140	30
alpha-Chlordane	5	40	140	20	166.7	40	140	30
Ametryn	5	40	140	20	166.7	40	140	30
Aniline	5	10	120	20	166.7	10	130	30
Anthracene	5	45	120	20	166.7	50	123	30
Atraton	5	40	140	20	166.7	40	140	30
Atrazine	5	40	130	20	166.7	29	148	30
Azinphos-methyl	5	40	140	20	166.7	40	140	30
Benz(a)anthracene	5	40	120	20	166.7	50	131	30
Benzaldehyde	5	35	120	20	166.7	45	120	30
Benzidine	5	10	120	20	166.7	10	120	30
Benzenethiol	5	30	130	20	166.7	30	140	30
Benzo(a)pyrene	5	45	120	20	166.7	50	130	30
Benzo(b)fluoranthene	5	50	120	20	166.7	50	137	30
Benzo(e) pyrene	5	40	140	20	166.7	40	140	30
Benzo(g,h,i)perylene	5	42	127	20	166.7	50	130	30
Benzo(k)fluoranthene	5	45	127	20	166.7	50	143	30
Benzoic acid	5	10	110	20	166.7	10	120	30
Benzyl alcohol	5	35	122	20	166.7	40	143	30
Beta-BHC	5	40	140	20	166.7	40	140	30

Table 24.3	Water Matrix (SW8270D/EPA 625/EPA 625.1)				Soil Matrix (SW-8270D)			
Analyte	SPK µg/L	Low %	High %	RPD %	SPK µg/Kg	Low %	High %	RPD %
Bis(2-chloroethoxy) methane	5	45	120	20	166.7	50	120	30
Bis(2-chloroethyl)ether	5	37	121	20	166.7	45	125	30
Bis(2-chloroisopropyl)ether	5	40	120	20	166.7	50	120	30
Bis(2-ethylhexyl)phthalate	5	40	139	20	166.7	21	148	30
Bromacil	5	40	140	20	166.7	40	140	30
Butachlor	5	40	140	20	166.7	40	140	30
Butyl benzyl phthalate	5	47	123	20	166.7	50	130	30
butylate	5	40	140	20	166.7	40	140	30
Caprolactam	5	35	134	20	166.7	50	135	30
Captan	5	40	140	20	166.7	40	140	30
Carbazole	5	42	127	20	166.7	50	140	30
Carboxin	5	40	140	20	166.7	40	140	30
Carbophenothion	5	40	140	20	166.7	40	140	30
Chlorobenzilate	5	40	120	20	166.7	40	140	30
Chlorothalonil	5	40	140	20	166.7	40	140	30
Chlorfenvinphos	5	40	140	20	166.7	40	140	30
Chlorpropham	5	40	140	20	166.7	40	140	30
Chlorpyrifos	5	40	140	20	166.7	40	140	30
Chrysene	5	43	120	20	166.7	50	130	30
Coumaphos	5	40	140	20	166.7	40	140	30
Cyanazine	5	40	140	20	166.7	40	140	30
Cycloate	5	40	140	20	166.7	40	140	30
Delta-BHC	5	40	140	20	166.7	40	140	30
Demeton-O	5	40	140	20	166.7	50	140	30
Demeton-S	5	40	140	20	166.7	50	140	30
Diallate	5	40	120	20	166.7	40	140	30
Diazinon	5	40	140	20	166.7	40	140	30
Dibenz(a,h)acridine	5	35	140	20	166.7	35	130	30
Dibenz(a,h)anthracene	5	45	125	20	166.7	50	130	30
Dibenz(a,j)acridine	5	35	140	20	166.2	35	130	30
Dibenzofuran	5	50	120	20	166.7	50	125	30
Dichlorvos	5	40	140	20	166.7	40	140	30
Dicofol	5	40	140	20	166.7	40	140	30
Dieldrin	5	40	140	20	166.7	40	140	30
Diethyl phthalate	5	41	120	20	166.7	50	125	30
Dimethyl phthalate	5	40	122	20	166.7	50	125	30
Di-n-butyl phthalate	5	45	123	20	166.7	50	130	30
Di-n-octyl phthalate	5	45	129	20	166.7	50	135	30

Table 24.3	Water Matrix (SW8270D/EPA 625/EPA 625.1)				Soil Matrix (SW-8270D)			
Analyte	SPK µg/L	Low %	High %	RPD %	SPK µg/Kg	Low %	High %	RPD %
Dimethoate	5	40	140	20	166.7	40	140	30
Dinoseb	5	40	140	20	166.7	40	140	30
Diaxathion	5	40	140	20	166.7	40	140	30
Diphenamide	5	40	140	20	166.7	40	140	30
Diphenylamine	5	45	120	20	166.7	40	132	30
Disulfoton	5	40	140	20	166.7	40	140	30
Disulfoton sulfone	5	40	140	20	166.7	40	140	30
Diuron	5	40	140	20	166.7	40	140	30
Endosulfan I	5	40	140	20	166.7	40	140	30
Endosulfan II	5	40	140	20	166.7	40	140	30
Endosulfan sulfate	5	40	140	20	166.7	40	140	30
Endrin	5	40	140	20	166.7	40	140	30
Endrin Aldehyde	5	40	140	20	166.7	40	140	30
Endrin ketone	5	40	140	20	166.7	40	140	30
EPTC	5	40	140	20	166.7	40	140	30
Ethion	5	40	140	20	166.7	40	140	30
Ethoprop	5	40	140	20	166.7	40	140	30
Ethyl methanesulfonate	5	40	140	20	166.7	40	140	30
Ethyl parathion	5	40	140	20	166.7	50	140	30
Etridiazole	5	40	140	20	166.7	40	140	30
Famphur	5	40	140	20	166.7	40	140	30
Fenamiphos	5	40	140	20	166.7	40	140	30
Fenarimol	5	40	140	20	166.7	40	140	30
Fensulfothion	5	40	140	20	166.7	40	140	30
Fenthion	5	40	140	20	166.7	40	140	30
Fluoranthene	5	45	125	20	166.7	50	131	30
Fluorene	5	49	120	20	166.7	50	125	30
Fluridon	5	40	140	20	166.7	40	140	30
Fonofos	5	40	140	20	166.7	50	150	30
Gamma-BHC	5	40	140	20	166.7	40	140	30
gamma-Chlordane	5	40	140	20	166.7	40	140	30
Heptachlor	5	40	140	20	166.7	40	140	30
Heptachlor epoxide	5	40	140	20	166.7	40	140	30
Hexachlorobenzene	5	48	120	20	166.7	50	124	30
Hexachlorobutadiene	5	40	120	20	166.7	50	125	30
Hexachlorocyclopentadiene	5	34	136	20	166.7	45	135	30
Hexachloroethane	5	40	120	20	166.7	45	125	30
Hexazinone	5	40	140	20	166.7	40	140	30

Table 24.3	Water Matrix (SW8270D/EPA 625/EPA 625.1)				Soil Matrix (SW-8270D)			
Analyte	SPK µg/L	Low %	High %	RPD %	SPK µg/Kg	Low %	High %	RPD %
Indene	5	40	130	20	166.7	20	120	30
Indeno(1,2,3-cd)pyrene	5	41	128	20	166.7	45	139	30
Isodrin	5	40	120	20	166.7	40	140	30
Isophorone	5	40	121	20	166.7	45	130	30
Isosafrole	5	40	120	20	166.7	40	140	30
Kepone	5	40	120	20	1667	40	140	30
Malathion	5	40	140	20	166.7	50	150	30
Merphos	5	40	140	20	166.7	50	150	30
Methapyrilene	5	40	120	20	166.7	40	140	30
Methoxychlor	5	40	140	20	166.7	40	140	30
Methyl chrysene	5	40	130	20	166.7	40	140	30
Methyl paraoxon	5	40	140	20	166.7	40	140	30
Methyl methanesulfonate	5	40	120	20	166.7	40	140	30
Methyl parathion	5	40	140	20	166.7	40	140	30
Metolachlor	5	40	140	20	166.7	40	140	30
Metribuzin	5	40	140	20	166.7	40	140	30
Mevinphos	5	40	140	20	166.7	40	140	30
MGK-264	5	40	140	20	166.7	40	140	30
MGK-264(1)	5	40	140	20	166.7	40	140	30
MGK-264(2)	5	40	140	20	166.7	40	140	30
Mirex	5	40	140	20	166.7	40	140	30
Molinate	5	40	140	20	166.7	40	140	30
Naphthalene	5	45	120	20	166.7	50	125	30
Napropamide	5	40	140	20	166.7	40	140	30
Nitrobenzene	5	44	120	20	166.7	50	125	30
Nitrobenzene-d5	5	41	120	20	166.7	37	125	30
N-Nitrosodiethylamine	5	30	140	20	166.7	30	140	30
N-Nitrosodimethylamine	5	30	121	20	166.7	20	140	30
N-Nitroso-di-n-butylamine	5	30	140	20	166.7	40	140	30
N-Nitrosodi-n-propylamine	5	40	120	20	166.7	45	120	30
N-Nitrosodiphenylamine	5	40	125	20	166.7	50	130	30
N-Nitrosomethylethylamine	5	30	140	20	166.7	30	140	30
N-Nitrosomorpholine	5	40	120	20	166.7	30	140	30
N-Nitrosopiperidine	5	30	140	20	166.7	30	140	30
N-Nitrosopyrrolidine	5	30	140	20	166.7	30	140	30
Norflurazon	5	40	140	20	166.7	40	140	30
Pebulate	5	40	140	20	166.7	40	140	30
O,O,O-Triethylphosphorothioate	5	40	140	20	166.7	30	140	30

Table 24.3	Water Matrix (SW8270D/EPA 625/EPA 625.1)				Soil Matrix (SW-8270D)			
Analyte	SPK µg/L	Low %	High %	RPD %	SPK µg/Kg	Low %	High %	RPD %
o-Toluidine	5	40	120	20	166.7	30	140	30
p-Dimethylaminoazobenzene	5	40	120	20	166.7	30	140	30
p-Phenylenediamine	5	40	120	20	166.7	10	140	30
Pentachlorobenzene	5	40	120	20	166.7	40	140	30
Pentachloronitrobenzene	5	40	120	20	166.7	30	140	30
Pentachlorophenol	5	19	121	20	166.7	23	135	30
Phenanthrene	5	45	121	20	166.7	50	125	30
Phenacetin	5	40	120	20	166.7	30	140	30
Phenol	5	20	124	20	166.7	45	130	30
Phenol-d6	5	20	120	20	166.7	40	125	30
Phorate	5	40	140	20	166.7	40	140	30
Phosmet	5	40	140	20	166.7	40	140	30
Prometon	5	40	140	20	166.7	40	140	30
Prometryne	5	40	140	20	166.7	40	140	30
Pronamide	5	40	120	20	166.7	40	140	30
Propachlor	5	40	140	20	166.7	40	140	30
Propazine	5	40	140	20	166.7	40	140	30
Pyrene	5	40	130	20	166.7	45	130	30
Pyridine	5	15	120	20	166.7	15	120	30
Quinoline	5	45	120	20	166.7	45	130	30
Ronnel	5	40	140	20	166.7	50	150	30
Safrole	5	40	140	20	166.7	40	140	30
Simazine	5	40	140	20	166.7	50	140	30
Simetryne	5	40	140	20	166.7	40	140	30
Stirofos	5	40	140	20	166.7	40	140	30
Sulfolane	5	40	140	20	166.7	40	140	30
Sym-Trinitrobenzene	5	40	120	20	166.7	40	140	30
Tebuthiuron	5	40	140	20	166.7	50	140	30
Terbacil	5	40	140	20	166.7	50	140	30
Terbufos	5	40	140	20	166.7	50	140	30
Terbutryn	5	40	140	20	166.7	50	140	30
Tetraethyldithiopyrophosphate	5	40	120	20	166.7	40	140	30
Thionazin	5	40	120	20	166.7	50	140	30
Triadimefon	5	40	140	20	166.7	50	140	30
Tricyclazole	5	40	140	20	166.7	50	140	30
Trifluralin	5	40	140	20	166.7	50	140	30
Tris(2,3-dibromopropyl) phosphate	5	40	140	20	166.7	50	140	30
Vernolate	5	40	140	20	166.7	50	140	30

Table 24.4 Number of Allowable Exceedances

Table 24.4 - Number of Allowable QC Exceedances	
Number of analytes	Sporadic Marginal Exceedances Allowed
5-15	1
16-30	2
31-45	3
46-60	4
61-75	5
76-90	6

Table 24.5 Summary of Calibration and QC Procedures for SW8270D/ EPA 625/EPA 625.1

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Check of mass spectral ion intensities using DFTPP and check DDT breakdown and benzidine/PCP tailing factors	Prior to Initial Calibration, daily Continuing Calibration Verification and every 12-hour period of sample analysis – 8270D and 625.1 **Method 625** Prior to initial calibration, sample analysis and every 24 hours of sample analysis.	Refer to DFTPP criteria listed in the Tables 11.2.1, 11.2.2 and 11.2.3. DDT breakdown must be <20% and benzidine & pentachlorophenol tailing factors <2. Recommendation is to use 625.1 since it is most stringent.	Retune instrument and verify. No samples shall be analyzed without a valid tune and tailing factor.
Multi-point initial calibration for all analytes including surrogates.	Initial calibration prior to sample analysis.	Average RF meet and each level RF should meet min RF criteria in Table 24.1 and %RSD ≤ 20% (≤15% for DoD projects) or one option below: Option 1 linear – least squares regression, r > 0.995 or Option 2 non-linear – COD > 0.990, 6 points	Correct problem then repeat initial calibration. Minimum 5 levels for linear and 6 levels for quadratic.

		shall be used for 2nd order.	
Second-source calibration verification (ICV).	Once per each new initial calibration.	All analytes within ±20% of expected value.	Correct problem then repeat initial calibration.
Retention time window calculated for each analyte.	RRTs may be updated based on the daily CCV.	Relative retention time (RRT) of the analyte within ±0.06 RRT units of the RRT of the standard.	Correct problem then reanalyze all samples analyzed since the last RT check.
Continuing Calibration Verification (CCV).	Daily, before sample analysis and every 12 hours of analysis time – 8270D/625.1. **Method 625** - Daily, before sample analysis and every 24 hours of analysis time.	CCV RF meets min RF criteria in Table 24.1. CCV RF is ≤ 20% difference (when using RFs) or ≤ 20% drift (when using linear or non-linear calibration models). CCV IS RT±30 seconds from RT of the mid-point standard in the ICAL. EICP area within -50% to +100% of ICAL mid-point standard. All reported analytes within 20% of true values.	Correct problem then repeat CCV. If second attempt fails then repeat initial calibration.
Continuing Calibration Verification (CCV) – closing for DoD projects.	At the close of an analytical sequence within tune window – 12 hours for 8270D/625.1 and 24 hours for 625.	All reported analytes within ±50% of true value	Recalibrate, and reanalyze all affected samples since the last acceptable CCV; or Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails, take corrective action(s) and re-calibrate; then reanalyze all affected samples since the last acceptable CCV.
Internal Standards for samples.	Immediately after or during data acquisition of	Retention time ±30 seconds from RT of the daily CCV. EICP	Check mass spectrometer and GC for malfunctions;

	calibration check standard.	area within -50% to +100% of daily CCV.	mandatory reanalysis of samples analyzed while system malfunctioned.
Method blank.	One MS/MSD per every 20 project samples per matrix for 8270D/625.1. One MS/MSD per every 10 project samples per matrix for 625..	No analytes detected > ½ LOQ; or analyte less than 5% of the regulatory limit, or analyte less than 5% of the sample result for the same analyte, whichever is greater.	Correct problem, then re-analyze method blank and all samples processed with the contaminated blank.
LCS for all analytes.	One MS/MSD per every 20 project samples per matrix for 8270D/625.1. One MS/MSD per every 10 project samples per matrix for 625.	QC acceptance criteria, Table 24.3. DoD samples must use DoD LIMS codes to ensure DoD recovery limits are used, see LIMS or DoD QSM for values.	Correct problem, then re- analyze the LCS and all samples in the affected preparation batch.
MS/MSD.	One MS/MSD per every 20 project samples per matrix for 8270D/625.1. One MS/MSD per every 10 project samples per matrix for 625.	QC acceptance criteria, Table 24.3 DoD samples must use DoD LIMS codes to ensure DoD recovery limits are used, see LIMS or DoD QSM for values.	Describe in Laboratory Review Checklist.
Surrogate spike.	Every sample, spiked sample, standard, and method blank.	QC acceptance criteria, Table 24.3. DoD samples must use DoD LIMS codes to ensure DoD recovery limits are used, see LIMS or DoD QSM for values.	Method 8000C, Section 9.6 Requirements. Describe in Laboratory Review Checklist.
Demonstrate ability to generate acceptable accuracy and precision using four replicate LCS analyses.	Once per analyst.	QC acceptance criteria, Table 24.3.	Recalculate results; locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria.
MDL study.	Once per 12 month period, per matrix for MDL and Quarterly for LOD and DCS.	Detection limits established shall be < 1/2 the LOQs in Table 21.1	Repeat LOD at higher level, but not greater than the PQL, substituting the

	For DoD, MDL and DCS (LOD) must be performed on all analytes including surrogate compounds.		higher LOD for the MDL, in case where the original LOD does not confirm the MDL.

END OF DOCUMENT

Analysis of Volatile Organic Compounds By GCMS Method 8260C, Method 624 and Method 624.1

DOCUMENT ID: HS-MSV001, REV 11.7

Approved By: Hoai. Van
Laboratory/Technical Director, Hoai Van

Date: 9/1/2020

Prepared By: Erica H Martinez
Quality Assurance Manager, Erica Martinez

Date: 09/01/2020

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1) Identification of the Method, Applicable Matrix, Scope and Applicability

1.1 Method 8260C is a GC/MS method used to determine volatile organic compounds in a variety of solid waste matrices, ground and surface waters, and various water-soluble soil extracts (methanol, TCLP and SPLP, etc.). The method is also applicable to those compounds that have boiling points below 200°C and are insoluble or only slightly soluble in water. Such compounds include low-molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. Table 2.4 is a list of compounds that can be analyzed for by the laboratory. The compound list is inclusive of various program lists such as the CLP Target Compound List and RCRA Appendix 9 List (40 CFR Part 264). The compound list reported will be the client-requested list.

1.2 Method 624/ 624.1 is a GC/MS method used to determine the certain volatile organic compounds in listed in Table 2.4 that are further identified with "*." These compounds are commonly found in municipal and industrial discharges as provided under 40CFR Part 136.1. The same GC/MS equipment performs Method 8260C and Method 624/624.1.

1.3 For both methods, volatile water-soluble compounds (e.g. Acrolein and Acrylonitrile) can be included in this technique, but their detection limits will be higher than water insoluble compounds.

1.4 This procedure uses two techniques by which the volatile compounds are introduced into the GC system. The techniques include the purge-and-trap (P/T) method (method 5030 and 624/624.1) for aqueous samples, and closed system P/T (method 5035A) for solid and waste oil samples. Tables in Section 22 list performance specifications for VOCs in waters and soil (LODs, LOQs, etc.).

1.4.1 Soil collection and handling requirements for closed system purge & trap (SW5035A): these procedures are described in SOP HS-QS010, Container Sub-sampling-volatile organics and Method SW5035A. The procedures describe field collection using a coring device (TerraCore™ or equivalent, etc.), sample shipment, and preservation requirements. SW5035A sample collection and preservation approaches lessen potential loss of VOCs from the time of sampling to the time of analysis.

1.4.2 Low Level Soil: The applicable concentration range of the low soil method when analyzed by the closed loop GC/MS system is in the 5 to 200 µg/kg range.

1.4.3 High Level Soil: Generally applicable to soils and other solid samples with VOC concentrations greater than 200 µg/kg. In the high level soil approach for SW5035A, the laboratory either receives methanol field preserved soil sample or a soil sample in a core device (TerraCore™, etc.). The core sample received must then be transferred into pre-tared 40 mL VOA vial and preserved with an addition of methanol within 48 hours, unless a QA Plan freezing option extends the transfer time requirement. The analysis of the methanol preserved sample is accomplished by typical injection of 100µL of methanol extract per 5-mL of organic free DI water. The diluted extract is transferred to a VOC vial for analysis with aqueous samples by method SW5030 (Section 2.1).

1.5 Bulk Soil Samples submitted in containers having minimal headspace:

1.5.1 Low level VOCs are analyzed by transferring a 5.0-gram portion of undisturbed soil from a bulk container into a pre-tared VOC vial containing a

stir bar, followed by the addition of 5mL of organic-free water. NOTE: If analysis is required with a 5035 prep, then prepare a MB and LCS and analyze within the acceptable time to minimize loss.

1.5.2 High level VOCs are analyzed by transferring a known weight (typically 5.0-grams) of undisturbed soil from the container into a pre-tared VOC vial, followed by the addition of known amount of (typically 5-mL) methanol.

1.6 High concentration oily waste method - generally applicable to oily samples with VOC concentrations greater than 200 µg/kg that can be diluted in a water-miscible solvent (e.g. methanol). Samples that are comprised of oils or that contain significant amounts of oil present additional analytical challenges. This procedure is generally appropriate for such samples when they are soluble in a water-miscible solvent.

2) Summary of Procedure

2.1 Water Samples: Volatile compounds are introduced into the gas chromatograph by the purge-and-trap method (SW-846 Method 5030 or as described in EPA 624/624.1). The components are separated via the GC and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information. The purge-and-trap process involves an inert gas bubbling through the 5-mL aqueous sample where the volatile components are efficiently transferred at ambient temperature from the aqueous phase to the vapor phase. The vapor is swept through a column where the volatile components are trapped. After purging is completed, the column is heated and backflushed with inert gas to desorb the components onto a GC column. The GC column is heated to elute the components, which are detected with a mass spectrometer.

2.1.1 A minor modification has been made to Method EPA 624: The desorb time has been modified to 1-2 minutes. Consistently passing PT samples, and QC samples with that desorb time is technical justification that the modification yields good results. Passing PT results can be found in the QA files and passing QC samples in LIMS.

2.2 Low Concentration Soil (SW5035A): Volatile organic compounds (VOCs) are determined following the field collection of approximately 5-g of sample using a coring device (TerraCore™, etc.). The field core sample is either transferred in the field into tared VOC vials containing preservative (i.e. 5-mL reagent water and bisulfate preservative if required) or it is submitted in the core device for laboratory preservation. Upon receipt of the sample/core device, the lab transfers the entire contents of the device into a pre-tared VOA vial that contains a stir bar (and solid sodium bisulfate if specified by project). A 5-mL aliquot of reagent water is added, then the vial is capped with a Teflon™ lined screw-cap and is ready for analysis. The entire vial is then placed, unopened, into the instrument carousel. The analysis cycle begins with the instrument injecting an additional aliquot of reagent water to the vial. The addition contains the surrogates and internal standards required for the analysis. The contents of the vial are then stirred at 40°C while the vial undergoes the purge and trap cycle of the analysis using an inert gas. Optionally, for soil samples having very fine particles that may clog the purge apparatus, the soil sample may be agitated using a vortex mixer and then placed on the instrument and purged at 40°C without further stirring. Purged components travel via a transfer line where they are captured onto an appropriate trap. When purging is complete, the trap is heated and backflushed with helium to desorb the trapped sample components into a gas chromatograph for analysis by the GC/MS

by method 8260C.

2.3 High Level Soil (SW 5035A): field collection of approximately 5-g of sample using a coring device (TerraCore™, etc.) is performed. The field core sample is either transferred in the field into tared VOC vial containing preservative (i.e. 5-mL methanol) or it is submitted in the core device for laboratory preservation using methanol. Upon receipt of the sample/core device, the lab transfers the entire contents of the device into a pre-tared VOA vial. The soil is extracted with a known volume of methanol. The analysis of the methanol-preserved sample is accomplished by typically injecting a 100-µL volume of the extract per 5-mL portion of organic free water. The diluted extract is transferred to VOC vial. The VOC vial is then analyzed with aqueous samples by method SW5030 as described in section 2.1 at ambient temperature.

2.4 The Limit of Quantitation (LOQ) of this method for an individual compound is approximately 5 µg/kg (wet weight) for low level soil/sediment samples, 0.5 mg/kg (wet weight) for wastes, and 1 µg/L for groundwater. This assumes a sample volume of 5 mL for water. LOQs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector. Refer to Table 24.1, 22.2 for listing of analyte LOQs.

Table 2.4 Characteristic Ions for Volatile Compounds

Compound * EPA 624/[1] EPA 624.1 analyte	Primary Ion	Secondary Ion(s)	Compound * EPA 624/[1] EPA 624.1 analyte	Primary Ion	Secondary Ion(s)
1,1,1,2-Tetrachloroethane [1]	131	133, 119	Cis-1,2-Dichloroethene *,[1]	96	61, 98
1,1,1-Trichloroethane *,[1]	97	99, 61	Cis-1,3-Dichloropropene *,[1]	75	77, 39
1,1,2,2-Tetrachloroethane *,[1]	83	85, 131	Cyclohexane	56	84
1,1,2-Trichlor-1,2,2-trifluoroethane	101	151	Dibromochloromethane *,[1]	129	208, 206
1,1,2-Trichloroethane *,[1]	83	97	Dibromomethane [1]	93	174, 95
1,1-Dichloroethane *,[1]	63	65, 83	Dichlorodifluoromethane [1]	85	87
1,1-Dichloroethene *,[1]	96	61, 63	Diethyl Ether [1]	59	74
1,1-Dichloropropene [1]	75	110, 77	Diisopropyl Ether (DIPE) [1]	45	59, 72
1,2,3-Trichlorobenzene [1]	180	182, 145	Epichlorohydrin [1]	57	49
1,2,3-Trichloropropane [1]	75	77	Ethanol [1]	45	-
1,2,3-Trimethylbenzene [1]	105	120	Ethyl acetate [1]	43	61, 70
1,2,4-Trichlorobenzene [1]	180	182, 145	Ethyl acrylate	55	99
1,2,4-Trimethylbenzene	105	120	Ethyl methacrylate [1]	69	41
1,2-Dibromo-3-chloropropane [1]	157	75, 155	Ethyl tert-Butyl Ether (ETBE) [1]	59	87
1,2-Dibromoethane (EDB) [1]	107	109, 188	Ethylbenzene *,[1]	91	106
1,2-Dichlorobenzene (ortho) *,[1]	146	111, 148	Ethylene Oxide [1]	44	--
1,2-Dichloroethane (EDC) *,[1]	62	64,98	Hexachlorobutadiene [1]	225	223, 227

1,2-Dichloropropane *,[1]	63	112	Iodomethane (methyl iodide)[1]	142	172, 141
1,3,5-Trimethylbenzene[1]	105	120	Isobutyl alcohol[1]	43	41, 42
1,3-Butadiene[1]	54	39	Isopropanol	45	59
1,3-Dichlorobenzene (meta) *,[1]	146	111, 148	Isopropylbenzene[1]	105	120
1,3-Dichloropropane[1]	76	78	M & P-Xylene *,[1]	106	91
1,4-Dichlorobenzene (para) *,[1]	146	111,148	Methacrylonitrile[1]	41	67, 39
1,4-Dioxane[1]	88	58	Methyl acetate[1]	43	74
1-Chlorohexane	55	91	Methyl acrylate[1]	55	85
2,2-Dichloropropane[1]	77	97	Methyl methacrylate[1]	41	69
2-Butanone (MEK) *,[1]	43	72	Methyl tert-butyl ether *,[1]	73	57
2-Chloro-1,3-butadiene (Chloroprene)[1]	53	88	Methylcyclohexane	83	55
2-Chloroethyl vinyl ether *,[1]	63	65, 106	Methylene chloride *,[1]	84	49, 86
2-Chlorotoluene[1]	91	126	Naphthalene *,[1]	128	129, 127
2-Hexanone[1]	43	58, 57	n-Butyl acetate	43	56, 87
2-Methylnaphthalene	142	141	n-Butyl acrylate	55	73, 85
2-Pentanone[1]	43	58	n-Butyl alcohol[1]	56	41
4-Chlorotoluene[1]	91	126	n-butylbenzene[1]	91	92, 134
4-Isopropyltoluene	119	134, 91	n-hexane	57	41, 43
4-Methyl-2-pentanone[1]	43	58, 100	n-pentane	43	42, 41
Acetaldehyde	44	43,42	n-Propanol[1]	42	59
Acetone *,[1]	43	58	n-propylbenzene[1]	91	120
Acetonitrile[1]	41	40, 39	o-Xylene *,[1]	106	91
Acrolein *,[1]	56	55, 58	Pentachloroethane[1]	167	130, 132 ,169
Acrylonitrile *,[1]	53	52, 51	Propionitrile	54	52, 55
Allyl alcohol[1]	57	39	Propylene oxide	43	58
Allyl Chloride[1]	41	76	Sec-Butylbenzene[1]	105	134
Amyl Alcohol	42	55,41	Styrene[1]	104	78
Benzene *,[1]	78	77, 51	tert-Amyl methyl ether[1]	73	55, 43
Benzyl chloride[1]	91	126, 65	tert-Butyl alcohol[1]	59	41
Bromobenzene[1]	156	77, 158	Tert-Butylbenzene[1]	119	91, 134
Bromochloromethane[1]	128	49, 130	Tetrachloroethene *,[1]	164	129, 131
Bromodichloromethane *,[1]	83	85, 127	Tetrahydrofuran[1]	42	71
Bromoform *,[1]	173	175, 254	Toluene *,[1]	92	91, 65
Bromomethane *,[1]	94	96, 79	Trans-1,2-Dichloroethene *,[1]	96	61, 98
Butyl methacrylate	41	69	Trans-1,3-Dichloropropene *,[1]	75	77, 39
Carbon disulfide[1]	76	78, 44	Trans-1,4-Dichloro-2-butene[1]	53	88
Carbon tetrachloride *,[1]	117	119, 121	Trichloroethene *,[1]	130	97, 95
Chlorobenzene *,[1]	112	114, 77	Trichlorofluoromethane *,[1]	101	103, 66
Chloroethane *,[1]	64	66, 49	Vinyl acetate[1]	43	86
Chloroform *,[1]	83	85, 47	Vinyl chloride *,[1]	62	64, 61
Chloromethane *,[1]	50	52, 49	Xylene (Total) *,[1]	106	91

3) Definitions

3.1 Batch: A defined set of one to 20 client samples of the same matrix, meeting the batch definition criteria, and prepared and analyzed within 24 hours (EPA 624) or 12 hours (SW8260C/EPA 624.1) on the same instrument, under the same calibration criteria. The **preparation batch** must also contain the required determinative method-defined batch QC samples (e.g. method blank, laboratory control samples, matrix spikes, duplicates, etc.). Analysis for VOCs by GC/MS (SW8260C/EPA 624.1) using the purge and trap is an example of the preparation/analytical batch which falls within each new 12 hour instrument tune and calibration verification.

3.2 Continuing Calibration Blank (CCB): Reagent water, or appropriate solvent, containing no analytes of interest.

3.3 Continuing Calibration Verification (CCV): The verification of the ICAL that is required during the course of analysis at periodic intervals. The CCV applies to both external standard and internal standard calibration techniques, as well as to linear and non-linear calibration models.

3.4 Demonstration of Capability (DOC): The analysis of QC samples in series to verify the ability to produce data of acceptable precision and bias (Current DOD QSM).

3.5 Exception Report: Appropriate comments reported with the associated sample batch that addresses sample anomalies such as demonstrated sample matrix effects.

3.6 GC/MS: Gas Chromatograph/Mass Spectrometer

3.7 Initial Calibration (ICAL) – Analysis of analytical standards at different concentrations that are used to determine and calibrate the quantitation range of the response of the analytical detector or method.

3.8 Initial Calibration Verification (ICV) (Second Source Calibration Verification): A known concentration of the target analyte(s). The ICV is prepared from a source different from that used to prepare calibration standards and CCV. This standard is analyzed immediately after the calibration to confirm the usability of the initial calibration.

3.9 Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

3.10 Laboratory Control Sample (LCS): A matrix same as the sample, free from the analytes of interest, spiked with known amounts of analytes or a material containing known and verified amounts of analytes.

3.11 Laboratory Duplicate: Two sample aliquots, taken in the laboratory from a single sample bottle, and analyzed separately with identical procedures. Analysis of duplicates indicate precision associated specifically with the laboratory procedures, removing any associated variables attributed by sample collection, preservation, or storage procedures.

3.12 Limit of Detection (LOD): an estimate of the minimum amount of a substance that an analytical process can reliably detect. The LOD is determined annually through the execution of a Method Detection Limit Study, and verified quarterly through the analysis of a Detectability Check Sample (DCS). See also Method Detection Limit (MDL)

3.13 Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a

target variable (e.g., target analyte) that can be reported with a specified degree of confidence. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met. The LOQ is performed quarterly.

3.14 Matrix Spike (MS): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available.

3.15 Matrix Spike Duplicate (MSD): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of recovery for each analyte.

3.16 Matrix: The substrate (e.g., water, soil, etc.) which may contain the analyte of interest.

3.17 Method Blank (MBLK): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analysis.

3.18 Method Detection Limit (MDL): The minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results. See also Limit of Detection (LOD)

3.19 Method Detection Limit (MDL) Study: A procedure in 40CFR Part 136, Appendix B, that describes how to produce an MDL, a reporting element of certain EPA methods. The MDL study is one approach to determine the LOD.

3.20 NCAR: Nonconformance Corrective Action Report (refer to SOP HS QS-003, current revision).

3.21 Organic Free Water: Deionized (DI) reagent water that meets the purity characteristics of Type I laboratory distilled water (daily resistance >17 megohm-cm). For additional purification before use, the DI water is purged using ultra pure nitrogen.

3.22 Retention Time Window: The length of time between sample injection and the appearance of a peak at the detector. The window of time is established for each analyte or group of analytes and is set for complete elution of analyte peaks. It is based upon a series of analyses and statistical calculations that establish the measured band on the chromatogram that can be associated with a specific analyte or group of analytes.

3.23 Surrogate (Surrogate Spike): An analyte added to a sample, which is unlikely to be found in any sample at significant concentration, and which is added directly to a sample aliquot in known amounts before any sample processing procedures are conducted. It is measured with the same procedures used to measure other sample components. The purpose of the surrogate analyte is to monitor method performance with each sample.

3.24 Tuning: The analysis of a standard compound to verify the mass spectrometer meets standard mass spectra abundance criteria prior to sample analysis.

4) Safety

4.1 Lab Safety: Due to various hazards in the laboratory, safety glasses and laboratory coats or aprons must be worn at all times while in the laboratory. In addition, gloves and a face shield should be worn when dealing with toxic, caustic, and/or flammable chemicals.

4.2 Chemical Hygiene: The toxicity or carcinogenicity of each reagent used has not been precisely defined; however, each chemical used should be treated as a potential health hazard. Exposure to laboratory reagents should be reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets (MSDS) is available to all personnel involved in these analyses.

4.3 Waste Management: The principal wastes generated by this procedure are the method-required chemicals and standards. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required. Laboratory procedures in SOP HS-SAF-001, Waste Disposal Procedures, must be followed.

4.4 Pollution Prevention: The materials used in this method pose little threat to the environment when recycled and managed properly. The quantities of chemicals purchased should be based on the expected usage during its shelf life. Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards or reagents to be disposed.

4.5 Job Safety Assessment

HAZARD ASSESSMENT		
Job Task #1:	**Hazards**	**Preventative Measures**
Sample handling.	Injury due to lifting and placing samples on storage locations and cuts from broken sample containers.	Use proper lift technique and cart to move coolers and stools/stepladder when working reaching above shoulder height in sample storage cooler. When transporting samples always use sample carrier or properly inspected cart. Wear proper PPE when handling sample container and have spill kits available.
Job Task #2:	**Hazards**	**Preventative Measures**
Sample Testing and/or standard and reagent/solvent use.	Exposure to possible hazardous chemicals.	Wear gloves, safety glasses, face shields (when needed) and lab coat. Work in fume hoods and avoid skin contact with solvents/acids/reagents. Know location of safety shower, first aid kits, spill kits and fire extinguisher when handling flammable material.
Job Task #3:	**Hazards**	**Preventative Measures**
Use of compressed gasses	Suffocation hazard and	Do not used in confined space, ensure

cylinders.	cylinder fall hazard. Fire hazard when using flammable gas.	proper ventilation and secure all cylinders to prevent falls. Ensure all regulators and gas lines are in good repair and does not leak.
Job Task #4:	**Hazards**	**Preventative Measures**
Glassware cleaning	Cuts from broken or chip glassware and exposure to cleaning solution such as acids and solvents.	Wear proper gloves, safety glasses and lab coat or apron at all times. When rinsing with solvents keep glassware in fume hood.
Job Task 5:	**Hazards**	**Preventative Measures**
Handling syringes	Pricking oneself with syringe.	Wear proper gloves, safety glasses, lab coat or apron and handle syringe with extreme care.

5) Maintenance

5.1 Routine preventative maintenance must be performed and documented to assure optimum instrument performance. Refer to the current revision of SOP HS-EQ004 for preventative maintenance schedules.

5.2 All instruments must be maintained by a trained analyst. Always check all gas sources in order to prevent any damage to an instrument that can cause a GC column to crack leading to unnecessary cleaning of the MS ion source.

5.3 All samples must be stored in the designated refrigerator or freezer before and after analysis. Document any occurrences where samples are not treated properly.

5.4 Volatile samples should be screened when possible to avoid contamination of the purge-and-trap system by samples that contain very high concentrations of purgeable material above the calibration range.

6) Interferences

6.1 Major Contaminant Sources: Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-Teflon™ thread sealants, plastic tubing, or flow controllers with rubber components must be avoided, since such materials out-gas organic compounds which are concentrated in the trap during the purge operation. Analyses of calibration and reagent blanks provide information about the presence of such contaminants. When potential interfering peaks are noted in blanks, the analyst must investigate the cause. Possible maintenance measures include changing the purge gas source and regenerating the molecular sieve purge gas filter. Subtracting blank values from sample results is not permitted. If reporting values without correcting for the blank results in what the laboratory feels is a false positive result for a sample, the laboratory must fully narrate this in text accompanying the uncorrected data.

6.2 Matrix Interferences: Matrix interferences purged or co-extracted from the samples will vary considerably from source to source, depending upon the particular sample or extract being tested. The analytical system, however, must be checked to ensure

freedom from interferences, under the analysis conditions, by analyzing method blanks.

6.3 Carryover Contamination: Contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. After the analysis of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to check for cross-contamination. Alternatively, if the sample immediately following the high concentration sample does not contain the volatile organic compounds present in the high level sample, freedom from contamination has been established.

6.4 Sample Specific Requirements: For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high concentrations of target compounds, it may be necessary to wash the purging device with a soap solution. The purging device is then rinsed with organic-free reagent water and dried in an oven at 105° C (Refer to SOP HS-GEN003, Glassware Cleaning Procedures). In extreme situations, the entire purge-and-trap device may require dismantling and cleaning.

6.5 Methylene Chloride Background Contamination: Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area must be isolated from all atmospheric sources of methylene chloride, otherwise, random background levels will result. Since methylene chloride will permeate through Teflon™ tubing, all gas chromatography carrier gas lines and purge gas plumbing must be constructed from stainless steel or copper tubing. Laboratory clothing worn by the analyst must be clean, since clothing previously exposed to methylene chloride fumes during liquid/liquid extraction procedures can contribute to sample contamination. The laboratory where volatile analysis is performed must be completely free of solvents.

6.6 Contamination by Diffusion: Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample container into the sample during shipment and storage. A trip blank prepared from organic-free reagent water and carried through the sampling, handling, and storage protocols can serve as a check on such contamination. A refrigerator blank is also used to monitor laboratory storage of samples.

6.7 Plumbing and Gas System: Impurities in the purge gas and from some organic compounds out-gassing from the plumbing ahead of the trap account for a significant number of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running reagent blanks. The use of non-Teflon™ plastic coating, non-Teflon™ thread sealant, or flow controllers with rubber components in the purging device must be avoided.

6.8 Miscellaneous: Various measures for the reduction and/or elimination include:

- 6.8.1 Baking out the column between analyses.
- 6.8.2 Changing the injector line.
- 6.8.3 Removing a portion of the analytical column, in cases of extreme contamination.
- 6.8.4 Including a post analysis bake out period in the GC temperature program to ensure that semivolatile hydrocarbons have been volatilized.

6.9 Effect of Headspace: Due to varying solubility and diffusion properties of gases in liquid matrices at different temperatures, it is possible for the sample to generate some headspace during storage. This headspace will appear in the form of micro

bubbles, and should not invalidate a sample for volatiles analysis. The presence of a macro bubble in a sample vial generally indicates either improper sampling technique or a source of gas evolution within the sample. The latter case is usually accompanied by a buildup of pressure within the vial, (e.g. carbonate-containing samples preserved with acid). Studies conducted by the USEPA (EMSL-Cincinnati unpublished data) indicate that "pea-sized" bubbles (i.e., bubbles not exceeding 1/4 inch or 6 mm in diameter) do not adversely affect volatiles data. These bubbles were generally encountered in wastewater samples, which are more susceptible to variations in gas solubility than are groundwater samples.

7) Personnel Qualifications and Responsibilities

7.1 General Responsibilities - This method is restricted to use by or under the supervision of analysts experienced in the method.

7.2 Analyst - It is the responsibility of the analyst(s) to:

- 7.2.1 Each must read and understand this SOP and follow it as written. Any deviations or non-conformances must be documented and submitted to the QA Manager for approval.
- 7.2.2 Produce method compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP (HS-QS-009).
- 7.2.3 Complete the required initial demonstration of proficiency before performing this procedure without supervision.
- 7.2.4 Complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 7.2.5 The analysts must submit data for peer or supervisor review.

7.3 Section Supervisor - It is the responsibility of the section supervisor to:

- 7.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.
- 7.3.2 Ensure analysts have completed the required initial demonstration of proficiency before performing this procedure without supervision.
- 7.3.3 Ensure analysts complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 7.3.4 Ensure analysts produce method compliant data that meet all quality requirements using this procedure and the Data Reduction, Review and Validation SOP.

7.4 Project Manager - It is the responsibility of the Project Manager to ensure that all method requirements for a client requesting this procedure are understood by the laboratory prior to initiating this procedure for a given set of samples.

7.5 QA Manager - The QA Manager is responsible for:

- 7.5.1 Approving deviations and non-conformances
- 7.5.2 Ensuring that this procedure is compliant with method and regulatory requirements,
- 7.5.3 Ensuring that the analytical method and SOP are followed as written through internal method and system audits.

8) Sample Collection, Handling, and Preservation

8.1 Aqueous samples for volatile organic analysis are received in several 40 mL glass VOA vials having Teflon™ lined septa lids. Presence of headspace must be noted at login. Ideally, a sample should have no headspace; however, up to 6 mm is acceptable. If headspace is observed, the condition must be noted in the final report. Aqueous VOC vials are stored in a dedicated refrigerator at a temperature of 0 to 6°C.

8.2 Analysis of volatile organic samples in a water matrix is performed within 14 days of sample collection, if the sample is acidified to pH <2; otherwise a 7 day holding time is used *EXCEPT* in the case of samples requiring Acrolein and/or Acrylonitrile. Samples requiring Acrolein and/or Acrylonitrile do not have an option to be preserved to pH <2. Unpreserved samples requiring Acrolein shall be analyzed within 72 hours of collection for Method 624/624.1. Samples requiring Acrylonitrile should be analyzed within 7 days for 8260/624/624.1 or 14 days if preserved to a pH of 4-5 per Table II of 40 CFR part 136.3.

NOTE: ALS Houston does not currently provide vials preserved to a range of pH 4-5.

8.3 The pH of water samples must be checked immediately after analysis to verify that it was properly preserved in the field and the pH paper lot number documented.

8.4 The TCLP leachate is performed within 14 days of collection and VOA analysis is completed within 14 days of the filtration of the TCLP leachate (if acidified, otherwise 7 days).

8.5 Samples with strong hydrocarbon odor are to be stored separately from routine environmental samples.

8.6 Refer to Table 8.4 for sample handling for both aqueous and soil samples:

Table 8.4 Volatile Organics Sample Collection, Preservation and Hold Time

Sample Matrix	Container	Preservative	Holding Time
Volatiles (water matrix)	Glass – 3 x 40 mL vials with Teflon™ lined lids, with no headspace	Cool >0 to 6°C; HCl to pH<2	14 Days
Volatiles, Unpreserved (water matrix)	Glass – 3 x 40 mL vials with Teflon™ lined lids, with no headspace	None	7 Days
Volatiles (water matrix WITH residual chlorine)	Glass – 3 x 40 mL vials with Teflon™ lined lids, with no headspace	Collect sample in 125 mL container that has been pre-preserved with 4 drops of 10 % sodium thiosulfate solution. Gently swirl sample to mix, then transfer to 3 - 40 mL vials with HCL to pH <2, Cool >0 to 6°C.	14 Days
Acrolein	Glass – 3 x 40 mL vials	None (624/624.1)	72 Hours

Sample Matrix	Container	Preservative	Holding Time
	with Teflon™ lined lids, with no headspace	Acidified with HCL to pH4-5	14 Days
Acrylonitrile	Glass – 3 x 40 mL vials with Teflon™ lined lids, with no headspace	None (624/624.1) None (8260) Acidified with HCL to pH4-5	72 Hours 7 Days (not indicated) 14 Days
Volatiles (low level soil by 5035A, where soil likely contains VOCs < 200 ppb)	Collect sample using approved coring device (TerraCore™,Encore, etc)	Cool >0 to 6°C; freeze* samples to -12 to -25 °C as an alternative to preservation with sodium bisulfate as a means to inhibit biodegradation.	48 hrs to (freeze*, then) transfer contents of core device (Encore) to 40 mL VOA vial , containing 5mL of organic free water & stir bar or freeze entire coring device; Terra Core 48 to freeze; analyze sample 14 days from collection
Volatiles (high level soil by 5035A, where soil may contain VOCs >200 ppb)	Collect sample using approved coring device (TerraCore™, Encore, etc)	Cool >0 to 6°C;	48 hrs to transfer core device (Encore) contents to a 40 mL VOA vial , containing 5 mL of purge and trap grade methanol; TerraCore preserved in field with methanol; analyze methanol preserved sample 14 days from collection
Volatiles, Solid Bulk Samples	4 oz widemouth glass with Teflon™ lined lids	>0 to 6°C	14 Days
* 5035A Option to "freeze" samples as a preservation step requires regulatory or QA Plan approval			

9) Equipment and Supplies

9.1 Syringe valve: Two-way, with Luer ends, if applicable to the purging device.

9.2 Syringe: 25 mL, 5 mL, 1 mL, 10 µl, 50 µl, 100 µl Hamilton GASTIGHT ® (1000, 1700 and 1800 series or equivalent, manufactured and pre-certified to ± 1% accuracy).

9.3 Balances: Analytical, capable of accurately weighing 0.0001 grams, and a top-loading balance capable of weighing 0.1 grams.

9.4 Glass vials: 40-mL, with screw cap and Teflon™ septa.

9.5 Volumetric flasks: 50-mL and 100-mL, class A with ground glass stoppers.

9.6 Spatula: Stainless steel.

9.7 Heater: Capable of maintaining the purging chamber to within ± 1°C over the temperature range of ambient to 40°C.

9.8 Purge and trap device: The purge and trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. These devices are often commercially available as a single unit.

9.8.1 Purge device: The purging chamber is designed to accept up to 25-mL samples with a water column at least 3 cm deep. The purge gas must pass through the water column as fine bubbles having diameters of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. Alternate sample purge devices may be utilized, provided equivalent performance is demonstrated.

9.8.2 Trap: Supelco K (Vocarb 3000) or equivalent.

9.9 GC Column: DB624 30 meter x 0.25 mm I.D., 1.4 µm film thickness capillary column, DB624 20 meter x 0.18 mm I.D., 1.0 µm film thickness capillary column or equivalent.

9.10 GC/MS interface: Any GC-to-MS interface that gives acceptable calibration points at 50 ng or less per injection for each of the analytes and the ions of 4-Bromofluorobenzene (BFB) may be used. HP and Agilent systems are used (See section 11.0).

9.11 Mass Spectrometer: Capable of scanning from 35-300 AMU every 3 seconds or less, using 70volts (nominal) electron energy in the electron impact mode and producing a mass spectrum that meets all the tuning criteria specified in the method when 50 ng of 4-bromofluorobenzene (BFB) are injected through the gas chromatograph inlet (see criteria in Table 11.3 when 50 ng of the tuning standard (BFB) are injected into the GC). To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC.

9.12 Purge and Trap (PT) Concentrator: The purge and trap is interfaced directly with the GC/MS system via a heated transfer line 150°C.

9.13 Gas Chromatograph: Programmable oven with interface to Purge and Trap and MS.

9.14 Data System:

9.14.1 Data Acquisition using Agilent ChemStation Software: Allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The software is interfaced to the mass spectrometer, providing a sequence log of run order for the data to be collected. The software also allows for searching any GC/MS data file for ions of a specified mass and plotting such ion abundance versus time or scan number. After data acquisition, collected data is automatically transferred into the Target Server for data processing.

9.14.2 Target DB Data Processing software: Target DB software is used for chromatographic data processing, data review and reporting where data and results can reside across multiple computers. Target complies with GALP using audit trails, validation checks, method and data locking, user security and data versioning, ensuring data integrity. The software allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundance versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Version NBS75K of the EPA/NIST Mass Spectral Library is used for data processing.

9.15 ALS employs a variety of instrument in the analysis of volatiles compounds by 8260/624/624.1

9.15.1 Computer Hardware for GC Units – Gas Chromatogram models:

9.15.1.1 Agilent 6890

9.15.1.2 Agilent 7890

9.15.2 Computer Hardware for MSD Units – Mass Selective Detectors models:

9.15.2.1 Agilent 5973

9.15.2.2 Agilent 5975

9.15.3 PT/Autosampler Combination Unit

9.15.3.1 Tekmar Atomx

9.15.3.2 Tekmar Atomx XYZ

9.15.3.3 Computer Software: Chem Station and Target

9.16 Vortex Mixer

9.17 Centrifuge

10) Standards and Reagents

10.1 Note: All *purchased* standards should be stored according to manufacturer specifications. Store *prepared* standard solutions (remaining stock, composite, calibration and surrogate) below 6 °C in glass containers having Teflon™ lined lids. All purchased stock standard solutions must be replaced after reaching the manufacturer's expiration date assigned to the standard. All laboratory prepared standard solutions must be replaced after six months or sooner if routine QC indicates a problem. An assigned expiration date of a lab prepared standard cannot exceed the manufacturer's expiration date for any component used in the standard formulation.

10.1.1 Standard purchased must meet the purity specified in method, for 8260 the minimum is 96%, see Section 7.7.3 of SW846 8260C.

10.1.2 In cases where purity is achieved, no adjust is needed see example below:

100 milligram (0.1 g) diluted to 100 mL = 1000 ug/L.

10.1.3 In cases where purity is NOT achieved then final concentration must be adjusted, see example below for 95% standard:

100 milligram (0.1 g) diluted to 100 mL = 1000 ug/L * 0.95 = 950 mg/L.

10.2 Standard Storage and Traceability

10.2.1 All *purchased* standards should be stored according to manufacturer specifications. Store *prepared* standard solutions (remaining stock,

composite, calibration and surrogate) below 6 °C in glass containers having Teflon™ lined lids.

10.2.2 Purchased stock standards must be certified by an approved vendor (e.g., Absolute Standards, AccuStandard, Restek, Supelco, Ultra, etc.)

10.2.3 All purchased standards and reagents must be logged into the Chemical Inventory Logbook upon receipt.

10.2.4 All prepared standards must be logged into the appropriate Standard/Reagent Preparation Logbook.

10.2.5 Refer to the most current version of SOP HS-QS001 for more information.

10.3 Methanol (MeOH): Purge and Trap grade (GC), ≥ 99.8%

10.4 Stock Standards – Must be replaced every 6 months at a minimum

10.4.1 Stock BFB (4-bromofluorobenzene) Tune Standard, 10,000 ug/mL

10.4.2 VOC Stock Surrogate Standard Mix, 2500 µg/mL: Restek 30240 or equivalent. This mix includes the following compounds: Dibromofluoromethane, toluene-d_8, 4-bromofluorobenzene and 1, 2-dichloroethane-d_4.

10.4.3 VOC Internal Standard Mix, 2500 mg/L: Restek 30074 or equivalent. This mix includes the following compounds: pentafluorobenzene, fluorobenzene, 1, 4-dichloro-benzene-d_4 and chlorobenzene-d_5.

10.4.4 VOC Calibration Stock Solutions, the following are typical of sources used, depending upon the application or regulatory requirement of the client:

10.4.4.1 Volatile Organic Compounds, Liquids in MeOH, 54 VOCs @ 2000 µg/mL (AccuStandard M-502A-R-10X or equivalent);

10.4.4.2 Volatile Organic Compounds, Gases in MeOH, 6 VOCs @2000 µg/mL (AccuStandard M-502A-R-10X or equivalent);

10.4.4.3 Acrolein & Acrylonitrile (A&A), in water, @10,000 µg/mL (AccuStandard M-502A-R-10X or equivalent);

10.4.4.4 Ketones, etc (acetone, 2-hexanone, carbon disulfide, etc) 8 compounds @ 2000 µg/mL (AccuStandard M-8260-ADD-10X or equivalent)

10.4.4.5 MTBE in methanol @ 2000 µg/mL (Restek # 30402 or equivalent)

10.4.4.6 Additional VOCs for Appendix IX Compounds in MeOH, (acetonitrile, allyl, isobutyl alcohol, etc,) 12 compounds @ 2000, 20,000 and 40,000 µg/mL (AccuStandard M-8240C-R3-10X or equivalent)

10.4.5 Calibration Verification Stock Standards: Second Sources must be acquired, similar to those in section 10.4.4, from a different vendor. If the same vendor must be used, the second source must of a different lot than those in section 10.4.4.

10.5 Working VOC Standards and Solutions – The following are concentrations and preparation procedures for working standards and solutions. These prepared solutions have an expiration date of one week* (See BFB Tune Solution).

10.5.1 BFB Tune Solution, 25 µg/mL: prepare by addition of 2.5-µL Stock BFB and into a final volume of 1.0-mL P/T methanol.

10.5.1.1 *BFB Tune solution is given an expiration date of 6 months due to the qualitative nature of its analysis.

10.5.2 Surrogate Auto Spiking Solution, 250 µg/mL: add 500 µL of Stock Surrogate Mix, 2500 µg/mL to P/T methanol and bring to a final volume of 5.0-mL.

10.5.3 VOC Internal Standard Auto Spiking Solution, 250 µg/mL: add 500 µL of Stock Internal Standard Mix, 2500µg/mL to P/T methanol and bring to a final volume of 5.0-mL

10.5.4 VOC Internal Standard/Surrogate Spiking Solution, 250 µg/mL: add 125 µL Stock Internal Standard Mix, 2000µg/mL and 125 µL Stock Surrogate Standard

Mix, 2000µg/mL to P/T methanol (10.3) and bring to a final volume of 1.0-mL.

10.5.5 Routine Working Calibration Standard, 25 µg/mL, prepare weekly, at a final volume of 1.0-mL:

10.5.5.1 Add 12.5 µL of a chosen Stock Standard Mix, @ 2000 µg/mL to P/T methanol and bring to a final volume of 1.0-mL.

10.5.5.2 Add 5.0-µL of Acrolein & Acrylonitrile Standard Mix, @ 10,000-µg/mL to P/T methanol; bring to a final volume of 1.0-mL.

10.5.5.3 Add 25.0 µL of a Ketones Stock Standard Mix, @ 2000 µg/mL (see 10.3.4) to P/T methanol and bring to a final volume of 1.0-mL.

10.5.6 Routine Working Calibration Standard, 250 µg/mL, prepare weekly, at a final volume of 1.0-mL:

10.5.6.1 Add 125 µL of a chosen Stock Standard Mix, @ 2000 µg/mL to P/T methanol and bring to a final volume of 1.0-mL.

10.5.6.2 Add 50-µL of Acrolein & Acrylonitrile Standard Mix, @ 10,000-µg/mL to P/T methanol; bring to a final volume of 1.0-mL.

10.5.6.3 Add 250 µL of a Ketones Stock Standard Mix, @ 2000 µg/mL (see 10.3.4) to P/T methanol and bring to a final volume of 1.0-mL.

10.5.7 Non-Routine Working Calibration Standard (App XI Applications, etc), 125/1500 /2500 µg/mL, prepare fresh weekly, at a final volume of 1.0-mL:

10.5.7.1 Add 62.5 µL of a multi-level Stock Standard Mix, @ 2000 / 20,000 / 40,000 µg/mL to P/T methanol and bring to a final volume of 1.0-mL.

10.5.8 Non-Routine Working Calibration Standard (App XI Applications, etc), 1250/15000/25000 µg/mL (or ppm), prepare fresh weekly, at a final volume of 1.0-mL:

10.5.8.1 Add 625 µL of a multi-level Stock Standard Mix, @ 2000 / 20,000 / 40,000 µg/mL to P/T methanol and bring to a final volume of 1.0-mL.

10.5.9 Routine Working LCS/MS Solution (Full List), 250 µg/mL: The second sources are used to prepare this standard. While LCS/MS/MSD spikes require full list spikes, the target analyte list is typically client dependent.

10.5.9.1 Full List LCS/MS Working Spike, 250 µg/mL: add 125 µL of the Calibration Stock Standard Mix, 2000µg/mL, to P/T methanol and bring to a final volume of 1.0-mL. Prepare weekly

10.6 Initial Calibrations Curve (ICAL) Standards are prepared for VOC and Low-Level VOC separately. For regular Level VOC: A minimum of eight (8) standard levels are prepared at the levels outlined in Table 10.6 starting from 2ppb level. For Low Level VOC: Nine standards are prepared at the levels outlined in Table 10.6. The concentrations in Table 10.5.6 are not applicable to Ketones, Acrolein and Acrylonitrile, which have concentrations twice the value listed. Also it not applicable for the non-routine compounds and alcohols which are ran at five times to ten times the listed concentrations.

Table 10 ICAL Levels for Aqueous VOC and Low Level –VOC

Volume of Std added (250ppm)	**0.5µL**	**1µL**	**2µL**	**5µL**	**2µL**	**4µL**	**10µL**	**20µL**	**30µL**	**40µL**
Final Volume (mL)	250	250	250	250	50	50	50	50	50	50

Water ICAL Curve Std. Conc., (µg/L)	0.5	1.0	2.0	5 .0	10.0	20.0	50.0*	100	150	200

*CCV level

10.6.1 CCB prepared by filling clean VOA vial with reagent water. Instrument will add surrogate and internal standards.

10.7 Soil Initial Calibration Standards: Add 5 g Ottawa sand to the purge vessel. Add 5-mL water. Eight different concentrations are prepared at the levels outlined in Table 10.7 by spiking the sand/water mixture with the appropriate working standard (§ 10.5) from a calibration standard mix (§10.5.5 or 10.5.6). The concentrations in Table 10.7 are not applicable to Ketones, Acrolein and Acrylonitrile, which have concentrations twice the value listed. Also it not applicable for the non-routine compounds and alcohols which are ran at five times to ten times the listed concentrations.

Table 10.7 ICAL Levels for Solid VOC

Volume of Std. Diluted to 5mL	**0.5µL** (25 ppm)	**1µL** (25 ppm)	**2µL** (25 ppm)	**4µL** (25 ppm)	**10µL** (25 ppm)	**20µL** (25 ppm)	**30µL** (25 ppm)	**40µL** (25 ppm)
Soil ICAL Std. Conc., (µg/kg)	2.5	5.0	10.0	20.0	50*	100	150	200

*CCV Level

10.7.1 Solid CCB, prepared by adding 5 grams of clean Ottawa sand to VOA containing a stirbar. Instrument will add internal standards and surrogate prior to analysis.

10.8 Methanol Initial Calibrations Curve (ICAL) Standards are prepared for solid medium level VOC separately. For medium Level VOC: A minimum of eight (8) standard levels are prepared at the levels outlined in Table 10.8 starting from 2ppb level. The concentrations in Table 10.8 are not applicable to Ketones, Acrolein and Acrylonitrile, which have concentrations twice the value listed. Also it not applicable for the non-routine compounds and alcohols which are ran at five times to ten times the listed concentrations.

Table 10.8 ICAL Levels for Solid Medium Level –VOC

Volume of Std added (250ppm)	**2µL**	**4µL**	**1µL**	**2µL**	**4µL**	**10µL**	**20µL**	**30µL**	**40µL**
Methanol volume added per flask (mL)	25	25	5	5	5	5	5	5	5
Final Volume (mL)	250	250	50	50	50	50	50	50	50
Water ICAL Curve Std. Conc., (µg/L)	1.0	2.0	5 .0	10.0	20.0	50.0	100	150	200

10.9 Reagent water is defined as water in which the analytes of interest and interfering compounds are not detected at the MDLs of the analytes of interest. It may be generated by passing deionized water, distilled water, or tap water through a carbon bed, passing the water through a water purifier, or heating the water to between 90

and 100˚C while bubbling contaminant free gas through it for approximately 1 hour. While still hot, transfer the water to screw-cap bottles and seal with a fluoropolymer-lined cap.

11) Method Calibration

11.1 GC/MS System general operating conditions: Any minor deviations to the below must be remain consistent for the initial calibration, and related calibration verifications, QC samples and client samples run on the specific instrument.

Table 11.1 Typical Purge & Trap and GC/MS System Conditions

System/Condition:	
Purge Flow:	40 mL/min
Preheat trap prior injection	240°C - 250°C
Purge time/temp:	11 min. at ambient (40°C for soils)
Desorb time/temp:	1-2 min at 250°C - 255°C
Bake time/temp:	4-6 min at 260°C - 270°C
Transfer line temp:	120°C - 150°C
Valve port temp:	120°C - 150°C
GC Conditions	
He gas flow rate	0.7 - 2 mL/min
Inlet Temp.	180°C - 220°C
Aux. Temp.	180°C - 200°C
Init. Oven Temp.	2-4 min at 35°C - 40°C
Temp Program:	35°C - 40°C to 190°C - 210°C at 10°C - 20°C/min
Final Temperature	190°C - 210°C
MS Source Temp:	230°C
Total run time	Approx. 15 - 22 minutes

11.2 Instrument Tuning with BFB: Inject 50 ng of 4-bromofluorobenzene and analyze. The GC/MS system must be hardware-tuned so that the BFB tune meets the criteria specified in table 11.2. The mass spectrum of BFB is to be acquired in the following manner: three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of BFB. Do not subtract background part of the BFB peak. Other tune option may not be employee, if tune is not met on a second attempt corrective action must be taken. Failure of tune is indication of need for maintenance and analyst must perform instrument maintenance, such as source cleaning, followed by new calibration after a successful tune.

11.2.1 The BFB tuning criteria must be met for initial and continuing calibration. This criterion must be demonstrated for every 12 hour time period of operation. Refer to Table 11.3 for the BFB tune criteria (most stringent requirement used).

Table 11.3 BFB Key m/z Abundance Criteria

Mass (m/z)	**Abundance Criteria 8260C/EPA 624/EPS 624.1**

Mass (m/z)	Abundance Criteria 8260C/EPA 624/EPS 624.1
50	15 to 40% of mass 95.
75	30 to 60% of mass 95.
95	Base Peak, 100% Relative Abundance.
96	5 to 9% of mass 95.
173	<2% of mass 174.
174	>50% of mass 95.
175	5.0 to 9.0 % of mass 174.
176	>95.0 % but <101.0 % of mass 174.
177	5.0 to 9.0 % of mass 176.

11.3 ICAL Standards: Analyze the standards prepared in Section 10.6 in order to initially calibrate the system and to determine linearity of response. An Initial calibration verification (ICV) is performed at the conclusion of every calibration using a second source standard (10.4.5), prepared near the midpoint of the curve. All anlaytes and surrogate must be in the multi-point calibration.

11.4 Internal standards (50 µg/L) are added to each calibration standard for quantitation and QA/QC purposes. Relative response factors (RRF) and percent relative standard deviation (%RSD) for each target compound at each calibration level are tabulated to assess them against method criteria. Calculate the average relative response factor (Ave. RRF) for each compound across the calibration concentrations using equations in Sec 15 (Target™ performs calculations).

11.5 Initial Curve RRF and the %RSD for each target compound at each calibration level is tabulated using the Target software. These results are generated using the calibration update and report programs of the software. For method 624, the resulting %RSD for each target analyte RRF must be <20% to assume linearity by the method.

11.6 8260C – Recommended Initial & Continuing Calibration Minimum RRF criteria:

Table 11.4 Recommended Calibration Minimum RRF criteria & IS assignment

Target Compound	IS	Min. RRF	Target Compound	IS	Min. RRF
1,1,1,2-Tetrachloroethane	3	(0.100)	cis-1,2-Dichloroethene	1	0.100
1,1,1-Trichloroethane	1	0.100	cis-1,3-Dichloropropene	2	0.200
1,1,2,2-Tetrachloroethane	3	0.300	Cyclohexane	1	0.100
1,1,2-Trichlor-1,2,2-trifluoroethane	1	0.100	Dibromochloromethane	3	0.100
1,1,2-Trichloroethane	3	0.100	Dibromomethane	2	(0.100)
1,1-Dichloroethane	1	0.200	Dichlorodifluoromethane	1	0.100
1,1-Dichloroethene	1	0.100	Diethyl Ether	1	0.050
1,1-Dichloropropene	2	(0.100)	Diisopropyl ether (DIPE)	1	(0.05)
1,2,3-Trichlorobenzene	4	(0.100)	Epichlorohydrin	2	0.005
1,2,3-Trichloropropane	4	(0.100)	Ethanol	1	(0.001)
1,2,3-Trimethylbenzene	4	0.100	Ethyl acetate	1	0.100
1,2,4-Trichlorobenzene	4	0.200	Ethyl acrylate	2	(0.100)
1,2,4-Trimethylbenzene	4	(0.100)	Ethyl methacrylate	3	(0.100)
1,2-Dibromo-3-chloropropane	4	0.050	Ethyl Tert-Butyl Ether (ETBE)	1	(0.100)

Target Compound	IS	Min. RRF	Target Compound	IS	Min. RRF
1,2-Dibromoethane	3	0.100	Ethylbenzene	3	0.100
1,2-Dichlorobenzene	4	0.400	Ethylene oxide	1	(0.05)
1,2-Dichloroethane	2	0.100	Hexachlorobutadiene	4	(0.100)
1,2-Dichloropropane	2	0.100	Iodomethane	1	(0.100)
1,3,5-Trimethylbenzene	4	(0.100)	Isobutyl Alcohol	1	0.005
1,3-Butadiene	1	(0.050)	Isopropanol	1	0.005
1,3-Dichlorobenzene	4	0.600	Isopropylbenzene	3	0.100
1,3-Dichloropropane	3	(0.100)	m,p-Xylene	3	0.100
1,4-Dichlorobenzene	4	0.400	Methacrylonitrile	1	(0.010)
1,4-Dioxane	2	(0.001)	Methyl acetate	1	0.100
1-Chlorohexane	3	(0.100)	Methyl acrylate	1	0.100
2,2-Dichloropropane	1	(0.100)	Methyl methacrylate	2	(0.05)
2-Butanone	1	0.100	Methyl tert-butyl ether (MTBE)	1	0.100
2-Chloro-1,3-butadiene (Chloroprene)	1	(0.050)	Methylcyclohexane	1	0.100
2-Chloroethyl vinyl ether	2	(0.050	Methylene chloride	1	0.100
2-Chlorotoluene	4	(0.100)	Naphthalene	4	(0.20)
2-Hexanone	3	0.100	n-Butyl acetate	3	0.050
2-Methylnaphthalene	4	(0.050)	n-Butyl acrylate	3	0.100
2-Pentanone	2	0.050	n-Butyl alcohol	2	(0.005)
4-Chlorotoluene	4	(0.100)	n-Butylbenzene	4	(0.05)
4-Isopropyltoluene	4	(0.100)	n-Hexane	1	(0.100)
4-Methyl-2-pentanone	3	0.100	n-pentane	1	(0.050)
Acetaldehyde	1	(0.025)	n-propanol	1	(0.005)
Acetone	1	0.100	n-Propylbenzene	4	(0.100)
Acetonitrile	1	(0.05)	o-Xylene	3	0.300
Acrolein	1	(0.02)	Pentachloroethane	4	(0.05)
Acrylonitrile	1	(0.05)	Proprionitrile	1	(0.01)
Allyl Alcohol	1	0.005	Propylene oxide	1	0.050
Allyl Chloride	1	(0.05)	sec-Butylbenzene	4	(0.100)
Amyl Alcohol	3	(0.005)	Styrene	3	0.300
Benzene	2	0.500	Tert-Amyl Methyl Ether (TAME)	2	(0.05)
Benzyl Chloride	3	0.050	Tert-Butyl Alcohol	1	(0.005)
Bromobenzene	4	(0.100)	tert-Butylbenzene	4	(0.100)
Bromochloromethane	1	(0.100)	Tetrachloroethene	3	0.200
Bromodichloromethane	2	0.200	Tetrahydrofuran	1	0.050
Bromoform	3	0.100	Toluene	3	0.400
Bromomethane	1	0.100	trans-1,2-Dichloroethene	1	0.100
Butyl Methacrylate	4	0.100	trans-1,3-Dichloropropene	2	0.100
Carbon disulfide	1	0.100	trans-1,4-Dichloro-2-butene	4	(0.05)
Carbon tetrachloride	2	0.100	Trichloroethene	2	0.200
Chlorobenzene	3	0.500	Trichlorofluoromethane	1	0.100
Chloroethane	1	0.100	Vinyl acetate	1	(0.100)
Chloroform	1	0.200	Vinyl chloride	1	0.100

Target Compound	IS	Min. RRF	Target Compound	IS	Min. RRF
Chloromethane	1	0.100			
Pentafluorobenzene- IS # 1	-	n/a	chlorobenzene-d5 IS # 3	-	n/a
1,4-Difluorobenzene – IS # 2	-	n/a	1,4-dichloro-benzene-d4-IS# 4	-	n/a
( ) = laboratory assigned min RRF, min RRF not defined for the analyte in SW 8260C					

11.7 Initial Calibration RSD Requirements: All target analytes must meet the minimum RRF requirements set in Table 11.4.

11.7.1 Response Factors (RF) and %RSD for each target compound at each calibration level are tabulated to assess them against method criteria.

11.7.2 Percent Relative Standard Deviation (% RSD): The RSD should be less than or equal to 20% for each target analyte by method 8260c and <35% for EPA 624/EPA624.1. Each target analyte should meet the minimum response factor noted in Table 11.4 (the most common target analytes identified by method 8260C). These are to be demonstrated for each individual calibration level as a means to ensure that these compounds are behaving as expected. In addition, meeting the minimum response factor criteria for the lowest calibration standard is critical in establishing and demonstrating the desired sensitivity. Due to the large number of compounds that may be analyzed by this method, some compounds may fail to meet the criteria. For these occasions, it is acknowledged that the failing compounds may not be critical (if not required target analytes) for the specific project. If required, their reporting would require use of data qualifier flags to indicate the data as estimated values (e.g. useable for screening purposes if acceptable in a client project plan). **Note** DOD QSM requires ≤15% RSD for average response, see Table 24.6

11.7.2.1 Analyst has two options (1) Create single calibration on with 15% RSD criteria or (2) create two curve from calibration with one using 20% method criteria and one with 15% DOD QSM criteria.

11.7.3 If more than 10% of the required target compounds included with the initial calibration exceed the 20% RSD limit and do not meet the minimum correlation coefficient (0.99) for alternate curve fits, then the chromatographic system is considered too reactive for analysis to begin. System maintenance must then be performed (e.g. clean or replace the injector liner, trap and/or capillary column, then repeat the calibration procedure).

11.8 Linearity of target analytes: If the RSD of any target analyte is 20% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation. If the RSD of any target analyte is greater than 20%, the linear or non-linear calibration options may be evaluated.

11.8.1 When the RSD exceeds 20% (≤15% for DOD projects), the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the GC system or analytes that exhibit poor GC behavior, etc.

11.8.2 Due to the large number of compounds that may be analyzed, some compounds may fail to meet either the 20% RSD (≤15% for DOD projects) or the minimum correlation coefficient criteria (0.99) for the acceptance criteria for alternative calibration fit procedures in Method 8000C. Either the linear or

non-linear calibration models described in Method 8000C may be used, but they must be used consistently. It is considered inappropriate once the calibration analyses are completed to select an alternative calibration procedure in order to pass the recommended criteria on a case by case basis. In order to report non-detects, it must be demonstrated that there is adequate sensitivity to detect the failed compounds at the applicable lower quantitation limit. NOTE: The option for non-linear calibration may be necessary but it may not be used to compensate for detector saturation or to avoid proper instrument maintenance. The calibration model must be continuous and monotonic. Linear fits require five levels minimally and non-linear (quadratic) fits require six levels minimally.

11.8.3 The method of linear regression analysis has the potential for a significant bias to the lower portion of a calibration curve, while the relative percent difference and quadratic methods of calibration do not have this potential bias. When calculating the calibration curves using the linear regression model, a minimum quantitation check on the viability of the lowest calibration point should be performed by re-fitting the response from the low concentration calibration standard back into the curve (See Method 8000C). It is not necessary to re-analyze a low concentration standard; rather the data system can recalculate the concentrations as if it were an unknown sample. The recalculated concentration of the low calibration point should be within ± 30% of the standard's true concentration. Should any recalculated analyte be greater than 30% at the MQL, the analyst must review the results (proper identification, area counts, calibration or response factors, and RSD). For those analytes affected, ensure that the problem is not associated with just one of the initial calibration standard. If the problem appears to be associated with a single standard, then that one standard may be reanalyzed once, to rule out problems due to a random chance, and the RSD or correlation recalculated. Replacing the standard may be necessary in some cases. All reanalysis of any calibration standard must be performed within the same tuning period for a GC/MS method. This reanalysis must also commence before any samples are analyzed. If this criterion cannot be met then repeat the entire initial calibration.

11.8.3.1 NOTE: Reanalyzing or replacing a single standard must NOT be confused with the practice of discarding individual calibration results for specific target compounds in order to pick and choose a set of results that will meet the RSD or correlation criteria for the linear model. The practice of discarding individual calibration results is addressed as a fourth alternative option and is very specific as to how a set of results are chosen to be discarded. If a standard is reanalyzed or a new standard is analyzed, then ALL of the results from the original analysis of the standard in question must be discarded. Further, the practice of running additional standards at other concentrations and then picking only those results that meet the calibration acceptance criteria is EXPRESSLY PROHIBITED, since the analyst has generated data that demonstrate that the linear model does not apply to all of the data.

11.9 Whichever calibration model is selected, the model can be checked to establish the applicability of the model over the extent of the calibration range. This check is performed by re-quantifying the calibration data using the new curve and comparing the calculated concentrations of the calibrations data against the concentration of the calibration level. Using % difference, the criteria for acceptability based upon the

additional check demonstrates the impact upon the usability of a calibration for quantitation.

11.9.1 Calculating the % difference is determined by using the following equation:

% Difference = (Cc – Ce)* 100 / Ce

where:
Cc = Calculated amount of standard, in mass or concentration units.
Ce = Expected amount of standard, in mass or concentration units.

11.9.2 The absolute value of the % difference between these two amounts for every calibration level should be less than or equal to 20%.

11.9.3 Corrective action may be required if the criteria for RSD, r, r^2 are not met. If any analyte for any calibration standard has a percent difference with an absolute value greater than 20% (or 30% for the exception stated in §11.8.3), a corrective action may be required. The calibration may not be used for quantitative analyses of that analyte when the RSD, r, or r^2 criteria are not met.

11.10 Initial Calibration using Linear Regression (First Order Fit Determinations): When the average response factor RSD is greater than 20% over the calibration range, linearity through the origin cannot be assumed. A linear regression (first order fit) of the response versus the concentration of the standards is evaluated. The instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). The regression produces the slope and intercepts terms for a linear equation in the following form:

$$y = a x + b$$

where,
y = instrument response in peak area or height
x = concentration of the calibration standard
a = Slope of the line (also called the coefficient of x)
b = the intercept

11.10.1 Linear Fit Criteria: The analyst must not force the line through the origin, but have the intercept calculated from the five data points minimally. The origin (0, 0) is NOT included as a sixth calibration point. The regression calculation will generate a correlation coefficient I that is a measure of the "goodness of the fit" of the regression line to the data. The linear fit correlation coefficient I must be 0.995 or better (or equivalently, coefficient of determination (r2) must be greater than or equal to 0.990).

11.11 Quadratic (second order non-linear) Fits: to use a quadratic fit, at least six data points are required. The origin is not included in the equation. The regression curve uses the following equation:

$$y = a + b x + c x^2$$

Where; a, b, and c are constants defined by the curve

11.11.1 The quadratic (non-linear) fit must generate a correlation coefficient I greater than or equal to 0.995 (or equivalently, coefficient of determination (r2) must be greater than or equal to 0.99). Response must increase with increasing

concentration.

11.12 Initial Calibration Verification (ICV): Using a second source standard, each new initial calibration must be verified. Typical verification will be at or near the midpoint of the curve or at 50 µg/L for a 5mL purge. The percent recoveries of the verification standard must fall within 80-120 % for all target analytes, with the exception of a range of 60-140% for poor performers such as alcohols, nitriles and ketones that are not routinely analyzed for. A 10 µg/L or 150 µg/L calibration verification standard should be run periodically in place of the 50 µg/L standard to evaluate a different point of the calibration curve. The same 80-120 % recovery criteria are applied for acceptance of the initial calibration.

11.13 Continuing Calibration Tune: Every twelve hour time period, the validity of the initial calibration is checked. A 50-ng sample of BFB is purged or injected to determine if tuning criteria are met above (Table 11.3).

11.14 Continuing Calibration Verification Standard (CCV) and Continuing Calibration Blank Standard (CCB): A calibration standard is analyzed at the 50 µg/L level. RRFs and %D for the continuing standard are compared to the average RRFs of the initial calibration. See section 15 for the calculation of the RRF and the %D.

11.14.1 Minimum RRF criteria for these compounds are in Table 11.4.

11.14.2 The Percent Difference (response factor calibration model) or Percent Drift (regression calibration curve fit) must less than or equal to 20% to demonstrate that the continuing calibration is valid. Corrective action is taken if either the CCV minimum RRF or %D (%Drift) do not meet criteria. Troubleshooting: Possible problems could be standard mixture degradation, column contamination, or active sites in the column or chromatography system.

11.14.3 CCV may only be analyzed after a successful tune with all compounds within ±20% of true value, see Table 24.6

11.14.4 CCB immediately following the CCV, with no target compounds present at level greater than ½ LOQ.

11.14.5 For DOD sample a closing CV is required, all sample must be bracketed by successful CCVs. This CCV must be analyzed within the 12 or 24 hour tune period. All analytes in the closing CCV must be within ±50% of the true value, see Table 24.6.

11.15 CCV/CCB Internal Standards – The CCV Internal Standard areas are to be within the -50% to +100% of the internal standard response of the most recent initial calibration standard (ICAL).

11.16 Sample Internal Standards – all sample and batch QC sample Internal Standard areas are to be within the -50% to +100% of the internal standard response of the daily CCV.

11.17 Internal Standard Retention Times: All sample and QC sample retention times most recent initial calibration (ICAL). If the retention times change more than 30 seconds, an appropriate maintenance and/or corrective action is initiated.

11.18 Surrogate Calibration: In addition to the generation of a surrogate initial calibration curve in the same manner as a target analyte as described in one of the sections 11.8 through 11.12, this SOP allows a second option for the surrogate calibration curve. In this option, a constant amount of each surrogate (and internal standard) is added to each variable target analyte calibration standard being run to establish the target analyte curve. When this procedure is utilized, the response factors of the surrogate are averaged to produce an average response factor for each surrogate. This surrogate

average response factor is then use for sample (and QC sample) surrogate quantitation.

11.19 Cleanup Blanks: Cleanup blanks are used after highly contaminated samples, QC samples that contain Naphthalene, 1-Methylnaphthalene, and 2-Methylnaphthalene, or any other observable sample where the latter compounds have the ability to carryover to the next sample.

12) Sample Preparation and Analysis

12.1 At the beginning of each batch, the instrument must be tuned and pass the tuning criteria. A continuing calibration, LCS and the method blank must be analyzed and meet the criteria before sample analysis begins. Tune must be repeated every 12 hours for 8260C/EPA 624.1 and every 24 hours for 624. All DoD project must be processed under DoD LIMS codes to ensure control limits from DoD QSM are achieved.

12.2 Laboratory Control Standard (LCS): The LCS is prepared from a second source calibration stock, containing the compounds on the standard reporting list and at the same concentration as the continuing calibration 20ppb. The LCS is analyzed after the continuing calibration passes as a check on the calibration standards. The LCS results must be within the spike control limits for the spiking compounds, see Table 24.3. All DoD project must be processed under DoD LIMS codes to ensure control limits from DoD QSM are achieved.

12.3 Method Blank: A method blank must be analyzed each twelve-hour shift of continuous operation. The method blank must always follow the calibration standard(s). Target compounds found in the method blank must be less than or equal to one half (1/2) of the Limit of Quantitation (LOQ) of each target compound or the Limit of Quantitation (LOQ) of the common lab contaminants (i.e. acetone and methylene chloride). The surrogate spike percent recoveries must be calculated and the values within acceptable ranges specified in Table 24.3.

12.4 Water Sample Analysis:

12.4.1 When retrieving samples from storage, samples received with headspace (<6mm) are noted and color tagged on the bottom of each affected vial. For samples where one or more vials had no headspace (or headspace <6mm) present, any untagged vial is to be used for the initial analysis. If a color tagged vial is required for an analysis (e.g. confirmatory or dilutions), indicate use of the vial in the Run Log and in the LIMS comments associated with the analysis data reported.

12.4.2 Allow samples to warm to room temperature.

12.4.3 For 1x dilutions, the entire 40-mL sample vial is loaded onto the autosampler. All DoD project must be processed under DoD LIMS codes to ensure control limits from DoD QSM are achieved.

12.4.4 For any prepared (diluted) sample, dilutions are made by an analyst and then placed into a VOA vial and loaded onto the autosampler. Dilutions are logged into the run log and Target.

12.4.5 When making a required sample dilution, chose a dilution that allows measurement of the major components to fall into the upper half of the calibrations curve.

12.4.6 The appropriate amount of each of the internal standard and surrogate solution will be added to the sample (or diluted sample) prior to purging by

the autosampler.

12.4.7 After sample analysis, each is to be checked for acid preservation using a narrow range pH paper (nominally pH 1 to 3).

12.5 For low level soil/sediment analysis, the purge device is heated to approximately 40°C, the blank is 5 g of Ottawa sand and 5 mL of DI water.

12.6 For medium level soil/sediment blank, a 50x dilution of MeOH into DI water is placed in a VOC vial for analysis. This blank checks for contaminants in the methanol used for high level extractions. Common contaminants are acetone and dichloromethane.

12.7 Assessment of Potential Carryover: If an analyzed sample has a compound that saturates the system, a reagent (method) blank must be analyzed to demonstrate that the system is free of contamination. If a sample analyzed after a sample having high VOCs shows levels of the VOCs, re-analysis of the sample must be performed after a new method blank has been analyzed and has demonstrated the system is free of carryover. The re-analysis results are used to confirm whether the first results were due to carryover. For additional information, refer to section 6.3.

12.8 Aqueous Dilutions – Prepared by the analyst prior to GC/MS analysis.

12.8.1 For example, a 10x dilution can be accomplished by filling a syringe with 5-mL of sample and adding it to a 50-mL Class A volumetric flask vial containing ~45-mL of organic free DI water. The flask is brought to volume, gently inverted three times and transferred into a new VOC vial for analysis.

12.8.2 A 100x sample dilution may be prepared by adding 500-µl of sample to a 50-mL volumetric flask vial containing ~49 mL of organic free DI water. The flask is brought to volume, gently inverted three times and transferred into a new VOC vial for analysis.

12.8.3 After the dilution has been made and transferred to a new VOC vial, cap and place on the autosampler. The internal standard/surrogate mix will be added by the autosampler.

12.9 Water-miscible Organic Samples – Samples should be diluted at least 50-fold in methanol. A methanol aliquot added to 50-mL of DI water is analyzed.

12.10 Soil/Sediment Samples, Low Level – Low level soils are analyzed using a 5-gram sample (or the contents of a core device). Using inert spatula, such as stainless steel, a 5-gram portion of sample is weighed into a tared VOA vial. Record weight to the nearest 0.01 gram using the weight module. The weight module will calculate the prep factor to calculate the final concentration. Using a 5-mL gas tight syringe, 5-mL of reagent water is added along with a stir bar. The vial is capped and placed on the autosampler. The samples are run using a heated-purge calibration (40 °C). If any target compound saturates the detector at the 5 gram level then the high level method (methanol extract) is used for analysis.

12.11 High Level soils – methanol extracts are analyzed at ambient temperature.

12.11.1 Weigh a 5-g sample into a tared VOC vial using an inert spatula, such as one made of stainless steel or like material. Record weight to the nearest 0.01 g in the weight module. The weight module will calculate the prep factor to calculate the final concentration. Add 5-mL of methanol using syringe. Seal the vial, mix sample on the vortex mixer for one to two minutes. Centrifuge sample up to 20 minutes to settle out fine particles in the samples. If a recorded weight exceeds 4 ± 0.04g, the actual weight must be used to calculate the dilution factor (DF), otherwise, the DF for this step is 1.0.

12.11.2 Add ~47 mL of DI water to a 50-mL volumetric flask vial, and then add 1000

µl (or less) of the sample methanol extract and dilute to final volume. Transfer to a new VOA vial and analyze with the water methanol curve. If any target compound is still above calibration range, then re-dilute an aliquot of the extract and analyze.

12.11.3 When high level soil extracts are analyzed as a matrix spike/matrix spike duplicate, then the spiked sample extract is analyzed in a similar fashion except that the spiking solution is added after the dilution is prepared.

12.11.4 LCS must be prepared using 1 mL of methanol in a 50 mL flask followed by spiking with spiking solution is added after the dilution is prepared. Invert flask three times and transfer sample to new 40 mL VOA vial.

12.11.5 Method blank is prepared by adding the spiking solution to DI water in a 50 mL Class A volumetric flask. Invert flask three times and transfer sample to new 40 mL VOA vial.

12.11.6 The volume of methanol in 5 mL of water being purge must be kept constant. Therefore, 5 mL purge water is equivalent to 100 uL or 1000 uL in 100 mL prep. If greater dilution is needed, dilute aliquot of methanol extract and then take 100 uL for analysis.

12.12 Qualitative Requirements: Analyte identification is performed by comparing the spectrum of the detected compound with that of a standard reference spectrum. The reference spectra are generated from the daily calibration check performed with the sample batch. The standard spectra are saved each time that the system is calibrated.

12.12.1 Note: Quantitation using secondary ions is not permitted.

12.12.2 Note: Isomers should be considered separately. A dilution is made when the concentration of either peak separately exceeds the initial calibration range. Examples of are total Xylenes and 1,2-dichloroethene (cis and trans).

12.13 The sample component RRT must be within ±0.06 RRT units of the RRT of the daily CCV. If there are interferences in the primary ion profile that makes the RRT determination difficult, the secondary ion must be used. For mass spectra comparisons, all ions in the standard spectrum at an intensity of >10% relative to the most abundant ion must be present in the sample spectrum. In addition, the above qualifying ions must agree within ±20%, unless in the judgment of the mass spectral interpreter, an identification is possible.

12.14 Upon request of the client, a library search will be performed on each sample to identify any components not matched to calibration standard spectra when requested. This search is performed using the data system in conjunction with the NBS/NIST Mass Spectral Library. Perform a search peaks whose total ion response is greater than 10% of the nearest internal standard. The interpretation specialist determines tentative identification of the results. Ions with relative intensities of >10% in the reference spectrum must be in the sample spectrum and agree within ±20%. The molecular ions present in the reference spectrum should be in the sample spectrum. Check for background contamination when ions that are not in the reference spectrum are in the sample spectrum. Final identification is made by the analyst reviewing the library search results and if no adequate match can be determined, the compound is reported as an UNKNOWN.

12.15 Sample Screening: Samples may be screened at dilution, either “off clock” using a GC/MS, or using another detector, such as a GC-FID, GC-PID or GC-FID/PID. If the latter option is employed, the analyst should start with an analysis of a standard at the CCV level.

13) Troubleshooting

13.1 Prepare new standards, check instrument maintenance, prepare a new curve as needed, etc.

13.2 Chloromethane may be lost if the purge flow is too fast. Bromoform may be lost if the purge flow is too slow, or if the transfer line has cold spots or active sites, or the ratio of m/z 174/95 is too low. Tetrachloroethane and 1,1-dichloroethane may deteriorate due to contamination and/or active sites in the purge and trap system.

13.3 Possible problems could be standard mixture degradation, column contamination, or active sites in the column or chromatography system.

14) Data Acquisition

14.1 Data Acquisition:
- 14.1.1 A sequence is run using Chemstation and automatically processed by Target.
- 14.1.2 The processed data are reviewed by the analyst using Target.
- 14.1.3 Finally, the final results are manually imported to LIMS for reporting.

14.2 Data Processing using Target
- 14.2.1 Typical Sample Labeling in Chemstation/Target DB:
  - 14.2.1.1 CCV
  - 14.2.1.2 VLCSW1-092807 (LCSW= water LCS; LCSS= soil LCS)
  - 14.2.1.3 VBLKW1-092807 (092807 = month, day, year)
  - 14.2.1.4 0106040-01A (Sample ID)
  - 14.2.1.5 0106040-01A MS (Matrix Spike)
  - 14.2.1.6 0106040-01A MSD (Matrix Spike Duplicate)

14.3 Importing Data from Target DB into the LIMS system for reporting.
- 14.3.1 Files to be transferred to LIMS are converted to CSV files using Target.
- 14.3.2 Data is imported into LIMS using the appropriate test code (8260_W / LCS or 8260_S / Samp, etc).

15) Calculation, and Data Reduction Requirements

15.1 Initial Calibration (ICAL) Calculation of Ave RRF: Calculate the average Relative Response Factor (Ave.RRF) for each compound across the five or more calibration concentrations using the below equations (The Target Software will perform this calculation):

$$\text{Ave. RRF} = \frac{A_x \times C_{is}}{A_{is} \times C_x}$$

where:

A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard.
C_x = Concentration of the compound being measured.

15.2 ICAL Percent Relative Standard Deviation (% RSD): Calculate the %RSD(s) for each compound as follows:

$$\%RSD = \frac{SD}{avgX} x\,100$$

where:
RSD = relative standard deviation.
avgX = mean of initial Response Factors (RFs) for a compound.
SD = standard deviation of average RFs for a compound.

15.3 Continuing Calibration Calculations:

15.3.1 Calculation of % drift (regression model curve fits) by using the following formula:

15.3.2 % Drift= [(Calculated conc – Theoretical conc) x 100] / Theoretical conc

15.3.3 Percent difference (response factor calibration fit) is calculated as follows:

$$Percent\ Difference = \frac{\overline{RRf}_I - RRf_C}{\overline{RRf}_I} x\,100$$

RRFi = average relative response factor from the initial calibration
RRF_C = relative response factor from current verification check standard

15.4 Analyte Calculations, Water and Water-Miscible Waste Samples

$$concentration\,(ug/l) = \frac{(A_x)(I_s)}{(A_{is})(RF)(V_o)}$$

where:

A_x =Area of the characteristic ion for the compound being measured.

I_s=Amount of internal standard injected (ng).

A_{is}=Area of the characteristic ion for the specific internal standard.

RRFi = Average Relative Response factor for the compound from ICAL.

V_o = Volume of water purged (mL)

15.5 High-level Soils (wet weight)

$$concentration\,(ug/kg) = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RRFi)(V_i)(W_s)}$$

15.6 Low-level Soils (wet weight)

$$concentration\,(ug/kg) = \frac{(A_x)(I_s)}{(A_{is})(RRFi)(W_s)}$$

where:
A_x, I_s, A_{is}, RRFi = same as for water.

V_t =volume of total extract (µl) (use 10,000 µl or a factor of this when dilutions are made).

V_i = volume of extract added (µl) for purging.

W_s = wet weight of sample purged (g).

15.7 Dry Weight, µg/Kg = wet weight, µg/Kg * 100 / (100 - % Moisture)

15.8 The internal standard method is used to calculate the estimated concentration of the Tentatively Identified Compounds (TICs). These equations are utilized in the vendor supplied library search program.

15.8.1 The analyst must know how to use the above equations. The equations are necessary tools for troubleshooting calibration files, ID files, and acquired data files. The sample concentration is quantified and a report generated utilizing computer software. The equations used for calculating concentrations of TICs are the same as those used for target compounds with the following modifications: peak areas are derived from the total ion instead of the extracted ion, and a RRF of 1 is assumed. TIC concentrations are always reported as estimated values and have an associated data qualifier reported.

15.9 Quantification Calculations

15.10 QC Calculations: LIMS calculates the percent recovery for various QC samples (LCS) according to the following equations:

15.10.1 % Recovery, %R (for MS and MSD Samples)

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SR = Sample Result (unspiked).
SA = Spike Amount Added (mg/L or mg/kg).

15.10.2 % Recovery, %R (for standards and LCS)

$$\%R = \frac{(SSR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SA = Spike Amount Added (mg/L or mg/kg).

15.10.3 RPD (for precision or duplicate evaluation)

$$RPD = \frac{|SR_1 - SR_2|}{½(SR_1 + SR_2)} \times 100$$

Where:

SR_1 = Sample result for duplicate 1.

SR_2 = Sample result for duplicate 2.

16) Quality Control, Acceptance Criteria and Corrective Action

16.1 Instrument Tuning:

16.1.1 Frequency: perform at start of each 12 hour shift (8260C/624.1) or each 24 hr shift (624).

16.1.2 Acceptance Criteria: refer to section 11.2 (Table 11.3); all criteria must be met

16.1.3 Tuning Criteria Failure Corrective action: discontinue operation, perform instrument maintenance. A passing tune must be achieved prior to resumption of operation/sample analysis; any samples run after a failing tune must be reanalyzed after corrective action has been performed.

16.2 Initial Calibration:

16.2.1 Frequency: A new curve must be generated when CCV criteria are not met, or after major instrument maintenance such as column replacement or changes in operating conditions

16.2.2 Acceptance Criteria:

16.2.2.1 Initial calibration curve must have 5-points minimally for all analytes; six points are required for second order curve fits.

16.2.2.2 Minimum RRF criteria, see section / table 11.4 for minimum RFs

16.2.2.3 The RSDs must be ≤ 20% (≤ 15% for DOD projects); and one of the following options (evaluate and choose best curve fit model):

16.2.2.4 Option 1 linear– RSD for all analytes greater than 20% (greater than 15% for DOD projects) squares regression r > 0.995 or

16.2.2.5 Option 2 non-linear – COD > 0.990 (6 points shall be used for second order).

16.2.2.6 When calculating the calibration curves using the linear regression model or non-linear curves, a minimum quantitation check on the viability of all calibration points should be performed by re-fitting the response from the low concentration calibration standard back into the curve (See Method 8000D for additional details). This check is the refitting of the calibration data back to the model or the comparison of the calculated amount of each of the standards against the expected amount. If any analyte for any calibration standard has a percent error > ±30% as described in Section11.5.4.1 of Method 8000D, corrective action may be needed

16.2.3 Curve Failure Corrective Action:

16.2.3.1 Check standards and or perform maintenance as necessary to correct problem, then generate new curve

16.3 Initial Calibration Verification (ICV):

16.3.1 Frequency: Perform this evaluation each time a new curve is generated.

16.3.2 Acceptance criteria: agreement between the curve and ICV results must be between 80 – 120 % of the ICV true values.

16.3.3 ICV Failure Corrective action: evaluate condition and age of standards being used and/or perform any needed system maintenance. Do not analyze samples until the criteria can be met or prepare new standards and /or generate new curve if criteria cannot be met.

16.4 Continuing Calibration Verification (CCV) and Continuing Calibration Blank (CCB)

16.4.1 Frequency: The calibration standard must be run at the beginning of every 12 hour analytical sequence for 8260C/624.1 and 24 hours for EPA 624.

16.4.2 Acceptance Criteria: CCV acceptance criteria for each compound must be ≤ 20% of the true value. Blank must have not compounds greater than ½ LOS and surrogate within 20% of true value.

16.4.3 Corrective Action: If the CCV does not meet the criteria, correct the problem and re-analyze the CCV. If the CCV is still out, prepare a new calibration curve. Samples associated with marginal exceedance target analyte can be reported when the result is "not detected". Corrective action must still be carried out to address the exceedance.

16.4.4 DOD samples require closing CCV with each compound within 50% of the true value. This CCV must be analyzed within the 12 or 24 hour tune period. DOD samples must be bracketed by successful CCV or samples re-analzyed.

16.5 CCV/CCB Internal Standard Area Requirements:

16.5.1 Frequency: every CCV/CCB is spiked with internal standards.

16.5.2 CCV IS Acceptance Criteria: Review the quantitation report for each sample and check the CCV IS retention time windows and the CCV IS areas.

16.5.2.1 The CCV IS retention time widow must be ± 30 seconds from the RT established in the ICAL.

16.5.2.2 The CCV IS areas must not differ from the areas established in the ICAL by more than a factor of two (-50 % to +100 %)

16.5.3 CCV Internal Standard RT window or Area Failure Corrective Action**:** If the CCV internal standard areas do not fall within CCV IS criteria for RT or areas, the system problem must be corrected prior to running any samples. If any samples were run after failing IS in a CCV, all those samples must be reanalyzed.

16.6 Method blank:

16.6.1 Frequency: Analyze the method blank at a frequency of one per analytical batch of 20 or less samples (it is prepared in that frequency). The method blank must be analyzed after the calibration standard, or at any other time during the analytical shift, to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples.

16.6.2 Acceptance Criteria: All analytes of interest must be less than the < ½ LOQ, except for certain common lab contaminants such as methylene chloride or acetone. The common lab contaminants must be less than the LOQ.

16.6.2.1 Other approved QA program requirements must be followed when the acceptable blank contamination specified in the approved quality assurance project plan differs from the above.

16.6.2.2 Analytes of interest must be less than 5% of the regulatory limit associated with an analyte or analytes of interest must be less than 5% of the sample result for the same analyte, whichever is greater.

16.6.3 Method Blank Contamination Corrective Action: If the method blank results do not meet the acceptance criteria above, then the laboratory must take corrective action to locate and reduce the source of the contamination and reanalyze any samples associated with the contaminated method blank. If samples cannot be re-run because of insufficient sample or other similar circumstances, a corrective action report must be initiated and issued to

project management and to the QA Manager. The NCAR must be detailed enough for preparation of the project narrative and all appropriate data flags are entered into LIMS for the final report preparation. Data reported with an associated contaminated method blank must be flagged with a "B", indicating the occurrence.

16.7 Laboratory Control Standard (LCS)

16.7.1 The LCS must be prepared using a second source standard.

16.7.2 LCS Frequency: The laboratory control sample is processed with each batch of 20 or less samples. All samples in the batch must be processed on the same 24 hour period.

16.7.3 Acceptance Criteria: refer to Tables 22.3 and 22.4 for criteria. Acceptance allowances provided for sporadic marginal exceedances according to Table 24.5, where water and soil matrix allowances are expanded to be between the control limit (three standard deviation) and four standard deviations from the statistical mean. See SOP QAQC-018, Sporadic Marginal Exceedance. For DOD samples, Current DOD QSM control limits must be used. To ensure application of Current DOD QSM control limits DOD LIMS codes and spec must be used. DOD control limits can be found LIMS or Current DOD QSM. For latest control limits see Testcode Specs in LIMS.

16.7.4 LCS failure Corrective Action: If the LCS recovery for the compounds of interest does not meet with the criteria, the sample batch must be re-analyzed. If reprocessing it is not possible due to lack of sample or expired hold time, report (narrate) the variance to the client and flag the associated data as estimated.

16.8 Matrix Spike and Matrix Spike Duplicate

16.8.1 Frequency: Perform MS and MSD at a frequency of at least one MS and MSD per 20 samples. If an MSD cannot be processed due to insufficient sample, a duplicate LCS shall be processed for the purpose of assessing duplicate RPD criteria.

16.8.2 Acceptance Criteria: Spike recovery criteria are specified in the tables 22.3 and 22.4 for criteria. If the MS/MSD native concentration is four times or more the spiking level, the recovery criteria do not apply. An RPD limit for waters is 20% and 30 % for soils. For DOD samples, Current DOD QSM control limits must be used. To ensure application of DOD QSM control limits DOD LIMS codes and spec must be used. DOD control limits can be found LIMS or DOD QSM For latest control limits see Testcode Specs in LIMS.

16.8.3 MS/MSD % Recovery Criteria Failure Corrective Action: If the MS and MSD have recoveries which are outside the target range, the poor recoveries in the MS and MSD may be due to matrix effects. The LCS, surrogate recoveries and calibration results must all be evaluated in order to determine if a matrix interference is present or if method performance is poor. Note that the MS and MSD are used to evaluate the matrix effect, not to control the analytical process. If both the Matrix Spike and Matrix Spike Duplicate are found to be out of control for the same analyte, a matrix effect is likely confirmed (assuming the LCS passes). For instance, if both matrix spikes exhibit low recovery but good precision then it can be assumed that matrix interference is present. However, if precision between the MS and the MSD is poor, technique error must be eliminated as a possible source of error before the data can be accepted. If recoveries of the MS/MSD pair are suspicious (laboratory error, etc), a corrective action must be performed or the situation must be described in a laboratory narrative. If matrix interference is highly

suspected, corrective action is not necessary unless a Quality Assurance Project Plan stipulates controlling based on MS/MSD recoveries (CLP, etc.). Exceedances due to confirmed matrix effects are reported as comments in LIMS for use in batch QC exception reporting as described in the VOC data review checklist.

16.8.4 MS/MSD RPD Criteria Failure Corrective Action: If the RPD fails, the data must be evaluated for error and perform sample/batch QC reprocessing is necessary.

16.9 Surrogates Recoveries

16.9.1 Frequency: Surrogates are spiked into each sample and QC sample. The recoveries must be evaluated for all samples and QC samples.

16.9.2 Criteria: Acceptance limits for are specified in the Tables 22.3 and 22.4. For DOD samples, DOD QSM control limits must be used. To ensure application of DOD QSM control limits DOD LIMS codes and spec must be used. DOD control limits can be found LIMS or DOD QSM For latest control limits see Testcode Specs in LIMS.

16.9.3 Surrogate Failure Corrective Action: If the surrogate recoveries do not meet the criteria above

16.9.3.1 Check for errors in calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly.

16.9.3.2 Examine chromatograms for interfering peaks and integrated peak areas.

16.9.3.3 If no calculation or integration errors are found, and the surrogate recovery remains outside the limit and the method blank and LCS is acceptable, re-analyze the sample to confirm analysis.

16.9.3.4 If the exceedances repeat and the recovery are outside limits, describe the exceedance in the data review checklist exception report.

16.9.3.5 Additionally, check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze. If the surrogate recoveries are available from a diluted sample, those recoveries may be used to evaluate potential matrix interference. However, the results of both the diluted and undiluted (or less-diluted) analyses should be provided to the data user.

16.9.3.6 If no instrument problem is found, the sample must be re-analyzed. If, upon re-analysis, the recovery is again not within limits, report the data as an "estimated concentration." If the recovery is within the limits in the re-analysis, provide the re-analysis data to the data user.

16.9.3.7 If the holding time has expired prior to the re-analysis, provide both the original and re-analysis results to the data user, and note the holding time problem in the data review checklist.

16.10 Internal Standard Area Requirements for samples (and QC samples except the CCV):

16.10.1 Frequency: All samples and QC samples are spiked with internal standards.

16.10.2 IS Acceptance Criteria: Review the quantitation report for each sample and check the IS retention time windows and the IS areas.

16.10.2.1 The IS retention time widow must be ± 30 seconds from the RT established in the CCV.

16.10.2.2 The IS areas must not differ from areas established in the ICAL midpoint by more than a factor of two (-50 % to +100 %)

16.10.3 Internal Standard RT window or Area Failure Corrective Action: If the internal standard areas do not fall within IS criteria for RT or areas, the sample(s) must be rerun as confirmation of matrix effect. Confirmed matrix effects will be

reported to project management for sample narrative comments. If the rerun internal standards do not confirm a matrix effect, review the calculations and check for error. If no errors are found, or if a sample cannot be re-run because of insufficient sample or other similar circumstances, a NCAR must be issued to project management and to the QAD. The NCAR detailed enough for preparation of the project narrative and all appropriate data flags must be entered into the LIMS for the final reporting.

16.10.4 NOTE: Several sample types exhibit matrix effects that make recovery of the internal standards and surrogates very difficult. These samples must be run at a dilution to achieve acceptable criteria. However, if target compounds are present in undiluted runs with failing QC (surrogates or internal standards) and are diluted out to achieve passing QC, it may be necessary to report the undiluted analyses with data qualifier flags and an appropriate discussion within the case narrative by project management.

16.11 The Data Assessment Checklist (Section 21) must be used for data review documentation (SOP HS-QS – 009) unless an alternative approved QA program document is required. The completed checklist is filed with the associated batch data.

16.12 Manual Integration: ALS procedures for Manual Integration, HS-QS016, must be followed.

16.13 Initial Demonstration of Capability (IDOC)

16.13.1 Purpose: Verify the ability to produce data of acceptable precision and bias for a specific instrument type, matrix, method, and analyst.

16.13.2 Frequency: Initially during method development, and any time there is a significant change in instrument type, personnel, methodology, or matrix

16.13.3 Acceptance Criteria: Four aliquots at one (1) to four (4) time the limit of quantitation and analyzed according to the method either concurrently or over a period of day. Calculate mean recovery and standard deviation for each analyte of interest. Compare recovery and standard deviation to the corresponding acceptance criteria for precision and accuracy in the method (if applicable) or to lab-generated acceptance limits. If any one compound does not achieve acceptance criteria, the performance is unacceptable for

16.13.4 Corrective Action: Identify and correct the source of error. Reanalyze the demonstration.

16.14 Continuing Demonstration of Capability (DOC)

16.14.1 Purpose: Verify the ability to produce data of acceptable precision and bias for a specific instrument type, matrix, method, and analyst.

16.14.2 Frequency: Annual to re-qualify analyst for analysts. If period of greater than one year lapse between DOCs, then analyst must repeat IDOC.

16.14.3 Acceptance Criteria: Four consecutive LCS analysis meeting stated LCS criteria or successful PT study. In the event that analyses fail on the PT being used, then four consecutive LCS analysis meeting stated LCS criteria will have to be provided for those analytes that failed.

16.15 Method Detection Level (MDL) or Detection Limit Procedure

16.15.1 Purpose: To establish the method detection limit, see SOP HS-QS006 for detail on MDL, LOD and LOQ procedures.

16.15.2 Frequency: Establish the initial MDL of an instrument by process a minimum of 7 spiked aliquots at the appropriate matrix spike level and 7 method blank samples through all steps of the method. The samples used for the MDL must

be prepared in at least three batches on three separate calendar dates and analyzed on three separate calendar dates. After analysis determine the MDLs (spiked MDL) and MDLb (blank MDL). Select the highest MDL as the initial MDL. MDL must be determined for each analyte per matrix per method.

16.15.3 Ongoing Data Collection: On a quarterly basis, two MDL spikes must be prepared at the MDL spiking level and analyzed. Ensure minimum of seven spiked samples and seven method blanks are completed for the annual verification. If only one instrument is in use, a minimum of seven spikes are still required.

16.15.3.1 If new instrument is added to group of instruments, analyze a minimum of two spike replicates and two method blanks. If both blank MDL and are below the MDL then instrument is considered valid. Combine new spied samples with existing MDL and recalculate the MDL. If the recalculated MDL does not vary by the specified factor then existing MDL is validated. If either one of these conditions are not met, then than the MDL must be regenerated.

16.15.4 Annual Verification

16.15.4.1 Recalculate the MDLs and MDLb from the spike samples and method blank from the last twenty four months, but only data with the same spiking level. Include initial MDL if data was within 24 months.

16.15.4.2 If the verified MDL is the greater of MDLs or MDLb. If the verified MDL is within 0.5 to 2.0 times the existing MDL and fewer than 3% of the method blank have numerical results above the existing MDL, then the existing MDL may be left unchanged. Otherwise adjust the MDL to the new verified MDL.

16.10.5 Current MDLs may be found in the Limits tab of each testcode in LIMS.

16.16 Limit of Detection (LOD) Verification

16.16.1 Purpose: Validates the established Detection Limit.

16.16.2 Frequency: Prior to sample analysis and verified quarterly Verification must is performed on each instrument. The LOD is spiked at 2-3 times the detection limit for single compound analyses and 1-4 times the detection limit for multi-analyte standards. Sample must be taken through all preparatory steps such as digestion, extraction clean-up, etc.

16.16.2.1 With each MDL study, all compound must be confirmed at a concentration equal to 1-2 time the calculated MDL. To achieve this confirmation multiple concentration may need to be analyzed. Remaining quarterly checks may be performed at 2-3 times the MDL until the next MDL study.

16.16.3 Acceptance Criteria: The apparent signal to noise ratio at the LOD must be at least three and the results must meet all method requirements for analyte identification (e.g., ion abundance, second-column confirmation, or pattern recognition.) For data systems that do not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least three standard deviations greater than the mean method blank concentrations.

16.16.4 Corrective Action: Repeat the Detection Limit Determination and LOD Verification at a higher concentration or perform and pass two consecutive LOD verifications at a higher concentration and set the LOD at the higher concentration.

16.16.5 Current LOD values may be found in LIMS under the QA Section in the Limit Manager feature.
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16.17 Limit of Quantitation (LOQ) Establishment and Verification:

16.17.1 Purpose: Validates the lower quantitation limit of the analysis. Can be performed at 1-2 X the LOQ. Sample must be taken through all preparatory steps such as digestion, extraction clean-up, etc.

16.17.2 Frequency: Prior to sample analysis and verified quarterly.

16.17.3 Acceptance Criteria: Data must empirically demonstrate precision and bias at the LOQ using LCS control limits.

16.17.4 Corrective Action: Identify and correct the source of error, reanalyze the LOQ. If failure persists re-evaluate the appropriateness of the LOQ.
Initial Demonstration of Proficiency – The laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operation annually and whenever new staff members are trained or significant changes in instrumentation are made.

16.17.5 LOQ at time of SOP creation is found in Table 24.1 of this SOP. For latest LOQ confirmation values, see Limit Manager feature in LIMS under the QA Section.

17) Data Records Management

17.1 All data is stored electronically and/or hard copy for a minimum of 5 years or greater as stipulated by regulations.

17.2 All analytical sequence IDs and standard preparation information must be recorded in the Run logbook. Hardcopy computer printouts of analytical sequences and raw data must be retained and initialed by the analyst (electronic initials are acceptable). To simplify standard and reagent tracking, analyst must attempt to use single lot of standards and reagent per batch or sequence.

17.3 Complete all pertinent sections in the respective logbooks. If not-applicable then line out the section. "Z" out or "X" out all large sections of the worksheet that are not used. Make all corrections with single line through, date and initial. Make NO obliterations when manually recording data.

17.4 Logbooks are controlled. Never remove a page from a logbook. Completed logbooks are returned to the QA department when filled and no longer needed in the work area.

17.5 Effect date of this SOP is the date noted in the header or last signature date, whichever is most recent.

17.6 As data is collected, the electronic files are stored on the network server. All electronic data which has been stored on the designated drive of the network server is backed up daily by the IT Manager on a tape drive.

18) Contingencies for Handling Out of Control or Unacceptable Data

18.1 When method required QC exceedances occur, in every case where sample data quality are affected, the source of the QC exceedance must be determined, corrected and sample reanalysis carried out when possible.

18.2 When affected sample analysis cannot be repeated due to limitations (i.e. sample

availability, or if reanalysis can only be performed after expiration of a sample hold time), the reporting of data associated with exceeded QC data must be appropriately flagged and narrated. This documentation is necessary to define for the data user the effect of the error has upon the data quality of the results reported (e.g. E flag data indicate the result to be only an estimate).

18.3 All analysts must report sufficient comments in laboratory data review checklist for exceeded QC associated with sample results so that project management can further narrate and ensure data qualifiers (flags) are properly assigned to the reported data.

18.4 NCARs must be issued for QC system exceedances. Matrix interferences are reported using the analyte reporting comment section in LIMS or using the Laboratory Data review checklist.

19) Method Performance

19.1 This method was validated through single laboratory studies of accuracy and precision. Refer to the reference method for additional method performance data available.

19.2 The method detection limit (MDL) is established using the procedure described in SOP *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (HS-QS006). Method Reporting Limits are established for this method based on the low calibration point and the MDL study results

19.3 Method performance is also determined and confirmed by:

19.3.1 The performance of LOD, and LOQ studies.

19.3.2 Quality control standards in each batch of data.

19.3.3 Performance Evaluation Samples.

20) Pollution Prevention and Waste Management

20.1 It is the laboratory's practice to minimize the amount of solvents, acids, and reagents used to perform this method wherever feasibly possible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvents and/or reagents used in this method can be minimized when recycled or disposed of properly.

20.2 The laboratory will comply with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Chemical Hygiene Plan and Lab Waste Management Plan.

20.3 Laboratory procedures in SOP SHWD-001, Waste Disposal Procedures, must be followed.

21) Training

21.1 Training outline

21.1.1 Review literature (see references section). Read and understand this SOP. Also review the applicable SDS for all reagents and standards used. Following the reviews, observe the procedure as performed by an experienced analyst at least three times.

21.1.2 The next training step is to assist in the procedure under the guidance of an

experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

21.1.3 Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

21.2 Training is documented following *SOP CE-QA003*).

21.3 When the analyst training is documented by the supervisor on the internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

22) Summary of Changes

Table 20.1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
11.7	9/01/2020	G. Moulton	Sec 19.15.3.3 – Added software
11.7	9/01/2020	G. Moulton	Sec 1: added scope and applicability, and Identification of the method.
11.7	9/01/2020	G. Moulton	Sec 9.15.1 and 9.15.3.3: Added computer hardware and software.
11.7	9/01/2020	G. Moulton	Changed sec 5 to maintenance.
11.7	9/01/2020	G. Moulton	Sec 19: Added method performance
11.7	9/01/2020	G. Moulton	Sec 20: Added Pollution prevention and waste management.
11.7	9/01/2020	G. Moulton	Sec 21: Added a training section.
11.7	9/01/2020	G. Moulton	Updated table numbers due to new sections that were added.
11.6	08/21/2019	G. Moulton	Included EPA 624 modification: desorb time of 1-2 minutes instead of 4 minutes.
11.6	08/21/2019	G. Moulton	Sec 8.3: Modified statement.
11.6	08/21/2019	G. Moulton	Modified table 8.3, 10.7, 11.7.2.1, 12.2
11.6	08/21/2019	G. Moulton	Modified sec 9.15.1.1/9.15.2.1 to remove old instrument models.

Revision Number	Effective Date	Document Editor	Description of Changes
11.6	08/21/2019	G. Moulton	Sec. 9.15.3.2 added correct instrument
11.6	08/21/2019	G. Moulton	Sec table 10. Changed some calibration volumes for the ICAL.
11.6	08/21/2019	G. Moulton	12.11.1: Corrected LCS preparation.
11.5 Sec page 1	10/15/2018	G. Moulton	Updated to new cover page, updated to include current QA Manager.
11.5 Sec 3.13	10/15/2018	G. Moulton	Included frequency of LOQ.
11.5 Sec 8.2	10/15/2018	G. Moulton	Included holding time of acrolein and acrylonitrile.
11.5 Sec 16.7.1	10/15/2018	G. Moulton	Second source needed for LCS.
11.5 Sec 17.1	10/15/2018	G. Moulton	Updated data storage time.
11.5 Sec 11.14.3	10/15/2018	G. Moulton	Criteria for using PT as CDOC if analytes fail for PT.
11.4	04/30/2018	T. Yen	New Organic Manager
11.4 – Section 4.6	04/30/2018	T. Yen	Job Safety Assessment
11.4 – Section 9.6 & 12.10	04/30/2018	T. Yen	Stainless steel spatula usage
11.4 – Section 10.1	04/30/2018	T. Yen	Standard minimum purity without needing correction for purity.
11.4 – Sections 10.6.1 & 10.7.1	04/30/2018	T. Yen	CCB prep – 10.6.1 aqueous and 10.7.1 solid.
11.4 – Section 10.8	04/30/2018	T. Yen	Medium methanol calibration level- constant methanol volume in calibration standard.
11.4 – Section 11.14.4	04/30/2018	T. Yen	CCB after CCV with no target analyte greater than ½ LOQ,
11.4 – Section 11.15	04/30/2018	T. Yen	CCB internal standard limits.
11.4 – Sections 11.7,2, 11.8, 16.2.2.3 & 16.2.2.4.	04/30/2018	T. Yen	DOD QSM 5.1.1- initial Calibration %RSD of ≤15%.
11.4 – Section 16.2.2.6	04/30/2018	T. Yen	Linear and none calibration refit of all levels on the calibration curve.
11.4 – Section 16.3	04/30/2018	T. Yen	ICV limits to 20% for all compounds
11.4 – Sections 11.14.3, 11.14.4 & 16.5.3.	04/30/2018	T. Yen	CCV Limits and DOD closing CCV limits.
11.4 – Section 16.	04/30/2018	T. Yen	CCB acceptance limits.

Revision Number	Effective Date	Document Editor	Description of Changes
11.4 – Section 12.1	04/30/2018	T. Yen	Tune period for Methods 82360C and 624.
11.4 – Sections 12.1, 12.2 & 14.4.3	04/30/2018	T. Yen	Use of DOD LIMS codes and specs to ensure DOD QSM control limits are applied to DOD samples.
11.4–Section 12.11	04/30/2018	T. Yen	Constant methanol volume in samples.
11.4–Section 12.11.1	04/30/2018	T. Yen	Vortex methanol sample to mix samples. Centrifuge samples up to 20 minutes to settle out fine particles.
11.4 – Section 12.8	04/30/2018	T. Yen	Aqueous Dilution usage of new VOC vials.
11.4 – Sections 16.7.2, 16.8.2 & 16.9.2.	04/30/2018	T. Yen	Use of DOD LIMS codes and specs to ensure DOD QSM 5.1.1 control limits are applied to DOD samples.
11.4 – Section 16.13	04/30/2018	T. Yen	IDOC updated
11.4 – Section 16.14	04/30/2018	T. Yen	DOC updated
11.4 – Section 16.15	04/30/2018	T. Yen	MDL Update
11.4 – Section 16.16	04/30/2018	T. Yen	LOD Update
11.4 – Section 16.17	04/30/2018	T. Yen	LOQ Update
11.4 – Sections 3.1, 16.7.2, 16.8.2, 16.9, 21 and Tables in 22	04/30/2018	T. Yen	References updated to DOD QSM 5.1.1
11.4 –Section 11.7.2 7 & Table 22.6	04/30/2018	T. Yen	Table 22.6 update for ICV and CCB criteria. DOD 15% RSD for initial calibration.
11.4 – Section 22	04/30/2018	T. Yen	Reference update
11.3 –Section 9.12	05/31/2014	T. Yen	Transfer line temp changed to 150 C.
11.3 – Table 21.1 & 21.2	05/31/2014	T. Yen	Reference to LIMS for current DL.
11.2	09/15/2013	T. Yen	New SOP Format, Signature Page – New Lab Director and QA Manager.
11.2 – Table 8.4 updated	09/15/2013	T. Yen	Data updated in table 8.4.
11.2 – Section 9	09/15/2013	T. Yen	Equipment List updated.
11.2 – Section 11.2	09/15/2013	T. Yen	Tune failures are symptom of

Revision Number	Effective Date	Document Editor	Description of Changes
			instrument in need of maintenance. Rather than used different allowed tuning procedures, analyst must perform instrument maintenance followed by recalibration after a successful tune is achieved.
11.2 – Section 11.3	09/15/2013	T. Yen	For DoD analysis, surrogates must be calibrated using a multipoint calibration.
11.2 – Section 17.2	09/15/2013	T. Yen	To simplify standard tracking, analyst must attempt to use single lots in sequence or batch.
11.2 – Section 17.5	09/15/2013	T. Yen	SOP effective date defined.
11.2 – Section 21.1.3	09/15/2013	T. Yen	Reference update - DoD QSM, Rev 5.0, July 2013.
11.2 - Table 0.6	09/15/2013	T. Yen	MDL must be performed annually for all analytes include surrogates and LOD Quarter for all analytes and surrogate compounds.
11.1	09/01/2012	J. Cady	Minor document revision. Format/font change. Clarification on procedure.
11.0	07/31/2011	J. Cady	Major document revision.

23) References and Related Documents

21.1 U.S. Environmental Protection Agency, "Method 8260C, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry", Test Methods for Evaluating Solid Waste Physical/Chemical Methods, Method Revision 3, August 2006.

21.2 U.S. Environmental Protection Agency, "Method 8000C (Revision 3, March 2003) Determinative Chromatographic Separations", Test Methods for Evaluating Solid Waste Physical/Chemical Methods, May 14, 2003.

21.3 Current Department of Defense/Department of Energy Quality Systems Manual for Environmental Laboratories.

21.4 U.S. Environmental Protection Agency, Method 624, Purgeables, Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, 40 CFR Part 136, Append A.

21.5 Current TNI Standards.

21.6 U.S. Environmental Protection Agency, Method 624.1, Purgeables by GCMS, EPA 821-R-16-008, December 2016.

24) Appendix

Table 24.1 SW8260C/EPA624.1 – Approximate LOQ values, 5 mL purge, at time of SOP revision. MDLs (DLs) are determined annually at a minimum, and are subject to change and latest values may be found in LIMS.

Analyte – water matrix 5 mL purge volume	LOQ µg/L	Analyte - solid/soil matrix based on 5 g dry weight sample	LOQ µg/Kg
1,1,1,2-Tetrachloroethane	1	1,1,1,2-Tetrachloroethane	5
1,1,1-Trichloroethane	1	1,1,1-Trichloroethane	5
1,1,2,2-Tetrachloroethane	1	1,1,2,2-Tetrachloroethane	5
1,1,2-Trichlor-1,2,2-trifluoroethane	1	1,1,2-Trichlor-1,2,2-trifluoroethane	5
1,1,2-Trichloroethane	1	1,1,2-Trichloroethane	5
1,1-Dichloroethane	1	1,1-Dichloroethane	5
1,1-Dichloroethene	1	1,1-Dichloroethene	5
1,1-Dichloropropene	1	1,1-Dichloropropene	5
1,2,3-Trichlorobenzene	1	1,2,3-Trichlorobenzene	5
1,2,3-Trichloropropane	1	1,2,3-Trichloropropane	5
1,2,3-Trimethylbenzene	1	1,2,3-Trimethylbenzene	5
1,2,4-Trichlorobenzene	1	1,2,4-Trichlorobenzene	5
1,2,4-Trimethylbenzene	1	1,2,4-Trimethylbenzene	5
1,2-Dibromo-3-chloropropane	1	1,2-Dibromo-3-chloropropane	5
1,2-Dibromoethane	1	1,2-Dibromoethane	5
1,2-Dichlorobenzene	1	1,2-Dichlorobenzene	5
1,2-Dichloroethane	1	1,2-Dichloroethane	5
1,2-Dichloropropane	1	1,2-Dichloropropane	5
1,3,5-Trimethylbenzene	1	1,3,5-Trimethylbenzene	5
1,3-Butadiene	1	1,3-Butadiene	5
1,3-Dichlorobenzene	1	1,3-Dichlorobenzene	5
1,3-Dichloropropane	1	1,3-Dichloropropane	5
1,4-Dichlorobenzene	1	1,4-Dichlorobenzene	5
1,4-Dioxane	20	1,4-Dioxane	100
1-Chlorohexane	1	1-Chlorohexane	5
2,2-Dichloropropane	1	2,2-Dichloropropane	5
2-Butanone	2	2-Butanone	10
2-Chloro-1,3-butadiene	2	2-Chloro-1,3-butadiene	5
2-Chloroethyl vinyl ether	2	2-Chloroethyl vinyl ether	5
2-Chlorotoluene	1	2-Chlorotoluene	5
2-Hexanone	2	2-Hexanone	10
2-Methylnaphthalene	1	2-Methylnaphthalene	5
2-Pentanone	2	2-Pentanone	10
4-Chlorotoluene	1	4-Chlorotoluene	5
4-Isopropyltoluene	1	4-Isopropyltoluene	5
4-Methyl-2-pentanone	20	4-Methyl-2-pentanone	10
Acetaldehyde	1	Acetaldehyde	10
Acetone	2	Acetone	20

Analyte – water matrix 5 mL purge volume	LOQ µg/L	Analyte - solid/soil matrix based on 5 g dry weight sample	LOQ µg/Kg
Acetonitrile	10	Acetonitrile	50
Acrolein	2	Acrolein	20
Acrylonitrile	2	Acrylonitrile	20
Allyl alcohol	20	Allyl alcohol	100
Allyl Chloride	1	Allyl Chloride	10
Amyl Alcohol	20	Amyl Alcohol	100
Benzene	1	Benzene	5
Benzyl Chloride	1	Benzyl Chloride	5
Bromobenzene	1	Bromobenzene	5
Bromochloromethane	1	Bromochloromethane	5
Bromodichloromethane	1	Bromodichloromethane	5
Bromoform	1	Bromoform	5
Bromomethane	1	Bromomethane	10
Butyl methacrylate	1	Butyl methacrylate	5
Carbon disulfide	2	Carbon disulfide	10
Carbon tetrachloride	1	Carbon tetrachloride	5
Chlorobenzene	1	Chlorobenzene	5
Chloroethane	1	Chloroethane	10
Chloroform	1	Chloroform	5
Chloromethane	1	Chloromethane	10
cis-1,2-Dichloroethene	1	cis-1,2-Dichloroethene	5
cis-1,3-Dichloropropene	1	cis-1,3-Dichloropropene	5
Cyclohexane	1	Cyclohexane	5
Dibromochloromethane	1	Dibromochloromethane	5
Dibromomethane	1	Dibromomethane	5
Dichlorodifluoromethane	1	Dichlorodifluoromethane	5
Diethyl Ether	1	Diethyl Ether	5
Diisopropyl ether	1	Diisopropyl ether	10
Epichlorohydrin	4	Epichlorohydrin	20
Ethanol	20	Ethanol	100
Ethyl acetate	1	Ethyl acetate	10
Ethyl acrylate	1	Ethyl acrylate	5
Ethyl Methacrylate	1	Ethyl Methacrylate	5
Ethyl tert-Butyl Ether (ETBE)	1	Ethyl tert-Butyl Ether (ETBE)	5
Ethylbenzene	1	Ethylbenzene	5
Ethylene oxide	2	Ethylene oxide	10
Hexachlorobutadiene	1	Hexachlorobutadiene	5
Iodomethane	2	Iodomethane	10
Isobutyl alcohol	20	Isobutyl alcohol	100
Isopropyl alcohol	20	Isopropyl alcohol	100
Isopropylbenzene	1	Isopropylbenzene	5
m,p-Xylene	2	m,p-Xylene	10
Methacrylonitrile	2	Methacrylonitrile	5
Methyl acetate	1	Methyl acetate	5
Methyl acrylate	2	Methyl acrylate	5
Methyl methacrylate	2	Methyl methacrylate	5
Methyl tert-butyl ether	1	Methyl tert-butyl ether	5
Methylcyclohexane	1	Methylcyclohexane	5

Analyte – water matrix 5 mL purge volume	LOQ µg/L	Analyte - solid/soil matrix based on 5 g dry weight sample	LOQ µg/Kg
Methylene chloride	2	Methylene chloride	10
Naphthalene	1	Naphthalene	5
n-Butyl acetate	5	n-Butyl acetate	5
n-Butyl acrylate	5	n-Butyl acrylate	5
n-Butyl alcohol	20	n-Butyl alcohol	100
n-Butylbenzene	1	n-Butylbenzene	5
n-Hexane	1	n-Hexane	5
n-Pentane	1	n-Pentane	5
n-Propanol	1	n-Propanol	5
n-Propylbenzene	1	n-Propylbenzene	5
o-Xylene	1	o-Xylene	5
Pentachloroethane	2	Pentachloroethane	5
Propionitrile	10	Propionitrile	50
Propylene oxide	2	Propylene oxide	10
sec-Butylbenzene	1	Sec-Butylbenzene	5
Styrene	1	Styrene	5
Tert-Amyl Methyl Ether	1	Tert-Amyl Methyl Ether	5
Tert-Butyl Alcohol	10	Tert-Butyl Alcohol	100
tert-Butylbenzene	1	Tert-Butylbenzene	5
Tetrachloroethene	1	Tetrachloroethene	5
Tetrahydrofuran	2	Tetrahydrofuran	5
Toluene	1	Toluene	5
trans-1,2-Dichloroethene	1	Trans-1,2-Dichloroethene	5
trans-1,3-Dichloropropene	1	Trans-1,3-Dichloropropene	5
trans-1,4-Dichloro-2-butene	1	Trans-1,4-Dichloro-2-butene	5
Trichloroethene	1	Trichloroethene	5
Trichlorofluoromethane	1	Trichlorofluoromethane	5
Vinyl acetate	1	Vinyl acetate	10
Vinyl chloride	1	Vinyl chloride	2
Xylenes, Total	3	Xylenes, Total	15

Table 24.2
EPA 624 - Approximate LOQs at time of SOP revision. MLDs (DLs) are determined annually at a minimum, and are subject to change and latest values may be found in LIMS.

Analyte - water matrix	LOQ µg/L	Analyte – water matrix	LOQ µg/L
1,1,1-Trichloroethane	5	Chlorobenzene	5
1,1,2,2-Tetrachloroethane	5	Chloroethane	5
1,1,2-Trichloroethane	5	Chloroform	5
1,1-Dichloroethane	5	Chloromethane	5
1,1-Dichloroethene	5	Cis-1,2-Dichloroethene	5
1,2-Dichlorobenzene	5	cis-1,3-Dichloropropene	5

Analyte - water matrix	LOQ µg/L	Analyte – water matrix	LOQ µg/L
1,2-Dichloroethane	5	Dibromochloromethane	5
1,2-Dichloropropane	5	Ethylbenzene	5
1,3-Dichlorobenzene	5	m,p-Xylene	5
1,4-Dichlorobenzene	5	Methylene chloride	5
2-Butanone	10	Naphthalene	5
2-Chloroethyl vinyl ether	10	o-Xylene	5
Acetone	10	Tetrachloroethene	5
Acrolein	20	Toluene	5
Acrylonitrile	20	trans-1,2-Dichloroethene	5
Benzene	5	trans-1,3-Dichloropropene	5
Bromodichloromethane	5	Trichloroethene	5
Bromoform	5	Trichlorofluoromethane	5
Bromomethane	5	Vinyl chloride	5
Carbon tetrachloride	5	Xylenes, Total	15

Table 24.3 SW8260C/EPA624.1 LCS Recovery Limits, at time of this SOP revision. LCS Recoveries are reviewed and/or updated annually and are subject to change, latest values may be found in LIMS. Note LIMS codes and specs must be used for DOD project/sample to ensure DOD QSM limits are used, for compounds not listed in DOD QSM internal lab limits will apply.

Aqueous Analytes (EPA 624.1/SW8260C)	SPK, ug/L	Low, %	High, %	RPD, %	Solid Analytes (SW8260C)	SPK, ug/kg	Low, %	High, %	RPD, %
1,1,1,2-Tetrachloroethane	50	80	120	20	1,1,1,2-Tetrachloroethane	50	79	121	30
1,1,1-Trichloroethane	50	80	120	20	1,1,1-Trichloroethane	50	79	124	30
1,1,2,2-Tetrachloroethane	50	72	120	20	1,1,2,2-Tetrachloroethane	50	75	123	30
1,1,2-Trichlor-1,2,2-trifluoroethane	50	73	123	20	1,1,2-Trichlor-1,2,2-trifluoroethane	50	79	125	30
1,1,2-Trichloroethane	50	80	120	20	1,1,2-Trichloroethane	50	79	120	30
1,1-Dichloroethane	50	76	120	20	1,1-Dichloroethane	50	75	124	30
1,1-Dichloroethene	50	73	124	20	1,1-Dichloroethene	50	80	122	30
1,1-Dichloropropene	50	74	123	20	1,1-Dichloropropene	50	80	122	30
1,2,3-Trichlorobenzene	50	70	123	20	1,2,3-Trichlorobenzene	50	74	126	30
1,2,3-Trichloropropane	50	74	121	20	1,2,3-Trichloropropane	50	71	125	30
1,2,3-Trimethylbenzene	50	80	120	20	1,2,3-Trimethylbenzene	50	78	126	30
1,2,4-Trichlorobenzene	50	75	130	20	1,2,4-Trichlorobenzene	50	74	128	30
1,2,4-Trimethylbenzene	50	68	123	20	1,2,4-Trimethylbenzene	50	79	123	30
1,2-Dibromo-3-chloropropane	50	65	125	20	1,2-Dibromo-3-chloropropane	50	66	129	30
1,2-Dibromoethane	50	80	120	20	1,2-Dibromoethane	50	79	120	30
1,2-Dichlorobenzene	50	80	120	20	1,2-Dichlorobenzene	50	79	120	30
1,2-Dichloroethane	50	78	120	20	1,2-Dichloroethane	50	73	121	30

Aqueous Analytes (EPA 624.1/SW8260C)	SPK, ug/L	Low, %	High, %	RPD, %	Solid Analytes (SW8260C)	SPK, ug/kg	Low, %	High, %	RPD, %
1,2-Dichloropropane	50	80	120	20	1,2-Dichloropropane	50	76	120	30
1,2-Dichlorotrifluoroethane	50	80	120	20	n/a				
1,3,5-Trichlorobenzene	50	70	130	20	1,3,5-Trichlorobenzene	50	70	130	30
1,3,5-Trimethylbenzene	50	80	120	20	1,3,5-Trimethylbenzene	50	80	123	30
1,3-Butadiene	50	69	126	20	1,3-Butadiene	50	80	120	30
1,3-Cyclopentadiene	50	80	120	20	1,3-Cyclopentadiene	50	70	130	30
1,3-Dichloro-2-propanol	2000	60	140	20	1,3-Dichloro-2-propanol	2000	60	140	30
1,3-Dichlorobenzene	50	80	120	20	1,3-Dichlorobenzene	50	79	120	30
1,3-Dichloropropane	50	80	120	20	1,3-Dichloropropane	50	79	120	30
1,4-Dichlorobenzene	50	80	120	20	1,4-Dichlorobenzene	50	77	120	30
1,4-Dichlorobutane	50	70	130	20	n/a				
1,4-Diisopropylbenzene	50	70	130	20	1,4-Diisopropylbenzene	50	70	130	30
1,4-Dioxane	1000	50	158	20	1,4-Dioxane	1000	65	132	30
1-Butene	50	61	128	20	1-Butene	50	70	130	30
1-Chlorobutane	50	60	140	20	n/a				
1-Chlorohexane	50	75	120	20	1-Chlorohexane	50	80	122	30
1-Hexene	50	70	130	20	1-Hexene	50	70	130	30
1-Methylnaphthalene	50	60	140	20	1-Methylnaphthalene	50	60	140	30
1-propanol	1000	54	151	20	1-propanol	1000	60	140	30
1-Propyl Acetate	50	70	130	20	n/a				
2,2-Dichloropropane	50	78	123	20	2,2-Dichloropropane	50	75	125	30
2,3-Dichlorobutane	50	80	120	20	2,3-Dichlorobutane	50	73	126	30
2,3-Dimethylbutane	50	62	131	20	2,3-Dimethylbutane	50	65	141	30
2-Butanol	1000	70	130	20	2-Butanol	50	70	130	30
2-Butanone	100	58	132	20	2-Butanone	100	65	130	30
2-Chloro-1,3-butadiene	50	73	121	20	2-Chloro-1,3-butadiene	50	72	125	30
2-Chloroethanol	4000	60	140	20	2-Chloroethanol	4000	60	140	30
2-Chloroethyl vinyl ether	100	74	120	20	2-Chloroethyl vinyl ether	100	63	128	30
2-Chlorotoluene	50	80	120	20	2-Chlorotoluene	50	79	120	30
2-Ethoxyethanol	1000	60	140	20	2-Ethoxyethanol	50	70	130	30
2-Ethyl-1-hexanol	1000	60	140	20	n/a				
2-Furfural	2000	60	140	20	2-Furfural	2000	60	140	30
2-Hexanone	100	61	130	20	2-Hexanone	100	65	133	30
2-Methoxyethanol	1000	60	140	20	2-Methoxyethanol	50	70	130	30
2-Methylnaphthalene	50	60	140	20	2-Methylnaphthalene	50	49	148	30
2-Methylpentane	50	67	129	20	2-Methylpentane	50	72	128	30
2-Methylpropane	50	57	132	20	2-Methylpropane	50	64	149	30

Aqueous Analytes (EPA 624.1/SW8260C)	SPK, ug/L	Low, %	High, %	RPD, %	Solid Analytes (SW8260C)	SPK, ug/kg	Low, %	High, %	RPD, %
2-Nitropropane	50	62	125	20	2-Nitropropane	50	70	130	30
2-Pentanone	100	58	125	20	2-Pentanone	100	67	131	30
3-Methyl-1-butanol	1000	60	140	20	3-Methyl-1-butanol	1000	70	130	30
3-Methylpentane	50	66	135	20	3-Methylpentane	50	70	130	30
4-Chlorotoluene	50	80	120	20	4-Chlorotoluene	50	80	120	30
4-Isopropyltoluene	50	79	120	20	4-Isopropyltoluene	50	80	125	30
4-Methyl-2-pentanol	1000	52	157	20	4-Methyl-2-pentanol	1000	70	130	30
4-Methyl-2-pentanone	100	65	127	20	4-Methyl-2-pentanone	100	69	130	30
4-Methylstyrene	50	60	140	20	n/a				
4-Vinyl-1-cyclohexene	50	80	120	20	4-Vinyl-1-cyclohexene	50	70	130	30
Acetaldehyde	200	58	133	20	Acetaldehyde	200	60	130	30
Acetone	100	59	137	20	Acetone	100	53	142	30
Acetonitrile	500	59	137	20	Acetonitrile	500	59	138	30
Acrolein	100	54	144	20	Acrolein	100	56	146	30
Acrylonitrile	100	61	130	20	Acrylonitrile	100	60	126	30
Allyl Alcohol	1000	50	150	20	Allyl Alcohol	1000	65	135	30
Allyl Chloride	50	60	137	20	Allyl Chloride	50	72	129	30
alpha-methylstyrene	50	70	130	20	alpha-methylstyrene	50	70	130	30
Amyl acetate	50	60	140	20	n/a				
Amyl Alcohol	1000	57	142	20	Amyl Alcohol	1000	60	140	30
Benzene	50	73	121	20	Benzene	50	79	120	30
Benzyl Chloride	50	69	120	20	Benzyl Chloride	50	68	129	30
Bromoacetone	100	60	140	20	Bromoacetone	100	60	140	30
Bromobenzene	50	80	120	20	Bromobenzene	50	80	120	30
Bromochloromethane	50	70	130	20	Bromochloromethane	50	78	121	30
Bromodichloromethane	50	75	125	20	Bromodichloromethane	50	79	121	30
Bromoform	50	70	130	20	Bromoform	50	74	122	30
Bromomethane	50	60	145	20	Bromomethane	50	68	131	30
Butyl acrylate	50	73	120	20	Butyl acrylate	50	74	125	30
Butyl methacrylate	50	70	130	20	Butyl methacrylate	50	70	130	30
Carbon disulfide	100	68	141	20	Carbon disulfide	100	80	124	30
Carbon tetrachloride	50	75	125	20	Carbon tetrachloride	50	74	126	30
Chlorobenzene	50	80	120	20	Chlorobenzene	50	79	120	30
Chloroethane	50	70	130	20	Chloroethane	50	76	126	30
Chloroform	50	70	130	20	Chloroform	50	78	120	30
Chloromethane	50	67	123	20	Chloromethane	50	69	129	30
Chloromethyl methyl ether	50	70	130	20	Chloromethyl methyl ether	50	70	130	30

Aqueous Analytes (EPA 624.1/SW8260C)	SPK, ug/L	Low, %	High, %	RPD, %	Solid Analytes (SW8260C)	SPK, ug/kg	Low, %	High, %	RPD, %
cis-1,2-Dichloroethene	50	78	120	20	cis-1,2-Dichloroethene	50	80	120	30
cis-1,3-Dichloropropene	50	80	120	20	cis-1,3-Dichloropropene	50	77	123	30
cis-2-Butene	50	50	144	20	cis-2-Butene	50	70	130	30
cis-2-Hexene	50	70	130	20	cis-2-Hexene	50	70	130	30
Crotonaldehyde	50	70	130	20	n/a				
Cyclohexane	50	66	125	20	Cyclohexane	50	74	126	30
n/a					Cyclohexanol	1000	60	140	30
Cyclohexanone	50	52	136	20	Cyclohexanone	50	70	130	30
Cyclohexene	50	70	130	20	n/a				
Cyclopentane	50	70	130	20	Cyclopentane	50	70	130	30
Dibromochloromethane	50	80	120	20	Dibromochloromethane	50	78	122	30
Dibromomethane	50	80	120	20	Dibromomethane	50	78	120	30
Dichlorodifluoromethane	50	63	125	20	Dichlorodifluoromethane	50	57	140	30
Diethyl benzene	50	60	140	20	n/a				
Diethyl Ether	50	78	125	20	Diethyl Ether	50	70	130	30
Diisopropyl ether	50	74	121	20	Diisopropyl ether	50	70	130	30
Dimethyl sulfoxide	50	60	141	20	n/a				
Divinyl benzene	50	60	140	20	n/a				
Epichlorohydrin	200	65	132	20	Epichlorohydrin	200	60	130	30
Ethanol	1000	60	140	20	Ethanol	1000	70	130	30
Ethyl acetate	50	64	128	20	Ethyl acetate	50	60	130	30
Ethyl acrylate	50	68	129	20	Ethyl acrylate	50	71	128	30
Ethyl methacrylate	50	70	130	20	Ethyl methacrylate	50	72	128	30
Ethylbenzene	50	80	120	20	Ethylbenzene	50	80	122	30
Ethylene oxide	100	53	137	20	Ethylene oxide	100	70	130	30
Hexachlorobutadiene	50	70	135	20	Hexachlorobutadiene	50	75	128	30
Hexachloroethane	50	60	140	20	n/a				
Iodomethane	100	57	150	20	Iodomethane	100	69	131	30
Isobutyl Acetate	50	70	130	20	n/a				
Isobutyl alcohol	1000	57	140	20	Isobutyl alcohol	1000	54	136	30
Isobutylene	50	60	140	20	Isobutylene	50	40	140	30
Isobutyraldehyde	50	71	126	20	Isobutyraldehyde	50	65	135	30
Isopentane	50	70	130	20	Isopentane	50	70	130	30
Isoprene	50	70	130	20	Isoprene	50	73	127	30
Isopropyl Acetate	50	70	130	20	n/a				
Isopropyl alcohol	1000	46	151	20	Isopropyl alcohol	1000	60	140	30
Isopropylbenzene	50	75	130	20	Isopropylbenzene	50	72	127	30
m,p-Xylene	100	78	121	20	m,p-Xylene	100	79	122	30

Aqueous Analytes (EPA 624.1/SW8260C)	SPK, ug/L	Low, %	High, %	RPD, %	Solid Analytes (SW8260C)	SPK, ug/kg	Low, %	High, %	RPD, %
Methacrylonitrile	50	71	126	20	Methacrylonitrile	50	69	131	30
Methyl acetate	50	60	130	20	Methyl acetate	50	69	123	30
Methyl acrylate	50	70	130	20	Methyl acrylate	50	70	130	30
Methyl Amyl Ketone	50	70	130	20	n/a				
Methyl formate	100	60	140	20	n/a				
Methyl methacrylate	50	74	120	20	Methyl methacrylate	50	73	122	30
Methyl tert-butyl ether	50	73	121	20	Methyl tert-butyl ether	50	76	121	30
Methylamine	50	60	140	20	n/a				
Methylcyclohexane	50	70	122	20	Methylcyclohexane	50	77	126	30
Methylcyclopentane	50	64	130	20	Methylcyclopentane	50	70	130	30
Methylene chloride	50	65	133	20	Methylene chloride	50	70	123	30
n-Amyl acetate	50	75	125	20	n/a				
n-Butyl acetate	50	60	140	20	n-Butyl acetate	50	70	130	30
n/a					n-Butyl acrylate	50	72	122	30
n-Butyl alcohol	1000	54	145	20	n-Butyl alcohol	1000	58	138	30
n-Butylbenzene	50	77	120	20	n-Butylbenzene	50	77	126	30
n-Butyraldehyde	50	60	140	20	n/a				
n-Heptane	50	68	126	20	n-Heptane	50	75	123	30
n-Hexane	50	61	136	20	n-Hexane	50	75	125	30
n-Pentane	50	79	120	20	n-Pentane	50	75	127	30
n-Propylbenzene	50	78	120	20	n-Propylbenzene	50	79	123	30
Naphthalene	50	65	135	20	Naphthalene	50	71	128	30
Nitrobenzene	50	70	130	20	Nitrobenzene	50	70	130	30
o-Xylene	50	80	120	20	o-Xylene	50	80	123	30
Pentachloroethane	50	60	140	20	Pentachloroethane	50	60	140	30
Propanal	1000	60	140	20	Propanal	1000	60	140	30
Propionitrile	500	60	140	20	Propionitrile	500	67	135	30
Propylene oxide	100	57	133	20	Propylene oxide	100	60	130	30
sec-Butylbenzene	50	78	120	20	sec-Butylbenzene	50	80	123	30
Styrene	50	80	120	20	Styrene	50	78	124	30
tert-Amyl Alcohol	1000	50	150	20	tert-Amyl Alcohol	50	80	120	30
tert-Amyl methyl ether	50	80	130	20	tert-Amyl methyl ether	50	70	130	30
Tert-butyl alcohol	1000	56	144	20	Tert-butyl alcohol	1000	59	141	30
tert-Butyl ethyl ether	50	60	140	20	tert-Butyl ethyl ether	50	70	130	30
tert-Butylbenzene	50	75	130	20	tert-Butylbenzene	50	79	124	30
Tetrachloroethene	50	79	120	20	Tetrachloroethene	50	73	129	30
Tetrahydrofuran	100	58	135	20	Tetrahydrofuran	50	70	130	30
Toluene	50	80	120	20	Toluene	50	79	120	30

Aqueous Analytes (EPA 624.1/SW8260C)	SPK, ug/L	Low, %	High, %	RPD, %	Solid Analytes (SW8260C)	SPK, ug/kg	Low, %	High, %	RPD, %
trans-1,2-Dichloroethene	50	78	120	20	trans-1,2-Dichloroethene	50	79	122	30
trans-1,3-Dichloropropene	50	80	120	20	trans-1,3-Dichloropropene	50	77	120	30
trans-1,4-Dichloro-2-butene	50	73	122	20	trans-1,4-Dichloro-2-butene	50	68	128	30
trans-2-Hexene	50	70	130	20	trans-2-Hexene	50	70	130	30
Trichloroethene	50	80	120	20	Trichloroethene	50	80	121	30
Trichlorofluoromethane	50	72	130	20	Trichlorofluoromethane	50	75	126	30
Vinyl acetate	100	67	139	20	Vinyl acetate	100	63	136	30
Vinyl chloride	50	70	127	20	Vinyl chloride	50	76	126	30
1,2-Dichloroethene, Total	100	78	125	20	1,2-Dichloroethene, Total	100	68	122	30
1,2-Dichloroethane-d4	50	70	125	20	1,2-Dichloroethane-d4	50	70	128	30
4-Bromofluorobenzene	50	72	125	20	4-Bromofluorobenzene	50	73	126	30
Dibromofluoromethane	50	71	125	20	Dibromofluoromethane	50	71	128	30
Toluene-d8	50	75	125	20	Toluene-d8	50	73	127	30

Table 24.4 EPA 624 LCS Recovery Limits, Approximate limits at time of SOP revision. LCS Recoveries are reviewed and/or updated annually and are subject to change, latest values may be found in LIMS. Note DOD LIMS codes and specs must be used for DOD project/sample to ensure DoD QSM limits are used, for compounds not listed in DOD QSM internal lab limits will apply.

Analyte - Water Matrix	SPK µg/L	Low	High	RPD	Analyte - Water Matrix	SPK µg/L	Low	High	RPD
1,1,1-Trichloroethane	20	80	133	20	Chloroform	20	79	127	20
1,1,2,2-Tetrachloroethane	20	73	133	20	Chloromethane	20	70	133	20
1,1,2-Trichloroethane	20	80	132	20	Cis-1,2-Dichloroethene	20	74	129	20
1,1-Dichloroethane	20	76	131	20	Cis-1,3-Dichloropropene	20	74	129	20
1,1-Dichloroethene	20	77	124	20	Dibromochloromethane	20	75	133	20
1,2-Dichlorobenzene	20	79	131	20	Ethylbenzene	20	75	137	20
1,2-Dichloroethane	20	79	126	20	m,p-Xylene	20	70	130	20
1,2-Dichloropropane	20	77	132	20	Methyl tert-butyl ether	20	70	130	20
1,3-Dichlorobenzene	20	77	130	20	Methylene chloride	20	80	126	20
1,4-Dichlorobenzene	20	74	125	20	Naphthalene	20	70	130	20
2-Butanone	40	70	130	20	o-Xylene	20	70	130	20

Analyte - Water Matrix	SPK µg/L	Low	High	RPD	Analyte - Water Matrix	SPK µg/L	Low	High	RPD
2-Chloroethyl vinyl ether	40	57	120	20	Tetrachloroethene	20	80	132	20
Acetone	40	65	140	20	Toluene	20	77	134	20
Acrolein	40	60	120	20	Trans-1,2-Dichloroethene	20	80	130	20
Acrylonitrile	100	60	120	20	Trans-1,3-Dichloropropene	20	76	128	20
Benzene	20	75	134	20	Trichloroethene	20	80	132	20
Bromodichloromethane	20	80	131	20	Trichlorofluoromethane	20	80	120	20
Bromoform	20	65	135	20	Vinyl chloride	20	70	125	20
Bromomethane	20	65	135	20	1,2-Dichloroethane-d4 (Surr)	20	70	130	20
Carbon tetrachloride	20	78	129	20	4-BFB (Surr)	20	77	121	20
Chlorobenzene	20	80	126	20	Toluene-d8 (Surr)	20	80	123	20
Chloroethane	20	78	125	20					

Table 24.5 - NUMBER OF ALLOWABLE SPORADIC MARGINAL EXCEEDANCES

Number of analytes	Sporadic Marginal Exceedances Allowed
0-11	0
11-30	1
31-50	2
51-70	3
71-90	4
>90	5

Table 24.6 Summary of Calibration and QC Procedures for Method SW8260C / 624

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Tune Check	Prior to ICAL and prior to each 12-hour period of sample analysis for method 8260C/EPA 624.1 **Method 624** - Prior to initial calibration, sample analysis and every 24 hours of sample	Specific ion abundance criteria of BFB, see Table 11.3.	Retune instrument and verify. No samples shall be analyzed without a valid tune and tailing factor.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
	analysis		
Multi-point initial calibration for all analytes, use six points if second order curve fit to be used.	Initial calibration prior to sample analysis. Minimum 5 levels for linear and 6 levels for quadratic	Average RRF : see Table 11.4; RSD for Target analytes <20% **(≤15% for DoD projects)**; or option below: Option 1 linear – least squares regression r > 0.995. Option 2 non-linear – r2 > 0.99 (must use 6 points at minimum). [Note: grand mean not allowed.]	Correct problem then repeat initial calibration.
Second-source (ICV) calibration verification.	Once per five-point initial calibration.	All analytes within ±20% of expected value. 624 – Analytes within ±20% of expected value, poor purging VOCs ±25% of true value. (Acrolein, Acrylonitrile, ketones) (DOD all reported analytes must be within ±20% of true value.	Correct problem then repeat initial calibration.
Retention Time Window position establishment	Once per ICAL and at the beginning of the analytical sequence.	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA.
Relative Retention Time evaluated for each analyte in ICAL.	Each sample	Relative retention time (RRT) of the analyte within ± 0.06 RRT units of the RRT of the ICAL midpoint.	Correct problem then re-run ICAL.
Continuing Calibration Verification (CCV)/CCB pair.	Daily, before sample analysis and every 12 hours of analysis time for 8260C/EPA 624.1. Daily, before sample analysis	All reported analytes and surrogates within ± 20% of true value. Blank with no compounds present greater than ½ LOQ and surrogate within ± 20% of true value.	Correct problem then repeat CCV/CCB. IF second attempt fails, then repeat initial calibration.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
	and every 24 hours of analysis time for 624.		
Continuing Calibration Verification (CCV) – Closing for DoD projects.	Daily at the end of 12 hours of analysis time for 8260C/EPA624.1 or 24 hours for 624.	All reported analytes and surrogates within ± 50% for end of analytical batch CCV.	Recalibrate, and reanalyze all affected samples since the last acceptable CCV; or Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails, take corrective action(s) and re-calibrate; then reanalyze all affected samples since the last acceptable CCV.
Internal Standards – samples and QC samples.	All samples and QC samples except the CCV	Retention time ±10 seconds from retention time of the CCV. EICP area within -50% to +100% of CCV.	Reanalyze sample to confirm IS failure due to matrix, and describe in lab review checklist.
Demonstrate ability to generate acceptable accuracy and precision using four LCS analyses.	Prior to initial analysis and annually afterwards.	QC acceptance criteria, Tables 22.3 and 22.4.	Recalculate results; locate and fix system problem and rerun demonstration for those analytes not meeting criteria.
Method blank.	One per preparation batch.	No analytes detected >½ LOQ; no common lab contaminants detected >LOQ.	Correct problem, then re-analyze method blank and all samples processed with contaminated blank.
LCS for all analytes.	One LCS per preparation batch.	QC acceptance criteria, Tables 22.3 and 22.4. DOD samples must use DOD LIMS codes to ensure DoD recovery limits are used, see LIMS or current Current DOD QSM for values	Correct problems, then re- analyze the LCS and all samples in the affected batch.
MS/MSD.	One MS/MSD per every 20 project samples per matrix.	QC acceptance criteria for % Recovery - Tables 22.3 and 22.4; 20% RPD limit for waters;	Describe in Laboratory Review Checklist. See section 16.7.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
		30% PRD Limit for Soils. DOD samples must use DOD LIMS codes to ensure DoD recovery limits are used, see LIMS or current DOD QSM for values	
Surrogate spike.	Every sample, spiked sample, standard, and method blank.	QC acceptance criteria, Table 24.2. DOD samples must use DOD LIMS codes to ensure DoD recovery limits are used, see LIMS or current DOD QSM for values	Method 8000C, Section 9.6 Requirements. Describe in Lab Review Checklist.
MDL study.	Once per 12 month period, per matrix for MDL and Quarterly for LOD and DCS. For DoD, MDL and DCS (LOD) must be performed on all analytes including surrogate compounds.	Detection limits established shall be < 1/2 the LOQs in Table 24.1	Repeat LOD at higher level, but not greater than the PQL, substituting the higher LOD for the MDL, in case where the original LOD does not confirm the MDL.

SOP TITLE: DATA REDUCTION, REVIEW, AND VALIDATION

DOCUMENT ID: HS-QS009, REV 8.5

Approved By: _____ Date: 11/05/18
Technical and Laboratory Director, Hoai Van

Prepared By: Erica M Howard Date: 11/05/2018
Quality Assurance Manager, Erica Howard

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1) Scope and Applicability

1.1 This procedure defines the approved process for the reduction, review and validation of all data produced in the laboratory, ensuring that the analytical results provided are of the type and quality required and expected by ALS Laboratory Group clients.

1.2 Specific tools used by the laboratory in this process are described, including checklists, spreadsheets, and data verification routines within the laboratory information management system (LIMS).

1.3 This document does not address method specific data handling procedures. Refer to individual analytical SOPs for method specific requirements

2) Summary of Procedure

2.1 This procedure involves the following processes:

2.1.1 Sample Receipt and Log-in: Sample receipts are assigned a unique LIMS work order, according to HS-SM001, current revision.

2.1.2 Initial Work Order Review: Each work order is reviewed by a project manager. This process ensures that internal work assignments agree with the client's request. The review must be performed prior to releasing samples for analysis.

2.1.3 Initial Data Reduction and Review: Performed by the analyst, this process ensures that samples are prepared and analyzed according to the work assignment in LIMS, and that samples are processed using correct calibrations, method requirements and calculations. Results are then reviewed to ensure that they comply with QC requirements. This process may be performed manually or using data acquisition and handling software.

2.1.4 Data Validation: Performed by a similarly qualified analyst or department supervisor, this process involves verification that sample and quality control results obtained meet method required acceptance criteria. This review is monitored in LIMS and is required before an analysis is considered complete.

2.1.5 Subcontract Data Review: Performed by a project manager, this process involves reviewing subcontractor reports to ensure that the final product is complete and accurate.

2.1.6 Project Management Review: Performed by a project manager, this process ensures that the final product is complete prior to its release to the client. The project manager reviews all batch QC samples, analytical comments, and the data assessment checklist prior to delivering the final report to the client.

2.1.7 Data Package Review: Performed initially by a department supervisor then by a Quality Assurance representative or designee, this process ensures that data packages are complete, and correct. Specifically, raw data is reviewed against LIMS generated reports to ensure that they agree. QC requirements are also evaluated for acceptance.

2.1.8 Sanity and Reasonableness Checks:

2.1.8.1 Analyst when possible must check for reasonableness such as comparing GRO data with VOA data, DRO with Semi, TCLP vs TOTAL, dilution comparison, etc.

2.1.9 Manual Integration verification – all manual integrations must be verified during second level review.

2.2 QA Manager Review: Performed by the Quality Assurance manager, this process involves the complete review of a representative sample of completed work orders to ensure that the final product meets the requirements of the laboratory. For DOD projects, complete data must be reviewed to ensure proper calculations, reporting and compliance to method criteria.

3) Definitions

3.1 Demonstration of Capability: The analysis of QC samples in series to verify the ability to produce data of acceptable precision and bias.

3.2 Exception Report: Appropriate comments reported with the associated sample batch that addresses sample anomalies such as demonstrated sample matrix effects.

3.3 Laboratory Control Sample (LCS): A sample matrix, free from the analytes of interest, spiked with known amounts of analytes or a material containing known and verified amounts of analytes.

3.4 Matrix Spike (MS): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available.

3.5 Matrix Spike Duplicate (MSD): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of recovery for each analyte.

3.6 Method Blank (MBLK): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analysis.

3.7 NCAR: Nonconformance Corrective Action Report (refer to SOP HSQS003, current revision).

3.8 Preparation Batch: A defined set of one to 20 client samples of the same matrix, meeting the batch definition criteria, and prepared for analysis within 24 hours. The preparation batch must also contain the required determinative method defined batch QC samples (e.g. method blank, laboratory control samples, matrix spikes, duplicates, etc.).

3.9 Surrogate: An analyte added to a sample, which is unlikely to be found in any sample at significant concentration, and which is added directly to a sample aliquot in known amounts before any sample processing procedures are conducted. It is measured with the same procedures used to measure other sample components. The purpose of the surrogate analyte is to monitor method performance with each sample.

3.10 Surrogate Spike: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environmental samples and is added for quality control purposes.

3.16 Batch: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** is composed of one (1) to twenty (20) environmental sample of the same quality systems matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be twenty-four (24) hours. An **analytical batch** is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.

3.11 Data Assessment: The evaluation of method-prescribed QC data produced against a set of defined acceptance criteria (e.g. evaluation of an LCS recovery of 72% for constituent A versus its acceptance limits of 70 (the LCL) to 130% (the UCL).

3.12 Data Assessment Checklist: A defined document used to aid and document the data assessment step.

3.13 Data Reduction: The process of transforming the number of data items by arithmetic or statistical calculations, standard curves, and concentration factors, and collating them into a more useful form. Data reduction is irreversible and generally results in a reduced data set and an associated loss of detail.

3.14 CN: Case Narrative – Narrative in final report documenting issues or difficulties encountered in the analysis of the samples.

3.15 TRRP: Texas Risk Reduction Program.

4) Health and Safety Warnings

4.1 Lab Safety: Due to various hazards in the laboratory, safety glasses and laboratory coats or aprons must be worn at all times while in the laboratory. In addition, gloves and a face shield should be worn when dealing with toxic, caustic, and/or flammable chemicals.

4.2 Chemical Hygiene: The toxicity or carcinogenicity of each reagent used has not been precisely defined; however, each chemical used should be treated as a potential health hazard. Exposure to laboratory reagents should be reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets (MSDS) is available to all personnel involved in these analyses.

4.3 Pollution Prevention: The materials used in this method pose little threat to the environment when recycled and managed properly.

4.4 Job Safety Assessment.

HAZARD ASSESSMENT		
Job Task #1:	**Hazards**	**Preventative Measures**
Fatigue from long period at desk & in front of the computer.	Fatigue, eye strain or injury from repetitive procedure.	Ensure proper ergonomics setup and take frequent breaks.

5) Cautions

5.1 All computer-based data processing tools developed by the laboratory must be validated and approved for use by the Quality Assurance Manager.

6) Interferences

6.1 Not Applicable to this SOP.

7) Personnel Qualifications and Responsibilities

7.1 General Responsibilities - This procedure is restricted to use by or under the supervision of analysts experienced in the method.

7.2 Analyst - It is the responsibility of the analyst(s) to:

- 7.2.1 Each must read and understand this SOP and follow it as written. Any deviations or non-conformances must be documented and submitted to the QA Manager for approval.
- 7.2.2 Produce method compliant data that meets all quality requirements using this procedure.
- 7.2.3 Complete the required initial demonstration of proficiency before performing this procedure without supervision.
- 7.2.4 Complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 7.2.5 The analysts must submit data for peer or supervisor review.

7.3 Section Supervisor - It is the responsibility of the section supervisor to:

- 7.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.
- 7.3.2 Ensure analysts have completed the required initial demonstration of proficiency before performing this procedure without supervision.
- 7.3.3 Ensure analysts complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 7.3.4 Ensure analysts produce method compliant data that meet all quality requirements using this procedure.
- 7.3.5 Data Validation – Supervisor or designated individual will review and validate data prior to releasing data for reporting.

7.4 Project Manager - It is the responsibility of the Project Manager to ensure that all method requirements for a client are understood by the laboratory.

- 7.4.1 Perform final review of report for completeness before reporting to the client.

7.5 QA Manager: The QA Manager is responsible for

- 7.5.1 Approving deviations and non-conformances
- 7.5.2 Ensuring that this procedure is compliant with method and regulatory requirements,
- 7.5.3 Ensuring that the SOP is followed as written through internal method and system audits. For DOD workorders a complete data review must be performing including calculations.

8) Sample Collection, Handling, and Preservation

8.1 Not Applicable to this SOP.

9) Equipment and Supplies

9.1 Applicable Preparation and Method SOPS: SOPs are found on the local QA portal.

9.2 Data Assessment Checklist: Section 22, Appendix A.

9.3 Data acquisition and processing software, as described in each analytical SOP.

9.4 LIMS – utilized in tracking sample progress, as well as validating and reporting data.

9.4.1 LIMS QC Data Check Tools are used in all levels of data review. These tools include the following:

9.4.1.1 Spike Ref Check – A LIMS tool that checks for correctness of links assigned between spiked samples (MS, MSD) and the background sample, to ensure recovery data calculations are correctly performed

9.4.1.2 RPD Ref Check - A LIMS tool that checks for correctness of links assigned between duplicate samples (MS and MSD; sample and duplicate; LCS and LCSD) and the background sample, to ensure duplicate RPD calculations are correctly performed

9.4.1.3 Batch QC Check – A LIMS tool used at the data entry level that checks for correctness of links assigned between all required QC within a single analytical batch. The check will identify a missing QC sample type.

9.4.1.4 Dilution Result Check – A LIMS tool used at the data entry level that checks results across dilutions allowing review for confirming the linearity of a result and that the correct dilution factor is reported.

9.4.1.5 QC Batch Report – A LIMS report summarizing the batch QC associated with a work order, used during project management review.

9.4.1.6 Duplicate Data Check - A LIMS tool used at the data entry and final report level to check for duplicated data results for the same sample.

9.4.1.7 Missing Data Check – A LIMS tool used at the final reporting step that searches for a missing analyte result.

9.5 NCAR form - A link to the NCAR database is found in the lab network to report NCARs.

10) Standards and Reagents

10.1 Not Applicable to this SOP.

11) Method Calibration

11.1 Refer to method SOPs for calculations

12) Sample Data Review Procedures

12.1 Work orders are assigned according to HS-SM001, current revision. All relevant information about each sample is entered into LIMS.

12.2 Initial Work Order Review: Upon creation of each WorkOrder (HS-SM001, current revision) the work order folder is submitted to the appropriate project manager for review.

12.2.1 The following items are reviewed for correctness against the chain of custody:

12.2.1.1 Client contact information

12.2.1.2 Project information

12.2.1.3 Client sample IDs, collection date and time

12.2.1.4 Sample matrix, preservation, container

12.2.1.5 Test Code assignments

12.2.1.6 Reporting requirements and turnaround time.

12.2.2 Any discrepancies found during this stage of review must be addressed. The project manager verifies the request with the client, in writing, and makes corrections as needed (HS-ADM003, current revision).

12.2.3 Once it has been determined that the above information is correct in LIMS, the project manager indicates that the review is complete by entering a complete date on the main view of the work order

12.3 Initial Data Reduction and Review:

12.3.1 Once sample analysis is complete, the analyst must reduce the raw data to a format that presents the information in a meaningful way.

12.3.1.1 Data reduction may be accomplished in one of the following ways:

- Manually calculate results using the calculations outlined in the SOP,
- Manually entering raw data for computer processing (i.e., spreadsheet calculations), or
- Initiating electronic data quantitation based on a predefined calibration file stored in the data processing software.

12.3.1.2 Data that is handled manually is recorded in the appropriate analytical logbook.

12.3.1.3 Data that is acquired electronically and reduced using data processing software is presented on a computer-generated summary report. A sequence logbook is maintained to document instrument activity and related notes.

12.3.1.4 All electronic data must be uniquely identified and protected against inadvertent changes.

12.3.2 Review of reduced data:

12.3.2.1 The primary analyst reviews 100% of the reduced data.

12.3.2.2 Typical initial data review includes the following:

- Evaluation of technical issues not previously addressed.
- Evaluation of anomalies in the raw data (i.e., baseline shifts, negative absorbance, omission, legibility, etc.)
- Evaluation of possible transcription errors (e.g., sample IDs, dilutions, sample weights, and standard IDs)
- Evaluation of results against working range of the procedure.
- Verification that all calibration verification requirements are met.
- Verification that batch QC requirements are met.
- Check manual integration for proper qualification.

12.3.3 At this point in the review process, any errors must be addressed with corrective actions. Typical corrective actions include:

12.3.3.1 Correction and recalculation of manual data entry errors;

12.3.3.2 Correction of transcription errors;

12.3.3.3 Manually integrate incorrectly processed chromatography peaks.

12.3.3.4 Reanalysis of samples associated with unacceptable CCVs/CCBs;

12.3.3.5 Re-extraction and/or reanalysis of samples associated with unacceptable batch QC;

12.3.3.6 Preparation of new standards for a CCV failure followed by re-analysis of associated samples;

12.3.3.7 Instrument maintenance and sample reanalysis if method blanks indicate system contamination;

12.3.4 Once this review is complete and corrective actions have been completed, the analytical results are imported into LIMS and the batch is calculated.

12.3.5 The LIMS batch scan is reviewed to ensure that batch QC is correctly referenced, and that data qualifiers are accurately applied.

12.3.6 The analyst makes note of any outstanding data quality issues on the sample or batch comment sections in LIMS and electronically signs and dates.

12.4 Peer/Supervisor Data Review: This stage of review is a completely independent review of sample results and batch QC by the Department Supervisor or an analyst qualified to perform the analysis.

12.4.1 The scope of this review includes raw data review and uploaded data, as appropriate to the method, verification of all batches QC, and a review of all comments and data qualifiers.

12.4.2 Review is performed in a systematic manner.

12.4.3 Various tools are available in LIMS to ensure proper data review, see Section 9.4 for listing of LIMS data check tools. These tools assist the reviewer in adequately assessing key data quality indicators. A NCAR may be issued based on the severity of the error.

12.4.4 Additionally, the reviewer must evaluate the data for correct interpretation of spectra, proper chromatogram integration, dual column P-flags, etc.

12.4.5 Manually processed data is validated by checking a representative sample of the data calculations and all of the final data entry for possible error

12.4.6 If an error(s) are detected in this stage of review, the raw data is returned to the primary analyst for correction.

12.4.7 The reviewer validates the LIMS batch by electronically approving data in LIMS which will document who reviewed and when approved.

12.4.8 Manual Integration Check – Reviewer must verify all manual integration for correctness and qualification/documentation (Reason for Manual Integration).

12.4.9 Dilution Checks - Using the dilution check feature in LIMS cross-check the results of the dilution compared to the lower dilution to ensure results are not off by any order of magnitude.

Such as	1X	– 5000		1X - 5000
	10x	– 4500	and NOT	10X – 11,000
	100X	- 6500		100X – 30,000.

If there is any discrepancy, then do not report sample until the result is verified or re-analyzed.

12.4.10 Sanity or "Reasonableness" Check – Reviewer and Analyst must consider if result being reported is reasonable across related methods. Example if GRO result was 5000 ug/L and the BTEX by 8021 or 8260 was ND, then this should alert data reviewer that there are inconsistencies. This review includes checking that all data is included in the report, verifying that all QC and project specific requirements have been met, and screening for logical inconsistencies in the data. A list of common checks is included in Appendix A. Additional comments regarding sample handling and quality control issues may be added at this time within the report case narrative

12.5 Subcontracted Data Review: This is 100% review of data reported by a subcontracted laboratory and performed by the Project Manager for completeness.

12.5.1 During this review, the Project Manager will:

12.5.1.1 Verify that all samples are accounted for and all the assigned tests have been performed;

12.5.1.2 Verify that all contract required QC samples are included; and

12.5.1.3 Verify that adequate explanations are given for data when QC results show exceedances.

12.5.2 Any errors discovered during this review are referred back to the subcontract laboratory for correction and reconciliation. The reviewer and the subcontract laboratory must agree on all data reported. It may be necessary to obtain a revised report from the subcontract laboratory.

12.6 Data Package Review: This is a 10% (DOD) review of raw data against results reported in e-LIMS. This review is performed by a member of the Quality Assurance Department if requested by project management.

12.6.1 Once a data package is compiled (See HS-ADM003, current revision) and reviewed by the department supervisor, or designee, the reviewer begins by generating work order analytical and QC reports in LIMS.

12.6.2 In this stage, the reviewer will:

12.6.2.1 Verify all results presented on the raw data agree with the results presented in LIMS

12.6.2.2 Verify that forms, logbook copies, and calibrations are present and correct,

12.6.2.3 Perform a random review of logbook completion.

12.6.2.4 Review all comments and data qualifiers appearing in the reports and raw data.

12.6.3 Any errors observed at this stage are referred to the department supervisor for correction. A NCAR may be issued if the severity of the error warrants.

12.7 Once all errors have been corrected, any changes to LIMS data requires that the final report be regenerated prior to releasing it to the client

12.8 Final Project Management Review: This review involves the compilation and review of the final report, all completed Data Assessment Checklists, the QC Check Summary report, and other pertinent information. (i.e., comments, data qualifiers, etc.). Review is performed systematically using a Laboratory Review Checklist (i.e., TRRP Checklist).

12.8.1 This level of review assesses the usability of the data, and assists the client in avoiding inappropriate use of the data. Various tools are used to complete this review, including the Laboratory Quality Assurance Manual, the Project Quality Assurance Plan, if available, and communication with the client concerning intended use of the data.

12.8.2 Final data reports must include the following information:

Table 12.8.2 Information Required on Reduced Data

Table 12.8.2. Information Required on Reduced Data	
Analysis/Method Number	Lab Sample ID
Batch ID	Matrix
Analyst	Extraction/Digestion Date/Time
pH, if applicable	Analysis Date/Time
Dilution Factor(s)	Instrument ID
Result(s)	% Moisture, if applicable
Method Detection Limit(s)	Units

Analyte	Qualifiers
	Method-required Batch QC Data

12.8.3 Other information may be required as it is deemed necessary to communicate information about the analysis

12.8.4 Errors noted during this stage of review require that an NCAR be issued to determine why the error was not discovered in the previous stages of review. The analytical department supervisor is notified of the error and initiates the appropriate corrective actions, which may include:

12.8.4.1 Completion of missing data,

12.8.4.2 Correction of typographical or transcription errors,

12.8.4.3 Reanalysis of data that does not meet the data quality objectives of the work order.

12.8.5 Once the work order is complete and accurate, the Project Manager assistant compiles all work order comments into a final Case Narrative, or TRRP Checklist Exception Report, when TRRP reporting is required.

12.8.5.1 Where no exceptions or comments are noted, the Case Narrative may be omitted from the final report. The TRRP Checklist is required for all TRRP reports.

12.8.6 The PM Review checklist (or TRRP Checklist) is signed and dated prior to releasing the final report to the client. This document is placed in the work order folder for future reference.

12.9 QA Manager Data Review – The QA Manager reviews approximately 5% (10% DoD) of all final reports issued by the laboratory. This review follows the QA checklist, or an equivalent document (i.e., TRRP Checklist). The QA manager also reviews laboratory records to evaluate the appropriateness of corrective actions taken during the course of analysis.

12.9.1 Errors discovered in this stage of review require the issuance of an NCAR. Report revisions recommended as part of a corrective action investigation will be coordinated with the Project Manager.

12.10 Periodic Document Reviews: Periodic reviews of laboratory documents verify that laboratory records are current and adequate at all times.

12.10.1 Monthly Supervisory Review of Department Laboratory Records: On a monthly basis, laboratory supervisor must review departmental records for completeness and consistency of information recorded in departmental records (maintenance logbooks, chemical inventory logbooks, standard and chemical preparation logbooks, sample preparation logbooks and instrument run logbooks).

12.10.2 Quarterly Quality Assurance Review of Department Laboratory Records: On a quarterly basis, the Quality Assurance department must review departmental records for completeness and consistency of information recorded in departmental records and the review of such records (maintenance logbooks, chemical inventory logbooks, standard and chemical preparation logbooks, sample preparation logbooks and instrument run logbook).

13) Troubleshooting

13.1 Refer to method SOPs.

14) Data Acquisition

14.1 Refer to method SOPs.

15) Calculation, and Data Reduction Requirements

15.1 For DOD data review, perform sample calculation for select number of compounds, ensure all calibration models use are checked.

16) Quality Control, Acceptance Criteria and Corrective Action

16.1 Tuning:
- 16.1.1 Purpose: Verifies the proper working of the mass spectrometer.
- 16.1.2 Frequency: Prior to ICAL, and at the beginning of each 12-hour period.
- 16.1.3 Acceptance Criteria: See analytical SOP.
- 16.1.4 Corrective Action: Identify and correct the source of error. Re-tune the instrument and reanalyze affected samples.

16.2 8270 Breakdown Check (DDT):
- 16.2.1 Purpose: Verifies the inertness of the injection port because DDT is easily degraded in the injection port.
- 16.2.2 Frequency: At the beginning of each 12-hour period, prior to the analysis of samples.
- 16.2.3 Acceptance Criteria: Degradation ≤20% for DDT. Benzidine and pentachlorophenol should be present at their normal responses, and should not exceed a tailing factor of 2.
- 16.2.4 Corrective Action: Identify and correct the source of error. Repeat the breakdown check.

16.3 8081 Breakdown Check (Endrin / DDT):
- 16.3.1 Purpose: Verifies the inertness of the injection port because Endrin and DDT are easily degraded in the injection port.
- 16.3.2 Frequency: At the beginning of each 12-hour period, prior to the analysis of samples.
- 16.3.3 Acceptance Criteria: Degradation ≤15% for both compounds.
- 16.3.4 Corrective Action: Identify and correct the source of error. Repeat the breakdown check.

16.4 Initial Calibration (ICAL):
- 16.4.1 Purpose: Establishes the calibration curve for the quantification of the analytes of interest.
- 16.4.2 Frequency: Prior to sample analysis, following significant instrument maintenance
- 16.4.3 Acceptance Criteria: The new ICAL curve must have a correlation coefficient equal to or greater than 0.995. [Method may have additional criteria]
- 16.4.4 Corrective Action: Identify and correct the source of error. Perform the ICAL again and reanalyze all affected samples. If correlation coefficient is outside their range, perform corrective action to determine the source of the error.

16.5 Initial Calibration Verification (ICV):
- 16.5.1 Purpose: Verifies the accuracy of the ICAL using a standard prepared from a source independent of the source of the standards for the ICAL and CCV.
- 16.5.2 Frequency: Analyzed immediately after each ICAL to verify the new curve, prior to sample analysis.
- 16.5.3 Acceptance Criteria: [Varies with method, typically 20%]

16.5.4 Corrective action: Identify and correct the source of error. Reanalyze the ICV. If failure persists, repeat the ICAL.

16.6 Continuing Calibration Verification (CCV):
- 16.6.1 Purpose: Verifies that instrument response is reliable and has not changed significantly from the current ICAL.
- 16.6.2 Frequency: [Varies with method]
- 16.6.3 Acceptance Criteria: [Varies with method].
- 16.6.4 Corrective Action: Reanalyze the CCV, if failure persists identify and correct the source of error and reanalyze all client samples that were bracketed by the failing CCV.

16.7 Low-Level Calibration Check Standard (LL-CCV):
- 16.7.1 Purpose: Confirms the accuracy of measurements at or near the RL.
- 16.7.2 Frequency: Daily, after ICAL.
- 16.7.3 Acceptance Criteria: Recovery ±20% of true value.
- 16.7.4 Corrective Action: Identify and correct the source of error, reanalyze.

16.8 Linear dynamic range (LDR):
- 16.8.1 Purpose: Verifies quantitative accuracy of data up to the high-level standard.
- 16.8.2 Frequency: Every 6 months.
- 16.8.3 Acceptance Criteria: Recovery ±10% of true value.
- 16.8.4 Corrective Action: Identify and correct the source of error, reanalyze.

16.9 Calibration Blank (CCB):
- 16.9.1 Purpose: Determines the zero point of the calibration curve for all initial and continuing calibrations.
- 16.9.2 Frequency: At the beginning of each sequence, after every 10 samples and at the end of each sequence immediately after the CCV.
- 16.9.3 Acceptance Criteria: No analytes detected >MDL.
- 16.9.4 Corrective Action: Identify and correct the source of error. Reanalyze all affected samples.

16.10 Internal Standard Verification:
- 16.10.1 Purpose: Determines analyte concentration using the ratio of analyte signal to internal standard signal.
- 16.10.2 Frequency: Every field sample, standard, and QC sample.
- 16.10.3 Acceptance Criteria: [Varies with method]
- 16.10.4 Corrective Action: Identify and correct the source of error and reanalyze all affected samples.

16.11 Method Blank (MBLK)
- 16.11.1 Purpose: Assess background interference or contamination in the analytical system that may lead to high bias or false positive data.
- 16.11.2 Frequency: Analyze one MB with each batch of 20 or less field samples.
- 16.11.3 Acceptance Criteria: No analytes detected >1/2 RL and >1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater). For common laboratory contaminants, no analytes detected >RL.
- 16.11.4 Corrective Action: Identify and correct the source of error, and re-prep and reanalyze the MBLK and all associated client samples.

16.12 Interference Check Solutions (ICS-A and ICS-AB):
- 16.12.1 Purpose: Verifies established correction factors by analyzing the interference check solution at the beginning of the analytical sequence:
- 16.12.2 Frequency: At the beginning of each analytical sequence, then every 12-hour.

16.12.3 Acceptance Criteria: ICS-A: Absolute value of concentration for all non-spiked analytes <LOD. ICS-AB: Within ±20% of true value.

16.12.4 Corrective Action: Stop analysis. Identify and correct the source of error. Reanalyze the ICS and all affected samples.

16.13 Laboratory Control Standard (LCS):

16.13.1 Purpose: Evaluates the performance of the entire analytical system, including all preparation and analysis steps. Assesses the ability of the laboratory/analyst to successfully recover the target analytes from a clean matrix. Contains all target analytes and surrogates.

16.13.2 Frequency: Once per preparation batch.

16.13.3 Acceptance Criteria: [Varies by method]

16.13.4 Corrective Action: Identify and correct the source of error. Re-prepare and reanalyze the affected preparation batch for failed analytes.

16.14 Matrix Spike Sample (MS):

16.14.1 Purpose: Assesses the performance of the method on a particular matrix.

16.14.2 Frequency: Once per preparation batch.

16.14.3 Acceptance Criteria: [Varies by method]

16.14.4 Corrective Action: If the spike results are outside the acceptance limits for recovery, first determine if the cause is a system error; if so, correct the problem and repeat the MS. If system error is not a factor, the data may only be reported if the associated LCS is acceptable. The sample MS results are flagged indicating matrix interference.

16.15 Matrix Spike Duplicate (MSD) or Laboratory Control Standard Duplicate (LCSD) :

16.15.1 Purpose: Assesses the performance of the method on a particular matrix. Also determines the precision of the analytical process for that matrix.

16.15.2 Frequency: Once per preparation batch depending on program 1 in 10, Wastewater or 1 in 20 samples, hazardous waste.,

16.15.3 Acceptance Criteria: [Varies by method].

16.15.4 Corrective Action: If the spike results are outside the acceptance limits for recovery, first determine if the cause is a system error; if so, correct the problem and repeat the MS. If system error is not a factor, the data may only be reported if the associated LCS is acceptable. The sample MS results are flagged indicating matrix interference.

16.16 Sample Duplicate

16.16.1 Purpose: Provides information on the heterogeneity of the sample matrix. Also determines the precision of the analytical process for that matrix.

16.16.2 Frequency: Once per preparation batch.

16.16.3 Acceptance Criteria: [Varies by method].

16.16.4 Corrective Action: Identify and correct the source of error. Reanalyze the affected batch. If system error is not a factor, reanalysis may not be necessary.

16.17 Surrogate Spike:

16.17.1 Purpose: Assess the ability of the method to successfully recover specific non-target analytes from an actual matrix; monitors recovery on a sample-specific basis.

16.17.2 Frequency: All field and QC samples

16.17.3 Acceptance Criteria: [Varies by method]

16.17.4 Corrective Action: Identify and correct the source of error. Re-prepare and reanalyze all affected sample. If obvious chromatographic interference with

the surrogate is present, it may not be necessary to reanalyze the sample.

16.18 Dilution Test:
- 16.18.1 Purpose: Assesses matrix interference
- 16.18.2 Frequency: One per preparatory batch.
- 16.18.3 Acceptance Criteria: Five-fold dilution must agree within ±10% of the original measurement
- 16.18.4 Corrective Action: Perform post digestion spike addition.

16.19 Post Digestion Spike Addition:
- 16.19.1 Purpose: Confirms the presence of matrix interference.
- 16.19.2 Frequency: One per preparatory batch.
- 16.19.3 Acceptance Criteria: Recovery within 75-125%
- 16.19.4 Corrective Action: Run all associated sample in the preparation batch by method of standard additions.

16.20 Confirmation of Positive Results:
- 16.20.1 Purpose: Verifies the identification of target analytes,
- 16.20.2 Frequency: All positive results must be verified (exception is 8015)
- 16.20.3 Acceptance Criteria: Results between initial or primary column and second column RPD ≤ 40%.
- 16.20.4 Corrective Action: Results are reported from higher column unless obvious co-elution is present. Data is qualified with a P-flag.

16.21 These procedures will be verified through the laboratory's internal audit process (HS-QC012, current revision)

17) Data Records Management

17.1 All data is stored electronically and/or hard copy for five (5) years or ten (10) years for data to be submitted to the state of Louisiana. Operational software is maintained for the same duration.

17.2 All analytical sequence IDs and standard preparation information must be recorded in the Run logbook. Hardcopy computer printouts of analytical sequences and raw data must be retained (electronic initials are acceptable).

17.3 Complete all pertinent sections in the respective logbooks. If not-applicable then line out the section. "Z" out or "X" out all large sections of the worksheet that are not used. Make all corrections with single line through, date and initial. Make NO obliterations when manually recording data.

17.4 Logbooks are controlled. Never remove a page from a logbook. Completed logbooks are returned to the QA department when filled and no longer needed in the work area.

17.5 SOP effective date is the date noted in the header or last signature date, whichever is most recent.

17.6 Document Storage:
- 17.6.1 Documents produced during data reduction, review and validation are stored electronically. Hard copy documents are stored with raw data. Refer SOP HS-QS-011, Records Archival Procedures, current version.
- 17.6.2 Documents produced during project management and data package reviews are stored in the appropriate work order folder. Refer SOP HS-ADM-003, Work Order Reporting, current version.

17.6.3 Documents produced during Quality Assurance reviews are maintained on file in the QA Department.

18) Contingencies for Handling Out of Control Data

18.1 Not Applicable to this SOP.

19) Method Performance

19.1 Not Applicable to this SOP.

20) Summary of Changes

Table 20.1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
8.5	11/05/2018	G. Moulton	Updated to new company cover page, updated new QA manager.
8.5	11/05/2018	G. Moulton	Modified sec 17.1 (data storage)
8.5	11/05/2018	G. Moulton	Modified sec 21.2.2 and 21.2.4
08.4	06/15/2017	T. Yen	New Lab Director.
08.4 – Sections 2.1.8 & 2.1.9	06/15/2017	T. Yen	Perform sanity/reasonableness check across method and manual integrations verification review at the second level review.
08.4 – Section 12.3.3	06/15/2017	T. Yen	Continuing Calibration Blank (CCB) – added with criteria.
08.4 – Section 12.4.9	06/15/2017	T. Yen	Dilution checks.
08.4 – Section 12.4.10 & Appendix B	06/15/2017	T. Yen	Sanity or "Reasonableness" Check
08.4 – Section 21	06/15/2017	T. Yen	Updated references.
08.3	09/15/2014	T. Yen	New SOP Format and lab Director.
08.3 – Sections 2.2, 12.9 and 15.1.	09/15/2014	T. Yen	Modified for DOD requirements
08.3 – Section 21	09/15/2014	T. Yen	Revised references and related documents
08.2	05/15/2013	T. Yen	Signature Page – New Department Supervisor, QA Manager and Lab Director.
08.2	05/15/2013	T. Yen	Document Footer – "A Campbell Brothers Limited Company" changed to "An ALS Limited Company" to reflect parent company name change.
08.2 – Section 10.5	05/15/2013	T. Yen	SOP effective date defined.

08.2 – Section 13.1.3	05/15/2013	T. Yen	TRRP 13 reference update.
08.1	04/15/2012	J. Cady	Minor document format revision.
08.0	07/15/2011	I. Williams	Major document format revision.

21) References and Related Documents

21.1 References

21.1.1 Test Methods for Evaluating Solid Waste, Chapter 1, SW-846, Third Edition, through Update IV, July 1992, OSWER.

21.1.2 Current TNI Standards.

21.1.3 "Review and Reporting of COC Concentration Data", TCEQ Regulatory Guidance, RG-366 / TCEQ Texas Risk Reduction Program - 13, May 2010.

21.1.4 Current DOD Quality Assurance Manual.

21.2 Related Documents

21.2.1 HS-ADM003, Work Order Reporting, current revision.

21.2.2 HS-QS003, Non-Conformance Corrective Actions, current revision.

21.2.3 HS-QS011, Records Archival Procedures, current revision.

21.2.4 HS-SM001, Sample Receipt and Log-In, current revision.

22) Appendix

Appendix A

Sanity Data Checks

Test(s)	**Relationship**
Solids (in waters)	Total solids ≥ TSS
	Total solids ≥ TDS
Nutrients	Total phosphorus ≥ ortho-PO_4
	Total phosphorus ≥ organic phosphorus
	TKN ≥ NH_3
	TKN ≥ Total organic nitrogen
	NO_3/NO_2 ≥ NO_3
	NO_3/NO_2 ≥ NO_2
Cyanide	Total cyanide ≥ Free cyanide
	Total cyanide ≥ Amenable cyanide
	Total cyanide ≥ Reactive cyanide
Demands	COD ≥ 1.5 x BOD
	COD ≥ Oil and Grease
	COD ≥ TOC (COD @ approximately TOC x 2.5)
Minerals	Total alkalinity ≥ carbonate alkalinity
	Total alkalinity ≥ bicarbonate alkalinity
	Total alkalinity ≥ hydroxide alkalinity
Others	Total ≥ Dissolved
	Influent ≥ Effluent
	Total ≥ TCLP
	Total sulfide ≥ Reactive sulfide
	Cr ≥ Cr^{+6}

	TDS ÷ Conductivity = 0.55 to 0.81
	TDS ≥ Total alkalinity
	TDS ≥ Hardness
	TDS ≥ Chloride
	TDS ≥ Sulfate
	If TDS = ND, metals should be ND (or very low)
	Measured TDS ÷ Calculated TDS = 1.0 – 1.2 • TDS_{calc} = 0.6(alkalinity) + Na + K + Ca + Mg, + Cl +SO_4 + SiO_3 + NO_3 + F
	COD, BOD, TSS, and Oil and Grease are all high or all low
	If TOC = ND, organic results should be very low level
	If a sample flashes, BTU ≥ 1000
	If a sample flashes, VOC data should show detections for BTEX and/or other flammable compounds
	Cation check[1]: (Ca + Mg + Na) ÷ Conductivity = 0.009 to 0.0124 • If this does not check out, check for other cations at high levels or low pH
	Anion check[1]: (Bicarbonate + carbonate + Cl + SO_4) ÷ Conductivity = 0.009 to 0.0124
	Ion balance check[1]: (Anions – Cations) ÷ (Anions + Cations) < .075
Organics	Gasoline pattern by GC/FID is consistent with BTEX, alkylbenzenes, and naphthalene data
	Diesel pattern by GC/FID is consistent with PAH data
	Chlorinated degradation products (DCE, DCA, DCM, etc.) in the presence of high TCE or PCE results
	PCB Aroclor 1016 results require careful evaluation.
	Mixtures of Aroclor 1242, 1254, and 1260 require careful evaluation and possible flagging of data due to a potential for double counting PCBs
	DDD and DDE in the presence of DDT
	Benzo(a)pyrene should be accompanied by other PAHs in a tissue samples (check for cholesterol if it is identified by itself).

[1] Applicable to clean samples with conductivity readings between 200 – 5,000 umhos/cm. Low conductivity, high viscosity, colored samples with high NH_3 content may not work for the cation, anion and ion balance checks.

SAMPLE LOG-IN PROCEDURES

DOCUMENT ID: HS-SM001, REV 10.7

Approved By: _____ Date: 8/3/2020
Department Supervisor, Nilesh Ranchod

Approved By: _____ Date: 8/3/2020
Technical and Laboratory Director, Hoai Van

Prepared By: _____ Date: 08/03/2020
Quality Assurance Manager, Erica Marinez

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1) Identification of the Method

1.1 N/A

2) Applicable Matrix or Matrices

2.1 N/A

3) Scope and Applicability

1.1 This procedure applies to the transportation, receipt, handling, protection, storage, and retention of all client samples received by ALS Laboratory Group.

3.2 Refer to the current version of SHWD-001, for sample disposal procedures.

3.3 The purpose of this document is to provide a general operating procedure for the receipt, log-in and storage of samples submitted to ALS Laboratory Group for environmental testing

4) Summary of Procedure

4.1 Samples arrive at the laboratory by one of the following methods:
- 4.1.1 Client delivery
- 4.1.2 ALS courier
- 4.1.3 A third party courier (i.e. FedEx, UPS)

4.2 Upon arrival at the laboratory, transfer of sample custody is noted on the Chain-of-Custody, and sample integrity is inspected. Any non-conformances are noted on the sample receipt checklist and the non-conformance is communicated to a member of project management.

4.3 The Chain-of-Custody is reconciled with the sample receipts. A unique identified work order is then initiated in LIMS to track all activity of the samples. Individual sample containers receive a unique fraction ID, which uniquely identifies samples within a work order and the work assigned to each sample container.

4.4 The sample administrator assigns the appropriate analysis to the corresponding sample container within the LIMS Log-In interface using information from the Chain-of-Custody or existing project information in LIMS.

4.5 Sample storage locations are assigned based on intended analysis and/or cooler space. This information, along with unique sample container identifiers, is recorded in LIMS and appears on backlog reports throughout the laboratory

4.6 Once the samples have been inspected and non-conformances noted, each container is labeled with: 1.) its internal workorder/fraction ID, container number, 2.) storage location, 3.) client sample ID, 4.) and the analyses assigned to the container.

4.7 All workorders are forwarded to a member of project management for final review and approval.

4.8 Internal Chain of Custody (ICOC) procedures must be used for all samples to track sample transfer within the lab from initial login to disposal. ICOC procedures utilize an internally assigned bar code tracking system for each sample container received, and are tracked electronically by analyst ID and sample location within the lab.

5) Definitions

5.1 Exception Report: Appropriate comments reported with the associated sample batch that addresses sample anomalies such as demonstrated sample matrix effects.

5.2 Matrix: The substrate (e.g., water, soil, etc.) which may contain the analyte of interest.

5.3 NCAR: Nonconformance Corrective Action Report (refer to SOP HSQS003, current revision).

5.4 Organic Free Water: Deionized (DI) reagent water meeting purity characteristics of Type I laboratory distilled water (daily resistance ≥17 megohms-cm). For additional purification, the DI water is passed through an activated carbon filter.

5.5 Chain of Custody (COC) form: A record that documents the possession of the samples from the time of collection to the time of receipt at the laboratory. The record generally includes the number and types of containers, collector, time of collection, preservation, and requested analyses.

5.6 Preservation: the process of protecting chemical and/or biological integrity of a sample. Generally involves refrigeration and/or the addition of reagents added to sample containers before and/or at the time of sample collection.

5.7 ICOC – Internal Chain of Custody

5.8 SRC – Sample Receipt Checklist – see appendix example

5.9 PM: Project Manager. Primary point of contact for clients and responsible for the management of client projects.

5.10 WOR: Work Order Report: a summary report generated by the login technician after completion of a client project login. The report is forwarded to the PM, for review along with the SRCL, COC documents, etc.

5.11 WOA: Work Order Acknowledgement: A report of the summary of samples & assigned tests logged into LIMS for a client sample delivery group. The WOA is sent to the client by the assigned PM, following the review of all information associated with the login process (chain of custody, SRCL, and other related information on file with the PM as provided by the client).

6) Safety

6.1 Lab Safety: Due to various hazards in the laboratory, safety glasses and laboratory coats or aprons must be worn at all times while in the laboratory. In addition, gloves and a face shield should be worn when dealing with toxic, caustic, and/or flammable chemicals.

6.2 Chemical Hygiene: The toxicity or carcinogenicity of each reagent used has not been precisely defined; however, each chemical used should be treated as a potential health hazard. Exposure to laboratory reagents should be reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets (MSDS) is available to all personnel involved in these analyses.

6.3 Waste Management: The principal wastes generated by this procedure are the method-required chemicals and standards. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required. Laboratory procedures in SOP HS-SAF-001, Waste Disposal Procedures, must be followed.

6.4 Pollution Prevention: The materials used in this method pose little threat to the environment when recycled and managed properly. The quantities of chemicals purchased should be based on the expected usage during its shelf life. Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards or reagents to be disposed.

6.5 Job Safety Assessment

HAZARD ASSESSMENT		
Job Task #1:	**Hazards**	**Preventative Measures**
Cooler and sample handling.	Injury due to lifting heavy coolers and placing samples on storage locations. .	Use proper lift technique, cart to move coolers and stools/stepladder when working reaching above shoulder height in sample storage cooler.
Job Task #2:	**Hazards**	**Preventative Measures**
Sample container handling and preservation checks.	Exposure to possible hazardous chemicals.	Use of proper PPE, i.e. Lab coats, safety glasses, gloves, etc.
Job Task #3:	**Hazards**	**Preventative Measures**
Use of utility knives to cut open cooler and seals.	Cuts.	Use proper safety with auto retracting blade and proper cutting techniques. Always cut away from body.
Job Task #4:	**Hazards**	**Preventative Measures**
Unpacking coolers and searching for samples within the coolers.	Possible cuts from broken sample containers.	Wear proper protective equipment such as Kevlar kit gloves and use of broken glass containers.

7) Maintenance

7.1 Routine preventative maintenance must be performed and documented to assure optimum instrument performance. Refer to the current revision of SOP HS-EQ004 for preventative maintenance schedules.

7.2 Routine preventative maintenance must be performed and documented to assure optimum instrument performance. Refer to the current revision of SOP HS-EQ004 for preventative maintenance schedules.

7.3 Waste Management: All samples should be treated as hazardous. All spills and broken sample containers should be immediately contained with the appropriate spill equipment and disposed of in a hazardous waste drum.

7.4 Shipment of containers, ice chests, samples, and suspected hazardous materials must meet all applicable International Air Transportation Association (IATA) and Department of Transportation (DOT) dangerous goods regulations.

7.5 Examine contents of each project cooler separately against the enclosed chain of custody to avoid sample identification or labeling errors, etc.

7.6 Samples submitted for volatile analysis (GC or GC/MS VOCs or GRO) are stored in the designated sample storage area in the Volatiles laboratory. Samples submitted for volatile analysis are never stored in general storage areas.

7.7 Aqueous samples submitted for oil and grease analysis by EPA1664 must not be checked for pH at log-in. The referenced method has a strict requirement the pH be checked in the laboratory.

7.8 On occasion it is necessary to divide samples in to sub-samples. Sub-samplers must be properly trained in sub-sampling techniques according to the appropriate standard operating procedure (HS-QS008 or HS-QS010). Note: Sub-sampling for volatiles analysis is not acceptable. Refer to HS-QS008 for guidance on samples being used for multiple analyses.

7.9 Preservation checks must be performed with care to prevent contamination of samples. Perform pH and residual chlorine tests using a fresh capillary tube. Collect the liquid by touching the tube to the surface of the sample. Release the liquid by touching the tip of the tube to the test strip. Use a new capillary tube for each sample.

8) Interferences

8.1 All areas where samples will be unpacked should be thoroughly cleaned after each set of samples to prevent cross contamination.

8.2 Samples from different clients should be grouped according to the client they were received from on the bench.

8.3 Clean utensils should be used for each sample if subsampling is being performed.

8.4 Samples that have an odor should be unpacked under the fume hood.

9) Personnel Qualifications and Responsibilities

9.1 General Responsibilities – These procedures should be used by or under the supervision of technicians experienced in sample management.

9.2 Project Manager - It is the responsibility of the Project Manager to ensure that all method requirements for a client requesting any procedure on their samples are understood by the laboratory prior to initiating any procedure for a given set of samples.

9.3 QA Manager: The QA Manager is responsible for
- 9.3.1 Approving deviations and non-conformances
- 9.3.2 Ensuring that laboratory procedures are compliant with method and regulatory requirements.

10) Sample Handling and Preservation

10.1 All samples should be handled carefully in the sample management area. See section 13 for procedures.

11) Equipment and Supplies

11.1 LIMS information system.

11.2 NIST-Traceable digital thermometer – calibrated quarterly and checked daily prior to use.

11.3 pH paper for preservation checks (various ranges - 0 to 4, 10 to 14, etc.) – log in pH paper in sample receipt login assign an internal ID number for tracking purpose.

11.4 Residual Chlorine Test Paper (Starch Iodide).

11.5 Safety glasses.

11.6 Protective gloves.

11.7 Ziploc® Bags, various sizes.

11.8 Coolers, various sizes – glass and plastic.

11.9 Durable refrigerator/freezer grade labels.

11.10 Computer Hardware and Software
- 11.10.1 This area uses mainly Dell computers and our LIMS.

12) Standards and Reagents

12.1 Note: Store purchased reagents for this area according to manufacturer specifications. Always document the lit number and or unique ID for proper traceability. The following reagents are used in the sample management department.

12.2 Nitric Acid, 1:1 - metals.

12.3 Nitric Acid, 1:9 – nitrate/nitrite.

12.4 Hydrochloric Acid, 1:1 – ferric iron.

12.5 Sodium Hydroxide, 1:1 - cyanide.

13) Sample Preparation/Analysis

13.1 Sample Receipt – Samples received by the laboratory must be inspected to ensure the integrity of the samples while protecting the interests of the laboratory and the client. **NOTE: ALS reserves the right to refuse any sample.**

13.2 The focus of the sample receipt inspection includes the following:

13.2.1 Sample Custody Requirements: Custody must be documented from collection to laboratory receipt. The individual responsible for sample collection must sign the Chain-of-custody when delivering the samples to the laboratory, relinquishing custody to the ALS courier, or when shipping samples via third party courier. The individual transporting the sample must sign the COC if possible. In the case of commercial couriers, shipping documents are sufficient proof of custody. Upon arrival at the laboratory an ALS representative must sign the COC to indicate that samples were received by the laboratory. This signed COC is forwarded to the client upon request. The client must be contacted if custody documents or required signatures are not present at sample receipt.

13.2.2 Time of Sample Receipt: The time of receipt must accurately correspond to the time a client relinquishes samples to ALS Laboratory Group at the lab, or courier service delivery time, or driver return to the lab.

13.2.3 Shipping Documents: Remove any shipping documents (bills of lading, air-bills, etc.) that arrive attached to the exterior of the shipped sample cooler. Examine the exterior of the cooler for evidence of tampering or breakage. Initial and remove all custody seals from cooler exterior, if applicable. If cooler seals have already been broken, document the information on the Sample Receipt checklist. Shipping documents and cooler custody seals are affixed to a blank sheet of paper and included in the work order file.

13.2.4 Initial Sample Inspection: Open the sample cooler and examine its contents. If broken sample containers or any type of offensive odors are discovered, immediately shut the lid and move the cooler to a well-ventilated area or under a fume hood before the samples are removed. If the chain of custody was sealed in the cooler, remove it and sign it at this time.

13.2.5 Sample Receipt Temperature: Using a traceable digital thermometer record the temperature of the temperature blank if present or a randomly chosen sample. IR thermometer must be check daily at two ranges, room temperature and near freezing against NIST traceable thermometers. Record day's temperature correction factors logbook in sample receipt area. If a temperature blank is available (usually a small plastic bottle) and clearly marked as such and read the temperature from the temp blank label with IR thermometer. The cooler's temperature must be >0 to 6 degrees Centigrade. If the temperature is outside this range, document the non-conformance on the sample receipt checklist, noting specific information about the affected bottles (i.e., sample ID, requested parameters), and immediately contact the project manager. Project Managers are required to contact the client immediately concerning any samples received outside the temperature requirement.

13.2.5.1 Sample Receipt Temperature Correction Factor: All temperature reading must be corrected for correction factor (CF) even if 0.0˚C. The CF must be applied to the measurement taken when the sample receipt temperature is measured, recorded and evaluated. Corrected and uncorrected temperatures are document on the electronic sample receipt checklist in LIMS.

Table 13.2.5.1 Sample Receipt Temperature Correction Factor

Device CF, ˚C	Temperature, uncorrected	Temperature, Corrected	Criteria Status
-0.2	6.0	5.8	Acceptable
-0.1	6.0	5.9	Acceptable
0.0	6.0	6.0	Acceptable
+0.1	6.0	6.1	Not-Acceptable
+0.2	6.0	6.2	Not-Acceptable

13.2.5.2 If samples are delivered to the laboratory soon after collection may have temperatures above the acceptable range. These samples are acceptable when it is apparent that the chilling process has begun. Record the temperature and note the attempt to chill the samples (i.e. “arrival on ice” or “insufficient time for cooling”).

13.2.5.3 If no temperature blank is provided in a cooler, use the NIST Traceable IR Temperature Gun to obtain a reading from the sample label. Record the temperature.

13.2.5.4 Next enter the ALS cooler tracking number(s) on the spaces provided on the SRC.

13.2.6 Samples are stored in original shipping cooler to maintain temperature until samples are ready to be processed. Work orders are prioritized for processing according to the following.

13.2.6.1 Holding Time

13.2.6.2 Turn Around Time

13.2.6.3 Order of Receipt

13.2.7 Prior notification of projects expected to have short hold parameters assists with resource allocation and work order priorities within client services.

13.2.8 Check the date of collection and associated holding time and verify whether samples have arrived past holding time. If any samples are received past their hold time, document as a nonconformance on the SRC and immediately report the issue to the project manager. The PM must contact the client in such circumstances for instruction on how to handle the sample.

13.3 Prior to processing a work order, samples are removed from the sample cooler and arranged on the bench in the order from left to right as they appear on the chain of custody. Sample names and bottle counts are compared to the chain of custody. Inform the project manager immediately of any discrepancies, including missing or broken containers.

13.4 Once the samples have been reconciled with the chain of custody, samples are evaluated

against our sample acceptance criteria. Any discrepancies are noted on the SRC and communicated to the Project Manager. Key items to note on the SRC include:

13.4.1 Missing/broken containers, or containers with limited sample volume

13.4.2 Unlabeled or illegible samples

13.4.3 Inappropriate sample or preservation for sample.

13.4.4 Preservation: If preservation is indicated on the chain of custody form as "pH<2" or "pH>12" verify this using appropriate pH paper.

13.4.4.1 DO NOT verify pH on samples submitted for VOC (8260, 8021, 8015-GRO) or Oil and Grease (La29B or EPA1664). Doing so could result in loss of analytes of interest. Preservation checks for these analyses are performed by the analyst.

13.4.4.2 If the pH for an aqueous metals analysis is >2, add HNO3 to bring the pH to <2. Note the ALS Sample ID, date and time of preservation, and Lot# of HNO3, in the preservation logbook. The sample must be allowed to equilibrate for 24 hours after which the pH must be checked again to ensure it is <2. If, after the 24 hours, the pH is still >2, inform the Project Manager immediately.

13.4.4.3 Where pH is not as indicated on the chain of custody, a pH adjustment may be necessary. Contact the Project Manager for guidance.

13.4.5 Residual Chlorine, check by analyst just prior to analysis: Residual chlorine checks are required for samples submitted for certain analysis. Perform this test by placing a small amount of sample on starch iodide paper. If the paper turns blue, the presence of residual chlorine is confirmed. Notify the project manager and make comments in LIMS.

13.4.6 Headspace: Aqueous samples in 40mL VOA vials are submitted with minimal headspace. A sample has headspace if it has an air-bubble larger than the size of a small pea. Check for headspace by turning the vial upside-down. Note the presence or absence of headspace on the SRC. Color-tag the bottom of the vial to notify the analyst of the presence of headspace. The analyst will avoid using the tagged vial in analysis unless absolutely necessary

13.4.6.1 SW-846 Note Concerning VOC Headspace: Due to different solubility and diffusion properties of gases in LIQUID matrices at different temperatures, it is possible for the sample to generate some headspace during storage. This headspace will appear in the form of micro bubbles, and should not invalidate a sample for volatile analysis. The presence of a macro (large) bubble in a sample vial generally indicates either improper sampling technique or a source of gas evolution within the sample. The latter case is usually accompanied by a buildup of pressure within the vial, (e.g. carbonate-containing samples preserved with acid). Studies conducted by the USEPA (EMSL-Cincinnati, unpublished data) indicate that "pea-sized" bubbles (i.e., bubbles not exceeding 1/4 inch or 6 mm in diameter) did not adversely affect volatiles data. These bubbles were generally encountered in wastewater samples, which are more susceptible to variations in gas solubility than are groundwater samples.

13.4.7 Subsampling Containers by Client services: In the event a project requires subsampling by the Client services department to fulfill project analytical requirements (e.g. subcontract sample submittals, etc.), this should be documented. See section 5.6 for cautions concerning VOC subsampling.

13.4.8 Samples received after hours regardless of project, must at minimum have a cooler receipt log created, and internal cooler temperature check and documented before being placed in the walk-in cooler for storage until processing. All DOD work must be checked for temperature and chemical preservation and documentation for check upon receipt, even if samples will be logged-in the next day.

13.5 All discrepancies must be noted on the LIMS SRC by the login technician and brought to the attention of the Project Manager as soon as possible (immediate for temperature, hold-time or sample ID/Label issues) so that immediate client contact can be made.

13.5.1 When short hold time samples are received, it is necessary to expedite processing to ensure hold times are met (see Sample Handling Guide, Section 11.5, for hold time information).

13.5.2 For samples received for parameters which are not routinely short hold, but have a hold time that will expire within 24 hours, alert the affected department supervisor so that necessary production schedule changes can be made.

13.5.3 For samples having no or illegible labels, client contact is required to clarify what was shipped and what test is required.

13.5.4 For a sample received that does not meet a pH preservation requirement,

13.5.4.1 Identify the sample in the SRC as not meeting preservation criteria.

13.5.4.2 Perform additional pH adjustment with proper preservative. Document initial and final pH also the amount and lot number of preservative in logbook.

13.5.4.3 For unpreserved metals samples, preserve and place sample on hold for at least 24 so the metals can go back into solution before releasing to the lab for analysis.

13.5.4.4 Note time of preservation in LIMS sample comments and document all actions taken on the SRC.

13.5.5 Temperature exceedances must be documented with enough detail to identify the cooler that was received outside of the acceptable temperature range, as well as each bottle/parameter received in the cooler. This information will facilitate decision making regarding the affected samples.

13.6 Log samples into LIMS utilizing the Chain of Custody. Use the projects and quotes features as much as possible to ensure the correct pricing and parameters are assigned.

13.6.1 Information to be logged in include: client sample identification; location of collection; date and time of collection; preservation type; sample container type; sample matrix type (e.g. water, soil, etc.) and any special remarks concerning the sample.

13.6.2 Additional client sample information (e.g. field pH or collector initials) is entered only if requested by a client.

13.6.3 Assign sample refrigerated storage locations based on sample matrix and type of analyses.

13.6.3.1 The proper storage of non-aqueous phase liquid waste VOA samples, or VOA samples with a strong hydrocarbon odor, is in the designated cooler (Nasty Sample Refrigerator), not with the standard environmental samples in the VOC Walk-in Refrigerator or refrigerator.

13.6.3.2 Water Trip blanks associated with soil samples are placed in the water sample refrigerator. Terra Core Trip Blanks are stored with the samples in the Freezer.

13.6.4 Samples must be labeled and stored as soon as possible to minimize the time

they are at ambient temperature. If work order processing is expected to exceed **20 minutes**, create receipt log and take internal temperature before placing VOA samples in the walk-in cooler on a cart or reach-in refrigerator in the login area. **If client requirements are more stringent, follow client specific protocol. Upon resolution of issue(s), samples are removed from removed from cooler and labeling completed followed by distribution to VOA storage. If resolution of issue(s) will take more than one hour ALL samples must be move to coolers to preserve the validity of each sample.**

13.6.5 Every effort should be made to ensure internal sample labels do not cover field-sampling labels (this may not always be possible).

13.6.6 Select storage tray(s) and transfer samples to tray locations in LIMS and place trays in the appropriate storage location. Documentation of samples transfer to storage is vital to ensure preservation of samples such as 5035 and TX1005/TX1006 are documented as being properly preserved within the 48 hours holding time.

13.6.7 Short hold samples such as ferrous iron, hexavalent chromium, nitrate, nitrite, etc., must be delivered to the lab along with a Short hold/Rush form as soon as possible. These samples will be physically delivered to the department that will perform the analysis and a signature obtained from the analyst on the short hold form.

13.6.8 If short hold samples delivered after hours or on weekend without prior knowledge WILL REQUIRE SAMPLE RECEIPT TO CONTACT PM AND REPSECTIVE LAB SUPERVISOR/MANAGER.

13.7 Once all samples are properly stored, the work order file must be completed. The log-in technicians will sign the Sample Receipt Checklist (SRC). All discrepancies and inconsistencies are noted on this document.

13.8 The Work Order Report, the Sample Receipt Checklist (SRC), the chain of custody, any shipping documents, custody seals, and all other relevant documentation must be placed in the work order file and forwarded to the project manager for review.

13.8.1 During the Project Management review, the PM must record the applicable client contact information on a Sample Receipt Checklist (LIMS SRC) for the non-conforming issues noted by Client services during the login process or document the client contact via email or fax. See example SRC in the appendix.

13.8.2 Upon completion of the login review, the PM forwards the Work Order Acknowledgement (WOA) to the client to document what was received and logged-in for testing.

13.9 Subcontracting Analytical Work

13.9.1 Upon inspection of the received sample containers, determine if separate containers were collected for the analyses to be performed by an outside laboratory. If separate containers were not provided, the sample must be sub-sampled (and preserved if necessary). The sample container type, the preservative, and the sample volume must meet the requirements for the analyses to be performed.

13.9.2 The sub-contract chain of custody is generated in LIMS and must accompany the samples to the sub-contract laboratory.

13.9.3 If samples are to be shipped out of town via air, proper package and shipment procedures must be followed. Glass sample containers are to be placed in bubble bags to prevent breakage. All water sample containers are to be placed in plastic Ziploc® bags to prevent leakage. The ice chest to be shipped is also

lined with a plastic garbage bag to prevent the cooler from leaking melted ice. A copy of the relinquished chain of custody and the courier's air bill is kept for tracking purposes.

13.9.4 Projects requiring NELAC approved test procedures must only be sent to laboratories having the appropriate NELAC accreditation for those test categories.

13.9.5 Samples to be picked-up by a local laboratory or courier service are to be placed in appropriate coolers and packed for shipment (e.g. use bubble bags, Ziploc® bags, ice as required, etc.) by the client services department. ALS Laboratory Group personnel relinquishing the samples must sign the chain of custody and ensure a copy is maintained for record keeping.

13.10 Internal Chain of Custody (ICOC) Procedures:

13.10.1 All internal sample transfer must be documented in the sample transfer module.

13.10.2 Once samples are placed in that designated area, removal and eventual return of samples must be documented using LIMS tracking module. The LIMS electronically records sample transfer within the laboratory by use of barcode scanner of manual sample transfer in LIMS.

13.10.2.1 Lab will tack transfer to satellite storage location, to long term storage and final sample disposal.

13.10.3 This report must be include in final report if requested by client.

13.11 Samples Compositing

13.11.1 Unless instructed by client with written compositing procedure, ALS will composite samples based on equal weights or volumes. When compositing sample, bear in mind the total volume or weight needed for the requested tests and adjust volumes and weight accordingly. Document weight and volume in composting logbook. When using weight, balance used must be identified. Exception is the VOA samples, all VOA sample will be composited by the analyst and not in Login.

13.12 CREATE "WORK ORDER"

13.12.1 Return to "Work orders" and [Add] new Work Order. [Add] is located in upper right hand corner of screen under [File].

13.12.2 Once the new work order is created, type in the client's ID and choose log-in using one of the following methods:

13.12.2.1 "Project" - test codes, reporting requirements, pricing are set-up for log-in by the assigned project manager

13.12.2.2 "Quote" - test codes and pricing are set-up by the marketing department

13.12.2.3 Note: "Project" is used as much as possible and must be set-up prior to log-in.

13.12.3 Enter "Report To" and "Project Information"

13.12.4 Enter "Laboratory Project Manager" and "Sales Person"

13.12.5 Enter required "QC level" and any required "Comments" for the Project Manager.

13.12.6 Enter "Received" date & time and the required "Turnaround Time"

13.12.7 Note: "REPORT OPTIONS" and "INVOICE INFO" should be built into "Project".

13.13 LOG-IN SAMPLES – entries are from the information provided by a client chain-of- custody, etc.

13.13.1 Go to [LOGIN] icon

13.13.2 Enter "Client Sample ID", as stated on client chain-of- custody, etc.

13.13.3 Enter "Collection Date/Time", client chain-of- custody, etc.
13.13.4 Enter "Matrix" type (e.g. water, soil, etc.)
13.13.5 Enter "Bottle Type" (choose from database of bottle types stored in LIMS)
13.13.6 Enter number of containers per fraction (this number is required to assure a label is printed for each container submitted).
13.13.7 Enter "Location" (database of sample storage locations is maintained in the LIMS configuration, designate TRAY which corresponds to specific coolers.)
13.13.8 Enter any "Comments" for laboratory personnel – these appear on analysts' backlogs
13.13.9 Enter appropriate "SA Code" (Sample Code – e.g. N = normal client sample, FB = Field Blank, RB = Rinse Blank, etc.)
13.13.10 If sample and sampler information in needed on final report Go to FIELD Info tab to document sampler's name & pH of preserved samples (e.g. <2 or >12), sample depth, etc.

13.14 ASSIGN TESTS to each sample or sample fraction
13.14.1 Enter TEST. If a Project is available, only applicable TestGroup for the project will appear. If not, entire test list is provided.
13.14.2 Bottles should be logged-in as separate fractions based on their preservative types or sample container type and volume.
13.14.3 After one sample has been created, MULTILOG can be used to replicate information for remaining samples. Only the SAMPLE ID and COLLECTED date/time have to be entered. All other information will be copied including analyses. If samples are to be logged-in for different analyses, MULTILOG may or may not be an efficient entry approach, depending on the complexity of the log-in.
13.14.4 A Grid may also be created "AUTO CREATE SAMPLE LIST GRID" if samples are identified in a sequential order (e.g. MW-1, MW-2, MW-3).
13.14.5 [POST] after all samples have been created to add samples to W.O.

13.15 LABEL SAMPLES & COMPLETE DOCUMENTATION
13.15.1 PRINT LABELS for all samples.
13.15.1.1 Initial "Logged By' on the SCR and give label to another technician who will be labeling the sample.
13.15.2 Complete the "Checklist", answering all questions, listing any discrepancies, and documenting cooler temperatures.
13.15.3 Print Rush/Short Hold Form as needed for all applicable laboratory departments.
13.15.4 Upon completion, if it ideal to get second staff member to review sample to ensure proper labeling.
13.15.5 RUN WO Check to check for anomaly found by LIMS made during Login, such as sampling date after receipt, wrong year, etc.
13.15.6 Sample Labeling
13.15.6.1 During the labeling process, check printed labels against information on sample container to ensure sample labels are correct.

14) Quality Control, Acceptance Criteria and Corrective Action

14.1 Please see the corrective action SOP CE-QA008 and HS-QS003 when issues or non-conformances arise.

14.2 Issues that arise pertaining to specific samples when received, are sent to the designated project manager to be resolved with the client.

15) Records Management

15.1 All data is stored for 5 years or longer if required.

15.2 Complete all pertinent sections in the respective logbooks. If not-applicable then line out the section and "Z" out or "X" out all large sections of the worksheet that are not used. Make all corrections with single line through, date and initial. Make NO obliterations when manually recording data.

15.3 Logbooks are controlled. Never remove a page from a logbook. Completed logbooks are returned to the QA department when filled and no longer needed in the work area.

16) Contingencies for Handling Out of Control Data

16.1 When sample preservation or thermal preservation does not method specification corrective action must be implement such as additional preservation added. In case of thermal preservation exceedance, the project manager should be notified so that the client can be contacted before proceeding with sample login.

16.2 Project Managers (PM) must be contacted for sample received in improper sample containers, Chain-of-Custody issue such as ID, signatures, broken containers, samples out of hold or out of temperature and all other issue relevant to proper sample custody.

17) Method Performance

17.1 Not Applicable to this SOP

18) Training

18.1 Training outline

18.1.1 Review literature (see references section). Read and understand this SOP. Also review the applicable SDS for all reagents and standards used. Following the reviews, observe the procedure as performed by an experienced analyst at least three times.

18.1.2 The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

18.2 Training is documented following *SOP CE-QA003*).

18.3 When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to

competently perform the analysis independently.

19) Summary of Changes

Table 20.1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
10.7	08/03/2020	G. Moulton	Added Sec1and 2: scope and applicability, and Identification of the method.
10.7	08/03/2020	G. Moulton	Sec 3.2: updated the ID for the sample disposal SOP SHWD-001.
10.7	08/03/2020	G. Moulton	Sec 8: added interferences.
10.7	08/03/2020	G. Moulton	Sec 14: Updated to include NCAR and corrective action SOPs.
10.7	08/03/2020	G. Moulton	Section 18: Included training.
10.7	08/03/2020	G. Moulton	Sec 20.7.3: updated reference section with the updated waste disposal policy.
10.6	10/30/2018	G. Moulton	Added new QA Manager on headers and cover. Updated new cover format.
10.6	10/30/2018	G. Moulton	Modified sections. 2.8, 12.2.2, 12.4.7, 12.4.8, 12.5.4.3, 12.5.4.4, 12.6.7, 12.10 to 12.12.1, 12.15.3, 18.1, 18.2, 21.1, 21.2, 21.6.3
10.6	10/30/2018	G. Moulton	Removed 7.2 to 7.3.4, 10.1
10.6	10/30/2018	G. Moulton	Added revised cooler receipt form
10.5 – Section 3	06/30/2017	T. Yen	Definition modified to reflect sample administration.
10.5- Section 12.2.4.4	06/30/2017	T. Yen	Document ALS cooler tracking number on SRC.
10.5 – sections 12.12 – 12.16	06/30/2017	T. Yen	LIMS Login procedure added.
10.5 – Sections 17 7 18	06/30/2017	T. Yen	Updated for LogIn procedures.
10.5 – Section 21	06/30/2017	T. Yen	References updated.
10.5 – Section 22	06/30/2017	T. Yen	Appendices updated
10.4 –	05/31/2015	T. Yen	New Lab Director.
10.4 – section 12.11	05/31/2015	T. Yen	Compositing procedure added

10.3	02/28/2015	T. Yen	New Department Supervisor.
10.3 – Section 12.4.5	02/28/2015	T. Yen	Chlorine checks by analyst prior to analysis.
10.3 – Section 12.6.4	02/28/2015	T. Yen	VOA vials must be stored in cooler or refrigerator if login will take longer than 20 minutes. If Login will take longer than one hour all samples must be move to walk until issues are resolved.
10.3 – Section 12.9	02/28/2015	T. Yen	Subsampling of samples, bottle lots and preservative must be tracked.
10.3 – Section 21	02/28/2015	T. Yen	Update reference sources – such as DOD Rev 5.0, TNI 2009, etc.
10.3 – Section 22	02/28/2015	T. Yen	Updated Appendices,
10.2	10/15/2013	T. Yen	New Format and Signature Page – New Department Supervisor, QA Manager and Lab Director.
10.2 – Section 2.8	10/15/2013	T. Yen	Internal sample tracking/transfer feature in LIMS must be used to document sample transfer within the lab.
10.2 – Section 12.6.6	10/15/2013	T. Yen	New procedure to place sample from same workorder in storage box(es) label with wordorder ID.
10.2 – Section 12.10	10/15/2013	T. Yen	Internal tracking module must be used for all samples when removed from cooler.
10.2 – Section 17	10/15/2013	T. Yen	Added documentation, record retention and effective date of SOP.
10.2 – Section 21.1	10/15/2013	T. Yen	Update reference sources – such as DOD Rev 5.0, TNI 2009, etc.
10.2 – Section 21.1	10/15/2013	T. Yen	Update reference sources – such as DOD Rev 5.0, TNI 2009, etc.
10.1	07/15/2012	J. Cady	Minor revision. Format/font change. Amendment additions.
10.0	09/01/2011	J. Cady	Major document revision.

20) References and Related Documents

20.1 Current TNI Standards.

20.2 Current Department of Defense Quality Systems Manual.

20.3 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Method 5030C, Purge-and-Trap for Aqueous Samples, U.S. Environmental Protection Agency, Revision 3, SW846, USEPA 2003.

20.4 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Method 5035A, Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste

20.5 Samples. U.S. Environmental Protection Agency, Revision 1, 2002.

20.6 Method 1664, Revision B, N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry. U.S. Environmental Protection Agency, EPA-821-R-10-001, February 2010.

20.7 Related Documents

20.7.1 HS-QS-008, Container Sub-Sampling for Metals and Semivolatile Organics, current revision

20.7.2 HS-QS-010, Subsampling for Volatile Organic Compounds, current revision.

20.7.3 SHWD-001, Waste Disposal Procedures

21) Appendix

21.1 Chain of Custody

☐ ALS Laboratory Group
10450 Stancliff Rd. #210
Houston, Texas 77099
(Tel) 281.530.5656
(Fax) 281.530.5887

Chain of Custody Form

Page _____ of _____

☐ ALS Laboratory Group
3352 128th Avenue
Holland, Michigan 49424
(Tel) 616.399.6070
(Fax) 616.399.6185

ALS Project Manager: | Work Order #:

Customer Information		Project Information		Parameter/Method Request for Analysis	
Purchase Order		Project Name		A	
Work Order		Project Number		B	
Company Name		Bill To Company		C	
Send Report To		Invoice Attn.		D	
Address		Address		E	
				F	
City/State/Zip		City/State/Zip		G	
Phone		Phone		H	
Fax		Fax		I	
e-Mail Address		e-Mail Address		J	

No.	Sample Description	Date	Time	Matrix	Pres.	# Bottles	A	B	C	D	E	F	G	H	I	J	Hold
1																	
2																	
3																	
4																	
5																	
6																	
7																	
8																	
9																	
10																	

Sampler(s): Please Print & Sign | Shipment Method: | Required Turnaround Time: ☐ STD 10 Wk Days ☐ 5 Wk Days ☐ 2 Wk Days ☐ 24 Hour ☐ Other _____ | Results Due Date:

Relinquished by:	Date:	Time:	Received by:	Notes:
Relinquished by:	Date:	Time:	Received by (Laboratory):	Cooler Temp.
Logged by (Laboratory):	Date:	Time:	Checked by (Laboratory):	

QC Package: (Check Box Below)
- ☐ Level II: Standard QC — ☐ TRRP-Checklist
- ☐ Level III: Std QC + Raw Data — ☐ TRRP Level IV
- ☐ Level IV: SW846 CLP-Like
- ☐ Other: _____

Preservative Key: 1-HCL 2-HNO3 3-H2SO4 4-NaOH 5-Na2S2O3 6-NaHSO4 7-Other 8-4 degrees C 9-5035

Note: Any changes must be made in writing once samples and COC Form have been submitted to ALS Laboratory Group.

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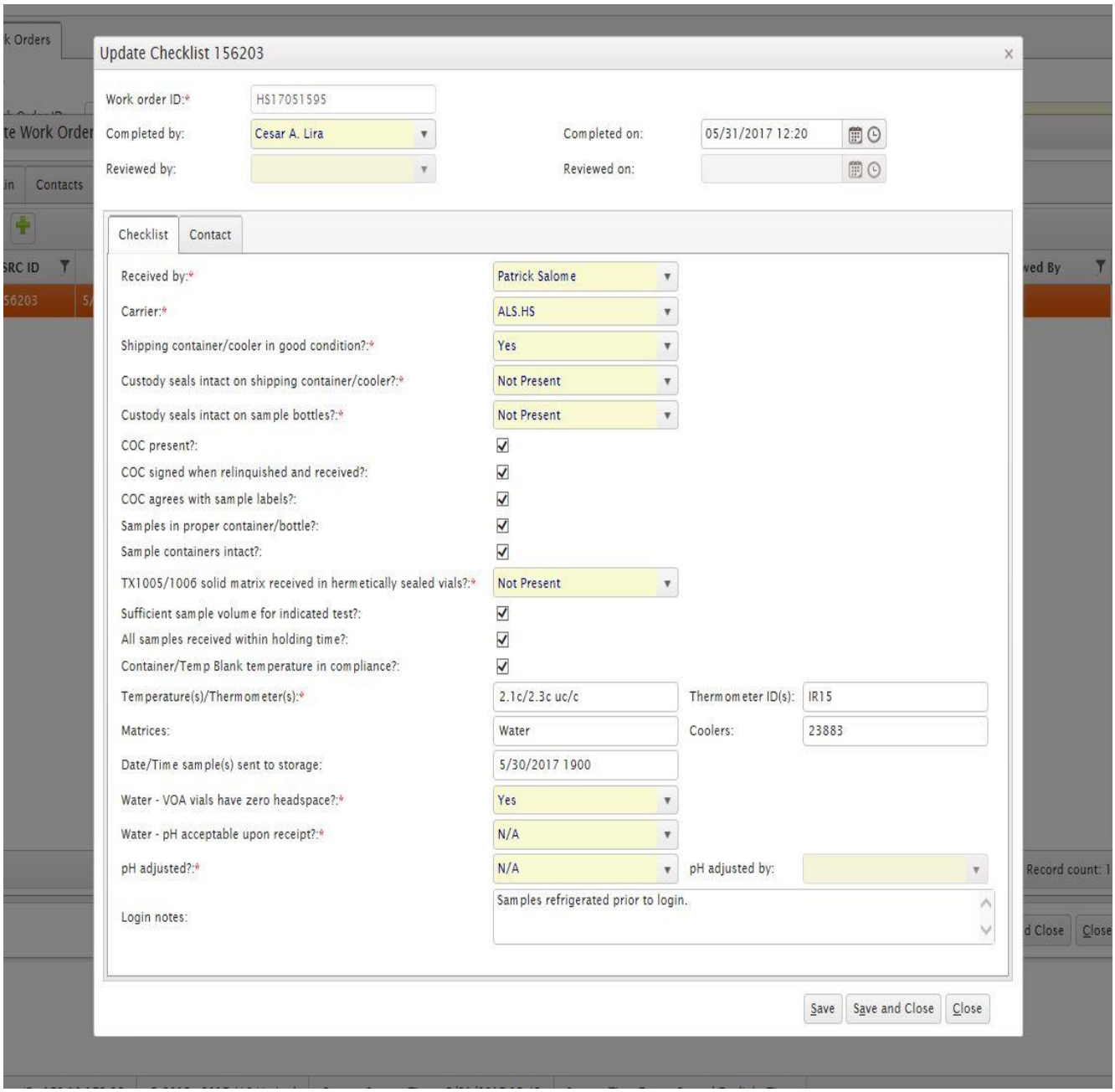
21.2 Sample Receipt Checklist



10450 Stancliff Road, Suite 210
Houston, TX 77099
T: +1 281 530 5656
F: +1 281 530 5887
www.alsglobal.com

Client: _____ Date: _____ WO#:_____

Time Received: _____ Received by: _____ BO#:_____

Matrices: Solid/Sludge Water Oil Wipes Hydrocarbon Liquid Other

Kit ID/Cooler ID	Trip Blank ID	Cooler Temp (C) Observed/Corrected	IR #	Temp BLK Present?
		/		Y N
		/		Y N
		/		Y N
		/		Y N
		/		Y N

Delivery Method: FedEx UPS Greyhound ALS Client Other_____

Date/Time of Unpacking: _____ Unpacked by: _____

Shipping container/cooler in good condition?	Yes	No	Not Present	
Custody seals intact on shipping container/cooler?	Yes	No	Not Present	
Custody seals intact on sample bottles?	Yes	No	Not Present	
Chain of Custody present?	Yes	No		
Chain of Custody signed when relinquished and received?	Yes	No		
Chain of Custody – Sampler's name present?	Yes	No		
Chain of Custody agrees with sample labels?	Yes	No		
Samples in proper container/bottle?	Yes	No		
VOA/TX1005/1006 Solids in hermetically Sealed Vials:	Yes	No	No VOA/TX1005/1006 Solid	
Sample containers intact?	Yes	No		
Sufficient sample volume for indicated test?	Yes	No		
All samples received within holding time?	Yes	No		
Container/Temp Blank temperature in compliance?	Yes	No		
Water - VOA vials have zero headspace?	Yes	No	N/A	No VOA submitted
Non-VOA waters preserved with HCl, H2SO4, HNO3 are pH <2?			Yes	No N/A
Waters preserved with NaOH/Ascorbic acid are pH>12?	Yes	No	N/A	
pH adjusted? Yes*	No	N/A	*See Preservation Logbook	

pH adjusted by: _____ **pH Paper Lot:** _____

RIGHT SOLUTIONS | RIGHT PARTNER

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Houston, TX 77099
T: +1 281 530 5656
F: +1 281 530 5887
www.alsglobal.com

Login Notes: _____

_____

_____

_____

_____

Client Contacted: _____ ___ Date Contacted: _____

Person Contacted: _____ Contacted By: _____

Regarding: _____

_____

Comments: _____

_____

_____

_____

Corrective Action: _____

_____

_____

_____

Logged by: _____

Labelled by: _____

Scanned by: _____

PM Review: _____

RIGHT SOLUTIONS | RIGHT PARTNER

21.3 Sample Acceptance Policy

Sample Acceptance Policy

Samples for which the laboratory is not suitably equipped and which pose a potential health and/or safety threat to laboratory staff (such as radioactive material, phosgene, vinyl chloride monomer, etc.) will not be accepted. These samples will be returned or, pending client instruction, forwarded to a different facility.

Samples requiring legal or evidentiary custody will not be accepted due to the required specialized handling, storage, and documentary procedures.

Samples received without a chain-of-custody or with an incomplete chain-of-custody will be retained* but not accepted until the missing information has been obtained. Upon receipt of the completed chain-of-custody, samples will be accepted.

The laboratory will accept samples received outside of normal EPA sampling guidelines for hold time, preservation, and/or container type. However, samples will not be processed until the anomaly has been resolved via contact between the client and the project manager.

The laboratory will provide multiple containers for collection of specified Quality Control (QC) samples, strongly recommends their use, and cautions that failure to provide sufficient QC volume may jeopardize data validation in the event of regulatory review and/or litigation. In the event that insufficient sample volume is submitted, the laboratory will process samples as requested but will not assume liability for any missing and/or incomplete QC criteria resulting from insufficient sample volume. The laboratory will make every reasonable effort to ensure that the required QC samples are processed and analyzed.

Samples with composite requirements will be accepted and processed according to the guidelines documented in the laboratory's procedures for container subsampling, HS-QS008.

* Acceptance is defined as assuming custodial responsibility for sample submittals.

Retained is defined as holding submittals in a secure facility without assuming custodial responsibility.
ALS reserves the right to refuse any samples.

21.4 Sample Handling Guide

Sample Handling Guidelines

Inorganic Parameters									
		WATER				SOIL			
Parameters	Method	Preservative	Holding Time	Container	Min. Volume*	Preservative	Holding Time	Container	Min. Volume*
Acidity	E305.1, SM2310B	≤6°C	14 Days	250 mL / P,G	50 mL	≤6oC	N/A	4 oz WMG	20g
Alkalinity	E310.1, SM2320B	≤6oC	14 Days	250 mL / P,G	50 mL	N/A	N/A	N/A	20g
Ammonia	SM4500NH3 B, F & D	≤6oC, H2SO4 to pH <2	28 Days	250 mL / P,G	50 mL	≤6oC	28 Days	4 oz WMG	20g
Anions- Sulfate, Bromide, Chloride, Fluoride	E300, SW9056 A	≤6oC	28 Days	125 mL / P,G	10 mL	≤6oC	28 Days**	4 oz WMG	10g
Anions- Nitrate, Nitrite, Phosphate, Ortho	E300.0, SW9056A	≤6oC	48 Hours	125 mL / P,G	10 mL	≤6oC	48 Hours**	2 oz WMG	20g
Anions - Nitrate-Nitrite	E300.0, SW9056A	≤6oC, H2SO4 to pH <2	28 Days	125 mL / P,G	10 mL	≤6oC	28 Days**	2 oz WMG	20g
Biochemical Oxygen Demand (BOD)/ Carbonaceous BOD (CBOD)	E405.1, SM5210B	≤6oC	48 Hours	1000 mL / P,G	500 mL	N/A	N/A	N/A	N/A
Burn Rate	SW1030	N/A	N/A	N/A	N/A	≤6oC	28 Days	4 oz WMG	30g
Chemical Oxygen Demand (COD)	E410.4, HACH8000	≤6oC, H2SO4 to pH <2	28 Days	125 mL / P,G	10 mL	N/A	N/A	N/A	N/A
Chlorine, Residual	SM4500-Cl F	≤6oC	15 minutes	125 mL / P,G	100 mL	N/A	N/A	N/A	N/A
Chromium VI (Hexavalent Cr)	SM3500-Cr, SW7196	≤6oC	24 Hours	250 mL / P,G	50 mL	≤6oC	24 H from Pr	4 oz WMG	20g
Color	E110.2, SM2120 B	≤6oC	48 Hours	250 mL / P,G	50 mL	N/A	N/A	N/A	N/A
Cyanide, Total & Cyanide, Amenable	E335.2, E335.3, E335.4, SW9010, SW9012, SW9014	≤6oC, NaOH to pH >12, Ascorbic Acid	14 Days	250 mL / P,G	50 mL	≤6oC	14 Days	4 oz WMG	20g
Ferrous Iron	SM3500FE B	≤6oC, HCL	48 hours	250 mL / P,G	50 mL	≤6oC	14 Days	4 oz WMG	20g
Flashpoint	SW1010A	≤6oC	28 Days	500 mL / P,G	80 mL	N/A	N/A	N/A	N/A
Fluoride	E 4500-F BC	≤6oC	28 Days	125 mL / P	10 mL	≤6oC	28 Days**	4 oz WMG	20g
Hardness	SM2340 B	≤6oC, HNO3 to pH <2	6 Months	250 mL / P,G	100 mL	≤6oC	6 months	2 oz WMG	N/A
Metals	E200.8, SW6020A	HNO3 to pH <2	6 Months	250 mL / P, G	100 mL	≤6oC	6 Months	2 oz WMG	20g
Metals (Dissolved-not field filtered)	E200.8, SW6020A	HNO3 to pH <2	2 days to filter	250 mL / P, G	100 mL	N/A	N/A	N/A	N/A
Mercury	E245.1, SW7470A, SW7471B	HNO3 to pH <2	28 Days	250 mL / P,G	40 mL	≤6oC	28 Days	2 oz WMG	20g
Nitrogen, Kjeldahl (TKN)	E351.3, SM4500-NH3 D	≤6oC, H2SO4 to pH <2	28 Days	250 mL / P,G	25 mL	≤6oC	28 Days	2 oz WMG	20g
Oil and Grease	E1664A, E1664B, SW9070A, SW907	≤6oC, H2SO4/HCL to pH<2	28 Days	1000 mL / WMG	1000 mL ***	≤6oC	28 Days	2 oz WMG	20g
Phenolics	E420.1, E420.4, SW9065, SW9066	≤6oC , H2SO4 to pH <2	28 Days	250 mL / G, Amber	50 mL	≤6oC	28 Days	2 oz WMG	20g
Phosphorous, Total	E365.3	≤6oC, H2SO4 to pH <2	28 Days	250 mL / P,G	50 mL	≤6oC	28 Days**	2 oz WMG	20g
Phosphate, Ortho	E365.3	≤6oC	48 Hours	250 mL / P,G	50 mL	≤6oC	48 Hours**	2 oz WMG	20g
pH	E150.1, SM4500-H+B SW9040C, SW9045D	≤6oC	15 minutes	125 mL / P,G	25 mL	≤6oC	48 Hours**	2 oz WMG	20g
Silica	SM4500-SiD	≤6oC	28 Days	100 mL / P	50 mL	≤6oC	28 Days**	2 oz WMG	20g
Solids, Dissolved (TDS)	E160.1, SM2540 C	≤6oC	7 Days	250 mL / P,G	50 mL	N/A	N/A	N/A	N/A
Solids, Suspended (TSS)	E160.2, SM2540 D	≤6oC	7 Days	1000 mL / P,G	1000 mL	N/A	N/A	N/A	N/A
Solids, Volatile (TVS)	E160.4	≤6oC	7 Days	250 mL / P,G	50 mL	N/A	N/A	N/A	N/A
Solids, Total (TS)	E160.3, SM2540 B	≤6oC	7 Days	250 mL / P,G	50 mL	N/A	N/A	N/A	N/A
Specific Conductance	E120.1, SM9050	≤6oC	28 Days	250 mL / P,G	50 mL	N/A	N/A	N/A	N/A
Sulfide	E376.1, SM4500 S F, WS 9030	≤6oC, ZnAc, NaOH to pH >9	7 Days	500 mL / P,G	200 mL	≤6oC, ZnAc to moist	7 Days	2 oz WMG	20g
Sulfite	377.1, 4500SO3B	≤6oC	15 minutes	250 mL / P,G	100 mL	≤6oC	48 Hours**	2 oz WMG	20g
Surfactants (MBAS)	425.1, 5540C	≤6oC	48 Hours	500 mL / G	400 mL	N/A	N/A	N/A	N/A
Total Organic Carbon (TOC)	E415.1, SW9060, Walkley Black(S)	≤6oC, H2SO4/HCl to pH<2	28 Days	2 x 40 ml vials	40 mL	≤6oC	28 Days	2oz WMG	20g
Turbidity	E180.1	≤6oC	48 Hours	250 mL / P,G	50 mL	N/A	N/A	N/A	N/A
LA29B	N/A	N/A	N/A	N/A	N/A	≤6oC		32oz WMG	500 g

* Please note the minimum volume should be used only in limited sample situations.
** Soil/Sludge holding time for anions is based upon aqueous HT and the time of preparation of aqueous deionized water leachate (10x typical) from the submitted soil/sludge.

Organic Parameters

		WATER				SOIL			
Parameters	Method	Preservative	Holding Time	Container	Min. Volume	Preservative	Holding Time	Container	Min. Volume
TPH---Texas Method	TX1005 and TX1006	≤6oC, HCl to pH <2	14 / 14 Days	3 x 40 mL	3 x 40 mL VOA	≤6oC or <-10oC	14 / 14 Days	2 oz WMG or Terra Core Kit	10g
Total Petroleum Hydrocarbons***	SW8015C	≤6oC	7 / 40 Days	2 x 1000 mL - Amb	1000 mL or calc on avail.	≤6oC	14 / 40 Days	8 oz WMG	30g
DRO, ORO Low Volume***	SW8015C	≤6oC	7 / 40 Days	3 x 40 mL / G-Amb	1 x 40 mL / G-Amb	N/A	N/A	N/A	N/A
DRO, ORO***	SW8015C	≤6oC	7 / 40 Days	2 x 1000 mL / G-Amb	1000 mL or calc on avail.	≤6oC	14 / 40 Days	4 oz WMG	30g
GRO**	SW8015C	≤6oC, HCl to pH <2	7 / 14 Days	3 x 40 mL VOA	1 x 40 mL VOA	≤6oC	14 Days	2 oz WMG	5g
GRO**	SW8015C/SW5035A	N/A	N/A	N/A	N/A	<-10oC	14 Days	Terra Core Kit /3 -Encore	5g
Methane, Ethane, Ethene	RSK-175	≤6oC, HCl to pH <2	7 / 14 Days	3 x 40 mL VOA	1 x 40 mL VOA	N/A	N/A	N/A	N/A
Glycols	SW8015C	≤6oC	14 Days	3 x 40 mL VOA	1 x 40 mL VOA	≤6oC	14 Days	4 oz WMG	30g
Explosives***	SW8330A/B	≤6oC	7 / 40 Days	2 x 1000 mL / G - Amb	1000 mL or calc on avail.	≤6oC	14 / 40 Days	4 oz WMG	30g
BTEX / MTBE**	SW8021B	≤6oC, HCl to pH <2	7 / 14 Days	3 x 40 mL VOA	1 x 40 mL VOA	≤6oC	14 Days	2 oz WMG	5g
BTEX / MTBE	SW8021B/SW5035A	N/A	N/A	N/A	N/A	<-10oC	14 Days	Terra Core Kit /3 -Encore	5g
Volatile Organics**	E624, SW8260C	≤6oC, H2SO4/HCl to pH <2	7 / 14 Days	3 x 40 mL VOA	1 x 40 mL VOA	≤6oC	14 Days	2oz WMG	5g
Volatile Organics	S8260C/SW5035A	N/A	N/A	N/A	N/A	<-10oC	14 Days (5035A)*	Terra Core Kit /3 -Encore	5g
Organochlorine Pesticides****	E608, SW8081B,	≤6oC, pH 5-8	7 / 40 Days	2 x 1000 mL / G-Amb	1000 mL or calc on avail.	≤6oC	14 / 40 Days or 1 year	4 oz WMG	30g
PCB *****	E608, SW8082A	≤6oC	7 / 40 Days	2 x 1000 mL / G-Amb	1000 mL or calc on avail.	≤6oC	14 / 40 Days or 1 year	4 oz WMG	30g
PCB Wipe	40CFR Part 761/8082	N/A	N/A	N/A	N/A	C6 (Hexane)	7 / 40 Days	250ml or 500 ml G jar	N/A
Organophosphorous Pesticides****	SW8270D	≤6oC	7 / 40 Days	2 x 1000 mL / G-Amb	1000 mL or calc on avail.	≤6oC	14 / 40 Days	4 oz WMG	30g
EDB, DBCP****	SW8011	≤6oC, H2SO4/HCl to pH <2	7 / 14 Days	3 x 40 mL VOA	1 x 40 mL / G-TLS	N/A	N/A	N/A	N/A
Chlorinated Herbicides****	SW8151A	≤6oC	7 / 40 Days	2 x 1000 mL / G-Amb	1000 mL or calc on avail.	≤6oC	14 / 40 Days	4 oz WMG	30g
Polynuclear Aromatic Hydrocarbons****	SW8270D	≤6oC	7 / 40 Days	2 x 1000 mL / G-Amb	1000 mL or calc on avail.	≤6oC	14 / 40 Days	4 oz WMG	30g
SVOC (Base/Neutrals/Acids)****	E625, SW8270D	≤6oC	7 / 40 Days	2 x 1000 mL / G-Amb	1000 mL or calc on avail.	≤6oC	14 / 40 Days	4 oz WMG	30g
Formaldehyde	SW8315	≤6oC	3 Days	1000 mL / G	500 mL	≤6oC	3 Days	4 oz WMG	20g
Dioxins and Furans	E1613, SW8280, SW8290,	≤6oC	30/45 Days	2 x 1000 mL / G-Amb	1000 mL or calc on avail.	≤6oC	14 / 40 Days	4 oz WMG	30g
Reactive Sulfide and Cyanide[1]	SW-846, Caphater 7	≤6oC	28 Days	125 mL / P,G	5g	≤6oC	28 Days	2 oz WMG	5g

*Must be frozen or preserved within 48 hours of collection; **Holding time - 7/14 days - not preserved/ preserved; *** Holding time - 7/14/14 days - not preserved/preserved/after extracted; **** Holding time - 7/40 days - not preserved/after extracted

***** Holding time - 7/40 days or 1 year (chek state reg)

[1]Samples anlayzed by ALS Michigan

TCLP Parameters

Parameters	Holding Time from Collection to TCLP Extraction	Preservative	Holding Time from TCLP Extraction to Preparative Extraction	Holding Time from TCLP/Preparative Extraction to Analysis	Total Elapsed Time
Volatiles	14 Days	≤6oC	Not Applicable	14 Days	28 Days
Semivolatiles	14 Days	≤6oC	7	40 Days	61 Days
Organochlorine Pesticides and PCBs	14 Days	≤6oC	7	40 Days	61 Days
Chlorinated Herbicides	14 Days	≤6oC	7	40 Days	61 Days
Organophosphorous Pesticides	14 Days	≤6oC	7	40 Days	61 Days
Mercury	28 Days	≤6oC	Not Applicable	28 Days	56 Days
Metals	180 Days	≤6oC	Not Applicable	180 Days	360 Days

Acronym Definitions

CLP - Contract Laboratory Program	H - Hours
G - Glass	D - Days
V-TLC - Glass Vial Teflon-lined Cap	M - Months
V-TLS - Glass Vial Teflon-lined Septum	T - TCLP
P - Polyethylene	Pr - Prep. Extraction
Amb - Amber	A - Analysis
WMG - Wide Mouth Glass Jar	C - CLP

ALS Analytical
10450 Stancliff Road, Suite 210
Houston, Texas 77099
281.530.5656 www.alsglobal.com 281.530.5887 (Fax)

Preservative

H_2SO_4 - Sulfuric acid
HNO_3 - Nitric acid
HCl - Hydrochloric acid
NaOH - Sodium Hydroxide
ZnAc - Zinc acetate
Asca - Ascorbic Acid
$NaHSO_4$ - Sodium bisulfate

21.5 Storage Area

Sample Storage Areas			
Storage Area	Description	Storage Area	Description
Long Term Storage	El Giante Walk-in Refrig	Sample Receiving	Long Term Storage
NSS	NSS	Sample Receiving	Nasty Sample Storage
Large Freezer	Walk-in Freezer	Sample Receiving	TX1005 Solid/5035
Foreign Refrig	Foreign Soil Refrigerator	Sample Receiving	Foreign and Regulated Soil
Small Walk IN	Walk-in Refrig	Sample Receiving	DRO/RSK/Gylcol
VOA WalkIn	VOA Walk-In	VOA Lab	VOA Long Term Storage.
VOA	Reach In Cooler	VOA Lab	VOA/GRO/BTEX Storage
Nasty Sample Storage (NSS)	Sample Refrigerator	Sample Receiving	VOA, GRO
SPA	Reach In Cooler	Extraction	Solid sample
Client Service	Reach In Cooler	LogIn	Temporary holding during LogIn
WET	Reach In Cooler	WET CHEM	Samples Storage
Metals	Shelf	Metals	Aqueous Metals Storage

21.6 Bottle and Cooler Custody Seals and Shipping Labels

Quality Seal of Excellence

ALS Environmental
10450 Stancliff Rd., Suite 210
Houston, Texas 77099
Tel: +1 281 530 5656

To: _____

Project #: _____

Deliver By: _____

Cooler ____ Of ____

Prepared By: _____ Initial and Date

Validated By: _____ Initial and Date

* Please review contents if seal has been broken *

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Pennsylvania • Texas • Utah • Washington • West Virginia

S-13730 ULINE 1-800-295-5510

ALS Environmental
10450 Stancliff Rd., Suite 210
Houston, Texas 77099
Tel. +1 281 530 5656
Fax. +1 281 530 5887

CUSTODY SEAL

Date: _____ Time: _____
Name: _____
Company: _____

Seal Broken By:

Date:

21.7 How to Complete SRC for Sample ID Discrepancies

ALS Group USA, Corp.
ALS Services USA, Corp.
ALS Industrial USA, LLC.
10450 Stancliff Road, Suite 210
Houston, TX 77099
T +1 281 530 5656 F +1 281 530 5887

How to document descriptive discrepancies between
Chain of Custody form (COC) and the **Sample Label/Matrix**

1. Containers should always unpack in sequential order based on the Sample Description that is listed on the COC.

2. If there are any discrepancies between the COC or Label/Matrix, these should be documented in the Login Notes on Page 2 of Sample Receipt Checklist (SRC).

Example:

10450 Stancliff Road, Suite 210
Houston, TX 77099
T: +1 281 530 5656
F: +1 281 530 5887
www.alsglobal.com

Login Notes: _____

2. The format for all Login Notes should be as follows:

Sample ID	COC	Label/Matrix
FGH-23	5/23/2017	5/24/2017
FGH-24	10:01 am	10:03 am
FGH-25	Solid	Water

- The sample should always under the correct matrix. If you are unsure if the Matrix is a solid, liquid, bi-phase or product (Solvent/Oil) – please talk to your Project Manager/Supervisor for guidance.

LIMS LOGIN PROCEDURE

DOCUMENT ID: HS-SM003, REV 4.3

Approved By: _____ Date: 11/18/18

Department Supervisor, Rajen Giga

Approved By: _____ Date: 11/20/18

Technical and Laboratory Director, Hoai Van

Prepared By: _____ Date: 11/20/2018

Quality Assurance Manager, Erica Howard

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2) Summary of Procedure 3
3) Definitions 3
4) Personnel Qualifications and Responsibilities 3
5) Procedure 4
6) Quality Assurance and Quality Control 5
7) Summary of Changes 5
8) References and Related Documents 6

LIMS LOGIN PROCEDURES

1) Scope and Applicability

1.1 The objective of this procedure is to provide a summary of the steps that are followed for logging samples received into LIMS (a Laboratory Information Management System).

2) Summary of Procedure

2.1 Samples are logged into the LIMS.

2.2 Client Services Login Personnel have assigned security rights granted by the IT Manager to perform entries of sample information associated with the samples received at the laboratory for testing.

2.3 Project Management Personnel have assigned security rights granted by the IT Manager to both perform entries of sample information associated with the samples received at the laboratory for testing and review the entries for correctness against information (chain of custody, etc.) before releasing samples for processing (preparation and analysis).

3) Definitions

3.1 COC: Chain of Custody

3.2 ICOC: Internal Chain of Custody

3.3 WO: Work Order

3.4 PM: Project Management

3.5 SA: Sample Administration (or equivalently stated, client services or sample management (SM).

3.6 Recommended Holding Time: The length of time after sample collection during which analysis should be performed to produce data of known quality.

4) Personnel Qualifications and Responsibilities

4.1 General Responsibilities - This method is restricted to use by or under the supervision of analysts experienced in the method.

4.2 Analyst - It is the responsibility of the analyst(s) to:

4.2.1 Read and understand this SOP and follow it as written. Any deviations or nonconformances must be documented and submitted to the QA Manager for approval.

4.3 Section Supervisor - It is the responsibility of the section supervisor to:

4.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.

4.4 Project Manager - It is the responsibility of the Project Manager to ensure that all method requirements for a client requesting this procedure are understood by the laboratory prior to initiating this procedure for a given set of samples.

4.5 QA Manager: The QA Manager is responsible for

4.5.1 Approving deviations and nonconformances

4.5.2 Ensuring that this procedure is compliant with method and regulatory

requirements,

4.5.3 Ensuring that the analytical method and SOP are followed as written through system audits.

4.6 Only individuals that have been trained in the basic use of LIMS, SOPs SM001 and SM002 (current revisions) can perform sample Login using LIMS.

5) Procedure

5.1 LIMS COOLER TRACKING/CHECK-IN

5.1.1 Find the "SAMPLE RECEIPTCHECKLISTFORM", located under the "ChkList" tab and check your coolers by including your coolers numbers in the form, or

5.1.2 Find cooler ID in "COOLER TRACKING", located under OPERATIONS (Cooler Inventory is maintained in "Bottle Orders".

5.1.3 Enter the Bottle Order No. in the "LOCATION" field (Cooler must be checked out when preparing bottle orders).

5.2 CREATE "WORK ORDER"

5.2.1 Return to "Work orders" and [Add] new Work Order. [

5.2.2 Once the new work order is created, type in the client's ID and choose log-in using one of the following methods:

5.2.2.1 "Project" - test codes, reporting requirements, pricing are set-up for log-in by the assigned project manager

5.2.2.2 "Quote" - test codes and pricing are set-up by the marketing department

5.2.2.3 Note: "Project" is used as much as possible and must be set-up prior to log-in.

5.2.3 Enter "Report To" and "Project Information"

5.2.4 Enter "Laboratory Project Manager" and "Sales Person"

5.2.5 Enter required "QC level" and any required "Comments" for the Project Manager.

5.2.6 Enter "Received" date & time and the required "Turnaround Time"

5.2.7 Note: "REPORT OPTIONS" and "INVOICE INFO" should be built into "Project" (§ 5.2.2.2 or § 5.2.2.3).

5.3 LOG-IN SAMPLES – entries are from the information provided by a client chain-of-custody, etc.

5.3.1 Go to [LOGIN] icon

5.3.2 Enter "Client Sample ID", as stated on client chain-of- custody, etc.

5.3.3 Enter "Collection Date/Time", client chain-of- custody, etc.

5.3.4 Enter "Matrix" type (e.g. water, soil, etc.)

5.3.5 Enter "Bottle Type" (choose from database of bottle types stored in LIMS)

5.3.6 Enter number of containers per fraction (this number is required to assure a label is printed for each container submitted).

5.3.7 Enter "Location" (database of sample storage locations is maintained in the LIMS configuration, designated cooler and shelves, etc.)

5.3.8 Enter any "Comments" for laboratory personnel – these appear on analysts' backlogs.

5.3.9 Enter appropriate "SA Code" (Sample Code – e.g. N = normal client sample, FB = Field Blank, RB = Rinse Blank, etc.)

5.4 ASSIGN TESTS to each sample or sample fraction

5.4.1 Enter TEST. If a Project is available, only applicable tests for the project will appear. If not, entire test list is provided.

5.4.2 Bottles should be logged-in as separate fractions based on their preservative types or sample container type and volume.

5.4.3 After one sample has been created, MULTILOG can be used to replicate information for remaining samples. Only the SAMPLE ID and COLLECTED date/time have to be entered. All other information will be copied including analyses. If samples are to be logged-in for different analyses, MULTILOG may or may not be an efficient entry approach, depending on the complexity of the log-in.

5.4.4 A Grid may also be created "AUTO CREATE SAMPLE LIST GRID" if samples are identified in a sequential order (e.g. MW-1, MW-2, MW-3).

5.4.5 [POST] after all samples have been created to add samples to W.O.

5.5 LABEL SAMPLES & COMPLETE DOCUMENTATION

5.5.1 PRINT LABELS for all samples.

5.5.2 Complete the "Checklist", answering all questions, listing any discrepancies, and documenting cooler temperatures.

5.6 INTERNAL CHAIN OF CUSTODY (ICOC) – use only if client & project designated

5.6.1 ICOC record keeping is initiated for client samples as requested through PM. The ICOC records are then maintained electronically by LIMS.

5.6.2 SA confirms that a PM has made an ICOC request by checking for the designation in [WorkOrders\ ReportOptions\ ReqICOC].

5.6.3 After designation confirmation, SA prints unique barcode labels and attaches them to the designated samples associated with the ICOC. The barcodes are generated using BARCODE Code 128, which generates a unique barcode from each unique WO sample ID number. SA places bar-coded samples in an LIMS designated cooler storage location.

6) Quality Assurance and Quality Control

6.1 Project Management performs a login review and approval step of information entered for each project entered into LIMS.

7) Summary of Changes

Table7.1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
4.3	11/20/2018	G. Moulton	Updated the cover page and QA manager.
4.3	11/20/2018	G. Moulton	Removed sections: 4.3.2, 5.3.10, 5.5.3, 5.6.4-5.6.4.3.
4.3	11/20/2018	G. Moulton	Modified 5.2.1
04.2	03/15/2013	T. Yen	Signature Page – New Department Supervisor, QA Manager and Lab Manager.
04.2	03/15/2013	T. Yen	Document Footer – "A Campbell Brothers Limited Company" changed to "An ALS Limited Company" to reflect parent company name change.
04.2 –	03/15/2013	T. Yen	Section 5.1.4 Removed -Reference to

Section 5.1.4.			bottle order.
04.2 – Section 5.2.2.1.	03/15/2013	T. Yen	Section 5.2.2.1 Removed –Client Default used to create log-in form scratch. Projects must be created before login in.
04.1	02/15/2012	J. Cady	Minor document revision.
04.0	05/30/2011	I. Williams	Major template revision.

8) References and Related Documents

8.1 Refer to LIMS Reference Guide.

Alkalinity by Method SM2320B-EPA 310.1

DOCUMENT ID: HS-WC001, REV 8.4

Approved By: Hoai. Van
Technical and Laboratory Director, Hoai Van

Date: 03/05/2020

Prepared By: Erica H Marinez
Quality Assurance Manager, Erica Marinez

Date: 03/05/2020

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1) Identification of the Method

1.1 This procedure describes the titrimetric method for determining Total Alkalinity and associated forms as $CaCO_3$, by Standard Methods 2320B and EPA 310.1.

2) Applicable Matrix or Matrices

2.1 This titrimetric procedure is applicable to water samples and to deionized water leachates of soil samples.

3) Scope and Application

3.1 This procedure is based on Standard Methods 2320B and EPA 310.1. Standard Methods 2320B further describes the approach to measure and report the various alkalinity forms such as bicarbonate, carbonate or hydroxide (as $CaCO_3$) when present.

3.2 Alkalinity of water is its acid-neutralizing capacity. It is the sum of all treatable bases. The measured value may vary significantly with the end-point pH used. Alkalinity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known.

3.3 The applicable concentration ranges for this procedure are 0 to 20 mg/L (low level) and 20 to 1000 mg/L.

4) Summary of Procedure

4.1 An unaltered water sample is titrated with standard sulfuric acid (0.020 or 0.10 N) to the inflection points at pH 8.3 and pH 4.5 using a pH meter. The amount of titrant required to drop the pH to 8.3 is used to calculate the carbonate and hydroxide concentrations of a sample as the phenolphthalein alkalinity. The total amount of titrant required to continue to a final pH to 4.5 (the methyl orange alkalinity) is used to calculate the bicarbonate, carbonate and hydroxide forms as total alkalinity. Both endpoints must be measured in order to calculate all of the forms present in a sample. The final calculation of the alkalinity forms present is dependent upon comparing volumes of standard acid to reach the respective endpoints. Table 18.5 describes the alkalinity relationships and is used for the final calculation of the respective form present. When only total alkalinity is required, the volume measurement at pH 8.3 is not required in the calculation.

4.2 Turbidity may cause some interference if due to suspended carbonate minerals such as caliche. Remove by pressure or gravity filtration. Oily samples may cause interferences by disrupting the response of the pH electrode.

5) Definitions

5.1 Analysis Batch: A group of no more than 20 field samples (Field sample analyses include only those samples derived from a field sample matrix. These include the initial field and duplicate field samples as well as all related matrix spike samples).

5.2 Demonstration of Capability: The analysis of QC samples in series to verify the ability to produce data of acceptable precision and bias.

5.3 Exception Report: Appropriate comments reported with the associated sample batch that addresses sample anomalies such as demonstrated sample matrix effects.

5.4 Initial Calibration (ICAL) – Analysis of analytical standards at different concentrations that are used to determine and calibrate the quantitation range of the response of the analytical detector or method.

5.5 Laboratory Control Sample (LCS): A known interference free matrix spiked a known concentration of the target analyte. The LCS is prepared from a source different from that used to prepare the calibration standards and CCV, and is used to assess laboratory method performance.

5.6 Limit of Detection (LOD): an estimate of the minimum amount of a substance that an analytical process can reliably detect. The LOD is determined annually through the execution of a Method Detection Limit Study, and verified quarterly through the analysis of a Detectability Check Sample (DCS).

5.7 Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met.

5.8 Matrix: The substrate (e.g., water, soil, etc.) which may contain the analyte of interest.

5.9 Method Blank (MBLK): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analysis.

5.10 Method Detection Limit (MDL) study: a procedure described in 40CFR Part 136, Appendix B, that describes how to produce an MDL, a reporting element of certain EPA methods. The MDL study is one approach to determine the LOD.

5.11 NCAR: Nonconformance Corrective Action Report (SOP HS QS-003, current revision).

5.12 Total Alkalinity as CaCO3: A defined parameter where the analytical result measures the cumulative presence of the basic ionic species (OH-, HCO3-, or CO3-2) present and uses the reporting unit “mg/L CaCO3”. This defined calcium carbonate equivalent (mg CaCO3) is the amount of titrant needed to reduce the sample pH to 4.5.

5.13 Bicarbonate Alkalinity as CaCO3: The form of alkalinity present if phenolphthalein alkalinity is less than half of the total alkalinity.

5.14 Carbonate Alkalinity as CaCO3: The form of alkalinity present when phenolphthalein alkalinity is more than zero but less than total alkalinity.

5.15 Hydroxide Alkalinity as CaCO3: The form of alkalinity present if phenolphthalein alkalinity is more than half the total alkalinity.

5.16 Methyl Orange Endpoint (M Endpoint): Defined as pH of 4.5. The original colorimetric alkalinity procedure employed a methyl orange endpoint indicator prior to the use of a pH meter to indicate pH 4.5.

5.17 Phenolphthalein Endpoint (P Endpoint): Defined as a pH of 8.3. The original colorimetric alkalinity procedure employed a phenolphthalein endpoint indicator prior to use of the pH meter to indicate pH 8.3.

5.18 Equivalence Point: The point in titration when the quantity of titrant is equal to the stoichiometric amount needed for complete reaction with analyte. The end point

occurs when there is an abrupt change in a physical property, such as pH or indicator color. Ideally, the end point is chosen to occur at the equivalence point.

5.19 pH: A measure of the hydrogen ion concentration expressed as a negative logarithm. It indicates a degree of the acidity or the alkalinity of a solution as measured on a scale ("pH scale") of 0 to 14. The midpoint of 7.0 on the pH scale represents neutrality, where the "neutral" solution is neither acid nor alkaline. A pH below 7 indicates acid conditions; a pH above 7 indicates alkaline conditions. The neutral point of 7.0 actually indicates the presence of equal concentrations of free hydrogen and hydroxide ions.

6) Health and Safety Warnings

6.1 Lab Safety: Due to various hazards in the laboratory, safety glasses and laboratory coats or aprons must be worn at all times while in the laboratory. In addition, gloves and a face shield should be worn when dealing with toxic, caustic, and/or flammable chemicals.

6.2 Chemical Hygiene: The toxicity or carcinogenicity of each reagent used has not been precisely defined; however, each chemical used should be treated as a potential health hazard. Exposure to laboratory reagents should be reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets (MSDS) is available to all personnel involved in these analyses.

6.3 Waste Management: The principal wastes generated by this procedure are the method-required chemicals and standards. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required. Laboratory procedures in SOP HS-SAF-001, Waste Disposal Procedures, must be followed.

6.4 Pollution Prevention: The materials used in this method pose little threat to the environment when recycled and managed properly. The quantities of chemicals purchased should be based on the expected usage during its shelf life. Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards or reagents to be disposed.

7) Cautions

7.1 Routine preventative maintenance must be performed and documented to assure optimum instrument performance. Refer to the current revision of SOP HS-EQ004 for preventative maintenance schedules.

7.2 Refer to manufactures instructions for care and storage of pH probes.

7.3 Interaction with atmospheric carbon dioxide may introduce a source of error. Maintain sample storage above 0 to 6°C and analyze the sample promptly upon receipt to minimize this interaction.

7.4 DO NOT dilute, filter, concentrate or otherwise alter the sample in any way.

8) Interferences

8.1 Physical Interferences: Suspended particulates or oily matter present in the sample, precipitates formed during the titration, or other waste material may cause a sluggish

electrode response.

8.2 Chemical Interferences

8.2.1 Dissolved Gases: Various dissolved gases contribute directly to acidity or alkalinity. Carbon dioxide (CO2) and hydrogen sulfide (H2S) both add acidity (i.e., increase free H+ ions) to aqueous samples (although CO2 can act as a buffering agent as well through conversion to carbonate and bicarbonate forms). Ammonia (NH3) will add alkalinity (i.e., decrease free H+ ions) to aqueous samples. Dissolved oxygen may contribute to either chemical (redox reactions) or biological activity that may alter the pH, buffering capacity, and acidity or alkalinity of a sample. The concentrations of these gases may also change in the solution during sampling, storage, or titration. Minimize the possible loss of these gases by titrating to the end point promptly after opening the sample container and removing the sample aliquot. Do not let the sample or sample aliquot stand open for extended periods, avoid vigorous shaking or mixing, and do not allow the sample to exceed 25°C.

8.2.2 Reactive Chemical Species: Samples containing significant quantities of hydrolizable or oxidizable ionic species such as ferrous and ferric iron, aluminum, or manganese that may have reaction rates that are slow to equilibrate. Due to impeded equilibrium, samples may exhibit a "rebound" effect where the sample pH initially reaches a value at or near the end point, but then drifts away from the measured value as the sample is mixed. In particular, aluminum in high concentrations makes an end point very hard to determine. This is normally observed as unusual pH drift when approaching the endpoint or as an abnormal response during the course of the titration.

8.3 Weak Acid Salts: Substances such as strong alkali salts of weak organic and inorganic acids present in large amounts may cause interference in the electrometric pH measurements.

9) Personnel Qualifications and Responsibilities

9.1 General Responsibilities - This method is restricted to use by or under the supervision of analysts experienced in the method.

9.2 Analyst - It is the responsibility of the analyst(s) to:

9.2.1 Each must read and understand this SOP and follow it as written. Any deviations or non-conformances must be documented and submitted to the QA Manager for approval.

9.2.2 Produce method compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP (HS-QS-009).

9.2.3 Complete the required initial demonstration of proficiency before performing this procedure without supervision.

9.2.4 Complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.

9.2.5 The analysts must submit data for peer or supervisor review.

9.3 Section Supervisor - It is the responsibility of the section supervisor to:

9.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.

9.3.2 Ensure analysts have completed the required initial demonstration of proficiency before performing this procedure without supervision.

9.3.3 Ensure analysts complete an ongoing demonstration of proficiency annually

when continuing to perform the procedure.

9.3.4 Ensure analysts produce method compliant data that meet all quality requirements using this procedure and the Data Reduction, Review and Validation SOP.

9.4 Project Manager - It is the responsibility of the Project Manager to ensure that all method requirements for a client requesting this procedure are understood by the laboratory prior to initiating this procedure for a given set of samples.

9.5 QA Manager: The QA Manager is responsible for

9.5.1 Approving deviations and non-conformances

9.5.2 Ensuring that this procedure is compliant with method and regulatory requirements,

9.5.3 Ensuring that the analytical method and SOP are followed as written through internal method and system audits.

10) Sample Collection, Handling, and Preservation

10.1 Aqueous samples: A minimum volume of 200-mL is collected in plastic or glass containers. The samples are stored above 0 to 6°C. The holding time for aqueous samples is 14 days.

10.2 Soil Samples: A minimum of 20 grams is collected in a 4 oz glass jar. The sample is stored above 0 to 6 °C prior to preparation. Once prepared, the soil leachate is also stored above 0 to 6 °C. There is no defined holding time for the preparation of soil samples. The holding time for the leachate is 7 days from the date of preparation.

11) Equipment and Supplies

11.1 Volumetric flasks, Class A. Various sizes.

11.2 Analytical Balance, capable of measuring to the nearest 0.0001g (0.1mg).

11.3 pH meter, glass electrode with Automatic Temperature Compensation (ATC), capable of reading 0.05 pH units. Standardize and calibrate according to the SOP for pH, WC-002, current revision

11.4 Mantech AutoMax 122, Automated meter for Alkalinity Determinations

11.5 Magnetic stirrer and Teflon™ coated stir bars

11.6 Buret: Various sizes, Class A buret, capable of measuring to nearest 0.1 mL

11.7 Micro-Buret: 10-mL Class A buret, capable of measuring to nearest 0.1 mL.

11.8 Pipets, Class A, TD- Assorted sizes (e.g. 100, 50, 25-mL).

11.9 Disposable plastic cups - 120 ml or Pyrex beakers, 100 or 200-ml.

12) Computer Hardware and Software

12.1 NA

13) Standards, Reagents and Consumable Materials

13.1 Note: Store purchased alkalinity standards according to manufacturer specifications. Store standard solutions (remaining stock) at room temperature in plastic containers. All purchased stock standard solutions must be replaced after reaching the

manufacturer's expiration date assigned to the standard. All laboratory prepared standard solutions must be replaced after six months or sooner if routine QC indicates a problem. An assigned expiration date of a lab prepared standard cannot exceed the manufacturer's expiration date for any component used in the standard formulation.

13.2 Deionized Water (DI) meeting the performance standard of Type I reagent water for conductance (produce inline resistance ≥ 17 megohm-cm @ 25°C).

13.3 All chemicals must be of ACS grade or equivalent.

13.4 Anhydrous Sodium Carbonate (Solid): Purchase this chemical from an approved vendor (VWR Cat # SC0401, or equivalent). Two sources of this chemical must be available at all times. The second source may be purchased from a different vendor, or from the same vendor (must be a different lot).
- 13.4.1 Dry this chemical for 4 hours at 250 °C.
- 13.4.2 This neat chemical must be recertified after 5 years.

13.5 Standard sodium carbonate solution (0.050N): Dissolve 2.5±0.2g of anhydrous sodium carbonate (10.3) in about 600ml of DI water and dilute to 1 liter (or use 1.25± 0.2g in 500ml).
- 13.5.1 Store this solution in a plastic bottle at room temperature
- 13.5.2 Prepare fresh weekly.

13.6 Sodium Carbonate Standard Solution, LCS (1000 mg/L as $CaCO_3$): This standard is prepared using the second source neat chemical (§13.4). To prepare 1000 mg/L standards dissolve 1.060 ± 0.2g of dried sodium carbonate in water and bring to 1 liter in a volumetric flask.
- 13.6.1 Store this solution in a plastic bottle at room temperature.
- 13.6.2 Prepare fresh weekly.

13.7 0.10 N Sulfuric Acid Titrant: Purchase commercially from an approved vendor.
- 13.7.1 Adhere to the manufacturer stated expiration date.

13.8 0.02 N Sulfuric Acid Titrant: Purchase commercially from an approved vendor.
- 13.8.1 Adhere to the manufacturer stated expiration date.

13.9 pH Standards: Purchase commercially certified standards of 4, 7, and 10 units.
- 13.9.1 Store pH standards at room temperature
- 13.9.2 Adhere to the manufacture's expiration date.

14) Calibration

14.1 Support Equipment Calibration Checks:
- 14.1.1 PH meter calibration must be performed daily prior to pH meter use as per SOP WC-002, current revision.
- 14.1.2 Quarterly Pipet Calibration checks must be current for the equipment used to measure portions of DI water and / or standard solutions required in this procedure. Quarterly pipet calibration checks are performed according to SOP HS-EQ-003, current revision.
- 14.1.3 Daily Balance Calibration Checks must be performed daily prior to balance use as per SOP HS-EQ-001, current revision, when solid materials are being tested.

15) Sample Preparation/Analysis

15.1 Allow all samples to come to room temperature.

15.2 Potentiometric titration:

15.2.1 Transfer a 50 mL aliquot of sample to a disposable beaker. DO NOT filter, dilute, concentrate, or otherwise alter the sample. Add a magnetic stir bar to the sample.

15.2.2 Gently stir the sample (no vortex).

15.2.3 Fill the buret with 0.02N standardized sulfuric acid. Ensure that the bottom of the meniscus of the acid is level with '0' on the buret when observed at eye level.

15.2.4 Rinse the pH and ATC probe and place them in the sample. Allow the pH meter to stabilize and record the initial pH.

15.2.5 If the sample pH is above 8.3, titrate the sample to just above pH 8.3. Slowly titrate drop wise to pH 8.3.

15.2.5.1 Record this value as the phenolphthalein endpoint (P).

15.2.6 Titrate the sample to pH 4.5.

15.2.6.1 DO NOT refill the buret.

15.2.6.2 Allow the buret to flow at a slow, steady rate until the pH nears 5.0

15.2.6.3 Titrate slowly to pH 4.5. Allow the pH to stabilize after each small addition.

15.2.6.4 Record the total volume used (including the volume used to reach P) as the methyl orange endpoint (M).

15.2.7 If the volume of titrant required to reach the methyl orange endpoint (M) is more than 50 mL, discard the sample aliquot and repeat 15.2.1 through 15.2.6 using 0.1N standardized sulfuric acid.

15.2.8 If the volume of titrant required to reach the methyl orange endpoint (M) using the 0.1N standardized sulfuric acid from 15.2.7 is more than 40 mL, discard the sample aliquot and repeat 15.2.1 through 15.2.6 using 0.1N standardized sulfuric acid, but at a lower sample volume. Perform each sample in duplicate to confirm high alkalinity results.

15.2.9 If the volume of titrant required to reach the methyl orange endpoint (M) is less than 1.5 mL, discard the sample aliquot and proceed to 15.3.

15.3 Potentiometric titration of low alkalinity – the following procedure is applicable to samples containing less than 20 mg/L alkalinity:

15.3.1 Transfer a 200 mL aliquot of sample to a disposable beaker. DO NOT filter, dilute, concentrate, or otherwise alter the sample. Add a magnetic stir bar to the sample.

15.3.2 Gently stir the sample (no vortex).

15.3.3 Fill the micro-buret with 0.02N standardized sulfuric acid. Ensure that the bottom of the meniscus of the acid is level with '0' on the buret when observed at eye level.

15.3.3.1 Note: The 10-ml Buret must always be used on water samples having low alkalinity, or typically less than 20-mg/L Alkalinity as $CaCO_3$.

15.3.4 Rinse the pH and ATC probe and place them in the sample. Allow the pH meter to stabilize and record the initial pH.

15.3.5 Titrate the sample to pH 4.2.

15.3.5.1 Allow the buret to flow at a slow, steady rate until the pH nears 5.0, allow the pH to stabilize.

15.3.5.2 Titrate slowly to pH 4.5, allowing the pH to stabilize after each addition. Record volume and exact pH. Carefully add titrant, drop-wise, to lower the pH by exactly 0.3 pH.

15.3.5.3 Record the total volume used

15.4 When using Mantech AutoMax 122, Automated meter, follow the manufacturer's recommended procedures.

15.4.1 Calibrate the instrument.

15.4.1.1 Calibrate first using the 1413, 2820, and 10,000 conductivity standards.

15.4.1.2 Calibrate the pH using the 4, 7, and 10 pH buffer solutions.

15.4.1.3 Ensure that the last position on the rack is the pH 4 buffer solution.

15.4.1.4 Load the samples in the autosampler and entering the sequence in the software.

15.4.1.5 Ensure that QC samples are run at the appropriate frequency.

15.4.1.6 Alkalinity will be based on the pH results

15.5 Calculate the alkalinity using the verified electronic electronic Spreadsheet.

15.6 Analysis of Soil from prepared leachate: Prepare a 10: 1 soil leachate for analysis by adding 100-ml of DI water to 10-grams of soil. Mix this slurry using a magnetic stirring device for 10 minutes. After 10 minutes of continuous stirring, allow the slurry to settle. Once settled, decant the appropriate amount of leachate for alkalinity analysis

16) Troubleshooting

16.1 Prepare new standards, check instrument maintenance, prepare a new calibration as needed, etc.

16.2 If the titrant is added too rapidly, the pH will surge downward, past the desired endpoint. If this occurs, discard the titrated sample and reanalyze with a fresh aliquot.

17) Data Acquisition

17.1 All data is manually recorded in controlled logbooks and manually entered into a validated electronic spreadsheet for calculation step prior to data entry into LIMS. LIMS will assign a batch ID to each batch entered.

17.2 P and T Alkalinity values in aqueous samples are calculated according to 18.3 using the e-spreadsheet. P and T Alkalinity values in soil samples are calculated according to §18.4. This data is used to calculate specific forms of alkalinity according to §18.5.

17.3 Calculate low-level alkalinity values according to §18.6.

17.4 Once the data has been entered into LIMS and all QC validation steps have been completed, data is further reviewed by project management for reporting.

18) Calculation, and Data Reduction Requirements

18.1 Quantification Calculations

18.2 Standardized Acid Normality:

$$\text{Normality, N} = \frac{A \times B}{53.00 \times C}$$

Where,

A = g Na_2CO_3 weighed into 1-L flask

B = mL Na_2CO_3 solution used for titration

C = mL acid used.

18.3 Phenolphthalein (P) and Total (T) Calculations for Aqueous Samples

18.3.1 Phenolphthalein Alkalinity (P) Endpoint:

$$\text{P. Alkalinity}\left(\frac{\text{mg}}{\text{L}}\text{as}\,\text{CaCO}_3\right)=\frac{\text{A}\times\text{N}\times 50{,}000}{\text{V}_{\text{Sample}}}$$

Where
A = mL of titrant needed to reach pH 8.3 and
N = normality of titrant
V_{Samp} = Volume of sample aliquot titrated

18.3.2 Total Alkalinity (T) Endpoint:

$$\text{T. Alkalinity}\left(\frac{\text{mg}}{\text{L}}\text{ as CaCO}_3\right)=\frac{\text{B}\times\text{N}\times 50{,}000}{\text{V}_{\text{Sample}}}$$

Where
B = mL of titrant needed to reach pH 4.5
N = normality of titrant
V_{Samp} = Volume of sample aliquot titrated

18.4 Phenolphthalein (P) and Total (T) Calculations for Soil Samples

18.4.1 Soil Leachate Preparation Factor, F:

$$\text{F}=\frac{\text{V}_{\text{ext}}}{\text{S}}$$

Where
S = grams of soil
V_{ext} = mL water used to leach the soil

18.4.2 Phenolphthalein Alkalinity (P) Endpoint:

$$\text{P. Alkalinity}\left(\frac{\text{mg}}{\text{L}}\text{ as CaCO}_3\right)=\frac{\text{A}\times\text{N}\times 50{,}000\times\text{F}}{\text{V}_{\text{Leach}}}$$

Where
A = mL of titrant for the sample to reach pH 8.3 and
N = normality of titrant
F = soil leachate preparation factor
V_{Leach} = Volume of leachate titrated

18.4.3 Total Alkalinity (T) Endpoint:

$$\text{T. Alkalinity}\left(\frac{\text{mg}}{\text{L}}\text{ as CaCO}_3\right)=\frac{\text{B}\times\text{N}\times 50{,}000\times\text{F}}{\text{V}_{\text{Leach}}}$$

Where
B = mL of titrant for the sample to reach pH 4.5
N = normality of titrant
F = soil leachate preparation factor
V_{Leach} = Volume of sample aliquot titrated

18.5 To report other alkalinity forms (bicarbonate, carbonate or hydroxide as CaCO3) in the water samples, refer to the table below:

Table 18.5 Alkalinity Forms Relationships

Table 18.5 - Alkalinity Forms Relationships			
Result of titration	Hydroxide Alkalinity as $CaCO_3$	Carbonate Alkalinity as $CaCO_3$	Bicarbonate Alkalinity as $CaCO_3$
P=0	0	0	T
P<0.5T	0	2P	T – 2P
P=0.5T	0	2P	0
P>0.5T	2P – T	2(T – P)	0
P=T	T	0	0
Where P is Phenolphthalein Alkalinity, and T is Total Alkalinity			

18.6 Low- Level Alkalinity Calculation

$$\text{T.Alkalinity}\left(\frac{\text{mg}}{\text{L}}\text{ as CaCO}_3\right)=\frac{(2\text{B}-\text{C})\times\text{N}\times 50{,}000}{\text{V}_{\text{Sample}}}$$

Where
B = mL of titrant needed to reach pH 4.5
C = Total mL of titrant needed to reach pH 0.3 unit lower
N = normality of titrant
VSamp = Volume of sample aliquot titrated

18.7 QC Calculations: LIMS calculates the percent recovery for various QC samples (LCS) according to the following equations:

18.7.1 % Recovery, %R (for MS and MSD Samples)

$$\%\text{R}=\frac{(\text{SSR}-\text{SR})}{\text{SA}}\times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SR = Sample Result (unspiked).
SA = Spike Amount Added (mg/L or mg/kg).

18.7.2 % Recovery, %R (for standards and LCS)

$$\%\text{R}=\frac{(\text{SSR})}{\text{SA}}\times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SA = Spike Amount Added (mg/L or mg/kg).

18.7.3 RPD (for precision or duplicate evaluation)

$$\text{RPD}=\frac{|\text{SR}_1-\text{SR}_2|}{½(\text{SR}_1+\text{SR}_2)}\times 100$$

Where:
SR_1 = Sample result for duplicate 1.
SR_2 = Sample result for duplicate 2.

19) Quality Control, Acceptance Criteria and Corrective Action

19.1 Titrant Standardization using 0.05N Sodium Carbonate:
- 19.1.1 Frequency: Standardize titrant prior to each use.

19.2 Method Blank (MBLK)
- 19.2.1 Purpose: Assess background interference or contamination in the analytical system that may lead to high bias or false positive data.
- 19.2.2 Frequency: Analyze one MB with each batch of 20 or less field samples.
- 19.2.3 Acceptance Criteria: No analytes detected >1/2 RL and >1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater). For common laboratory contaminants, no analytes detected >RL.
- 19.2.4 Corrective Action: Identify and correct the source of error, and re-prep and reanalyze the MBLK and all associated client samples.

19.3 Laboratory Control Standard (LCS):
- 19.3.1 Purpose: Evaluates the performance of the entire analytical system, including all preparation and analysis steps. Assesses the ability of the laboratory/analyst to successfully recover the target analytes from a clean matrix. Contains all target analytes and surrogates.
- 19.3.2 Frequency: Once per preparation batch.
- 19.3.3 Acceptance Criteria: Refer to table 26.2
- 19.3.4 Corrective Action: Identify and correct the source of error. Re-prepare and reanalyze the affected preparation batch for failed analytes.

19.4 Sample Duplicate
- 19.4.1 Purpose: Provides information on the heterogeneity of the sample matrix. Also determines the precision of the analytical process for that matrix.
- 19.4.2 Frequency: Once per preparation batch.
- 19.4.3 Acceptance Criteria: Refer to table 26.3
- 19.4.4 Corrective Action: Identify and correct the source of error. Reanalyze the affected batch. If system error is not a factor, reanalysis may not be necessary.

20) Training

20.1 Training to perform the procedures for this method should take the following into consideration:

- 20.1.1 Review literature (see references section). Read and understand this SOP. Also review the applicable SDS for all reagents and standards used. Following the reviews, observe the procedure as performed by an experienced analyst at least three times.

- 20.1.2 The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

- 20.1.3 Perform initial Demonstration of Capability (IDOC) study as described above for water samples. Summaries of the IDOC are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IDOC studies should be performed in order to be equivalent

to NELAC's Initial Demonstration of Capability.

20.2 Training is documented following *SOP CE-QA003*).

20.3 When the analyst training is documented by the supervisor on internal training documentation forms (HS-QAFORM010 and HS-QAFORM038) the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

21) Data Records Management

21.1 All data is stored electronically and/or hard copy for 5 years or 10 years for the state of Louisiana.

21.2 All analytical sequence IDs and standard preparation information must be recorded in the alkalinity logbook. Hardcopy computer printouts of e-spreadsheets and raw data must be retained and initialed by the analyst (electronic initials are acceptable). To simplify sample tracking, the analyst must attempt to use only one lot of standard and reagent per batch.

21.3 Complete all pertinent sections in the respective logbooks. If not-applicable then line out the section. "Z" out or "X" out all large sections of the worksheet that are not used. Make all corrections with single line through, date and initial. Make NO obliterations when manually recording data.

21.4 Logbooks are controlled. Never remove a page from a logbook. Completed logbooks are returned to the QA department when filled and no longer needed in the work area.

21.5 This SOP is effect on the date noted in the header or the last signature date, whichever is most recent.

22) Contingencies for Handling Out of Control Data

22.1 When method required QC exceedances occur, in every case where sample data quality are affected, the source of the QC exceedance must be determined, corrected and sample reanalysis carried out when possible.

22.2 When affected sample analysis cannot be repeated due to limitations (i.e. sample availability, or if reanalysis can only be performed after expiration of a sample hold time), the reporting of data associated with exceeded QC data must be appropriately flagged and narrated. This documentation is necessary to define for the data user the effect of the error has upon the data quality of the results reported (e.g. E flag data indicate the result to be only an estimate).

22.3 All analysts must report sufficient comments in laboratory data review checklist for exceeded QC associated with sample results so that project management can further narrate and ensure data qualifiers (flags) are properly assigned to the reported data.

22.4 NCARs must be issued for QC system exceedances. Matrix interferences are reported using the analyte reporting comment section in LIMS or using the Laboratory Data review checklist.

23) Method Performance

23.1 Method performance is determined by acceptable quality control outcomes for each batch of analysed samples and acceptable PT studies.

24) Summary of Changes

Table 24 .1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
8.4	03/05/2020	G. Moulton	Added sections 1 and 2 Identification of the method and Applicable matrix or matrices
8.4	03/05/2020	G. Moulton	Added section 12 for computer Hardware and software information
8.4	03/05/2020	G. Moulton	Added training in section 20
8.4	03/05/2020	G. Moulton	Corrected table number for table 18.1
8.3	10/15/2018	G. Moulton	Updated to new cover page and added new QA Manager
8.3	10/15/2018	G. Moulton	Modified Header 1
8.3	10/15/2018	G. Moulton	Modified storage time for data. 17.1
8.3	10/15/2018	G. Moulton	Modified sec 21.3 and 21.4
08.2	11/15/2013	T. Yen	Signature Page – New QA Manager and Lab Director.
08.2	11/15/2013	T. Yen	New SOP format.
08.2 Section 17.2	11/15/2013	T. Yen	To simplify standard tracking, analyst must attempt to use single lots in sequence or batch.
08.2 Section 17.5	11/15/2013	T. Yen	SOP effective dates
08.2 Section 21	11/15/2013	T. Yen	Update reference documents.
08.1	02/15/2012	J. Cady	Minor document revision.
08.0	03/31/2011	I. Williams	Template document revision. Added semi-automated procedures.

25) References and Related Documents

25.1 Referenced Documents

25.1.1 American Public Health Association, “Method 2320B, Alkalinity”, Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005

25.2 U.S. Environmental Protection Agency, “Method 310.1, Alkalinity”, Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020 (revised March

25.3 Current TNI Standards.

25.4 Current Department of Defense Quality Assurance Manual.

26) Tables, Diagrams, Flowcharts and Validation Data

Table 26.1 Titrimetric Alkalinity Forms - LODs and LOQs, at time of SOP revision.

Table 26.1- Titrimetric Alkalinity Forms - LODs and LOQs, at time of SOP revision. LODs are determined annually at a minimum, and are subject to change.					
Analyte – water matrix	LOD mg/L	LOQ mg/L	Analyte – solid matrix	LOD mg/Kg	LOQ mg/Kg
Total Alkalinity as CaCO3	2	5	Total Alkalinity as CaCO3, Soluble	2	5

Table 26.2 Titrimetric Alkalinity Forms - LCS Recovery Limits

Table 26.2 - Titrimetric Alkalinity Forms - LCS Recovery Limits							
Analyte - Aqueous	SPK mg/L	Low %	High %	Analyte - Solid/Soils	SPK mg/Kg	Low %	High %
Total Alkalinity as CaCO3	1000	80	120	Total Alkalinity as CaCO3, Soluble	1000	80	120

Table 26.3 Summary of Calibration and QC Procedures

Table 26.3 Summary of Calibration and QC Procedures for SM 2320B - EPA Method 310.1 and EPA Method 310.2			
QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Laboratory Control Sample (LCS)	Once per each batch of 20 or less field samples, perform prior to running samples.	Analyte within ±20% of expected value.	Correct problem then repeat LCS analysis and all samples associated with the LCS
Method blank.	One per batch of 20 or less field samples.	Alkalinity not detected above the LOQ.	Correct problem, and then re-analyze method blank and all samples processed with the contaminated blank.
Duplicate	One duplicate per every 20 or less field samples	RPD <20%	Describe in Laboratory Review Checklist.
Initial Demonstration of ability to generate acceptable accuracy and precision using four replicate LCS.	Once per analyst, renewed annually	QC acceptance criteria, Analyte within ±20% of expected value.	Recalculate results; locate and fix problem with system, then rerun demon-Stratton.

TOTAL ORGANIC CARBON - WATER BY SW5310B/EPA 415.1/SW 9060A

DOCUMENT ID: HS-WC021, REV 6.6

Approved By: _____ Date: 9/24/2020
Technical and Laboratory Director, Hoai Van

Prepared By: _____ Date: 09/24/2020
Quality Assurance Manager, Erica Marinez

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1) Identification of the Method

1.1 Methods to be used in this SOP is Total Organic Carbon by SW846-9060A, Standard Methods 5310B, and EPA 415.1.

2) Applicable Matrices

2.1 The procedure in this SOP is intended for the determination of Total Organic Carbon (TOC) in aqueous samples. EPA 415.1 is not approved for use in NPDES reporting.

3) Scope and Applicability

3.1 This procedure yields results for total Non-Purgeable Organic Carbons, as Total Organic Carbons.

3.2 This procedure yields reporting limit of 1.0 mg/L

3.3 Method SW9060A has been modified in this SOP to perform a single analysis of each sample versus analysis in quads as written in the method.

4) Summary of Procedure

4.1 Acidified samples are received and homogenized in 40-mL VOC vials. Each vial is placed on the instrument auto-sampler

4.2 The instrument withdraws an aliquot of sample for analysis.

4.3 The pre-acidified sample aliquot is sparged to remove inorganic carbon (carbonate and bicarbonate forms). This process also removes purgeable organic carbon from the sample (the remaining fraction is total Non-Purgeable Organic Carbon, reported as Total Organic Carbon)

4.4 For combustion method, organic Carbon is oxidized to carbon dioxide CO_2 in a heated reaction chamber packet with oxidative catalyst.

4.5 The calibrated NDIR measures the evolved carbon dioxide for each sample aliquot. The final mean result of NPOC is reported (as TOC)

5) Definitions

5.1 Dissolved Organic Carbon (DOC) – The fraction of TOC that passes through a 0.45 µm particulate filter.

5.2 Total Carbon (TC) – The sum of organic and inorganic carbon fractions in a sample.

5.3 Total Inorganic Carbon (TIC) - This fraction includes inorganic forms of carbon, including carbonate and bicarbonate.

5.4 Purgeable Organic Carbon (POC) - The fraction of organic carbon that is removed by acidification and sparging. Contribution of these organic carbon forms are negligible to Total Organic Carbon in many surface and groundwater sources, and are not included in the TOC determination.

5.5 Non-purgeable Organic Carbon (NPOC) - The fraction of organic carbon that is not removed by acidification and sparging. This fraction is reported as Total Organic Carbon, due to the negligible contribution of POC to Total Organic Carbon in many

surface and groundwater sources.

5.6 Analytical Batch: A group of no more than 15 field samples (Field sample analyses include only those samples derived from a field sample matrix. These include the initial field and duplicate field samples as well as all related matrix spike samples). See Table 25.2 for batch size requirements.

5.7 DI Water: Deionized reagent water meeting purity characteristics of Type I laboratory distilled water (daily resistance ≥17 megohm-cm).

5.8 Matrix: The substrate (e.g., water, soil, etc.) which may contain the analyte of interest.

5.9 Demonstration of Capability: The analysis of QC samples in series to verify the ability to produce data of acceptable precision and bias.

5.10 Limit of Detection (LOD): an estimate of the minimum amount of a substance that an analytical process can reliably detect. The LOD is determined annually through the execution of a Method Detection Limit Study, and verified quarterly through the analysis of a Detectability Check Sample (DCS).

5.11 Method Detection Limit (MDL) study: a procedure described in 40CFR Part 136, Appendix B, Revision 2, that describes how to produce an MDL, a reporting element of certain EPA methods. The MDL study is one approach to determine the LOD.

5.12 Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met.

5.13 Initial Calibration (ICAL): Analysis of analytical standards at different concentrations that are used to determine and calibrate the quantitation range of the response of the analytical detector or method.

5.14 Continuing Calibration Verification (CCV): The verification of the ICAL that is required during the course of analysis at periodic intervals.

5.15 Second Source Calibration Verification (ICV): A standard obtained or prepared from a source independent of the source of standards for the ICAL. Its concentration should be at or near the middle of the calibration range. It is performed after the ICAL.

5.16 Duplicate Sample: Two identical portions of material collected for chemical analysis, and identified by unique alphanumeric codes. The duplicate may be portioned from the same sample, or may be two identical samples taken from the same site. The two portions are prepared and analyzed identically.

5.17 Method Blank (MBLK): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analysis.

5.18 Laboratory Control Sample (LCS): A sample matrix, free from the analytes of interest, spiked with known amounts of analytes or a material containing known and verified amounts of analytes.

5.19 Matrix Spike (MS): A sample prepared by adding a known mass of target analyte to a

specified amount of matrix sample for which an independent estimate of target analyte concentration is available.

5.20 Matrix Spike Duplicate (MSD): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of recovery for each analyte.

5.21 NCAR: Nonconformance Corrective Action Report (refer to SOP HS QS-003).

5.22 Exception Report: Appropriate comments reported with the associated sample batch that addresses sample anomalies such as demonstrated sample matrix effects.

5.23 Globally Harmonized System of Classification and Labeling of Chemicals (GHS) – common and coherent approach to classifying chemicals and communicating hazard information on labels and safety data sheets.

5.24 Safety Data Sheets (SDS): Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

6) Safety

6.1 Lab Safety: Due to various hazards in the laboratory, safety glasses and laboratory coats or aprons must be worn at all times while in the laboratory. In addition, gloves and a face shield should be worn when dealing with toxic, caustic, and/or flammable chemicals.

6.2 Chemical Hygiene: The toxicity or carcinogenicity of each reagent used has not been precisely defined; however, each chemical used should be treated as a potential health hazard. Exposure to laboratory reagents should be reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets (MSDS) is available to all personnel involved in these analyses.

6.3 Waste Management: The principal wastes generated by this procedure are the method-required chemicals and standards. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required. Laboratory procedures in SOP SHWD001, Waste Disposal Procedures, must be followed.

6.4 Pollution Prevention: The materials used in this method pose little threat to the environment when recycled and managed properly. The quantities of chemicals purchased should be based on the expected usage during its shelf life. Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards or reagents to be disposed.

6.5 Job Safety Assessment

HAZARD ASSESSMENT		
Job Task #1:	**Hazards**	**Preventative Measures**
Sample handling.	Injury due lifting and placing	Use proper lift technique and cart to

	samples on storage locations and broken sample containers.	move coolers and stools/stepladder when working reaching above shoulder height in sample storage cooler. When transporting samples always use sample carrier or properly inspected cart. Wear proper PPE when handling sample container and have spill kits available.
Job Task #2:	**Hazards**	**Preventative Measures**
Sample Testing and/or standard and reagent/solvent use.	Exposure to possible hazardous chemicals.	Wear gloves, safety glasses and lab coat. Work in fume hood and avoid skin contact with solvents/acids/reagents. Know location of safety shower, first aid kits, spill kits and fire extinguisher when handling flammable material.
Job Task #3:	**Hazards**	**Preventative Measures**
Use of compressed gasses cylinders.	Suffocation hazard and cylinder fall hazard. Fire hazard when using flammable gas.	Ensure proper ventilation and secure cylinders to prevent falls. Ensure all regulators and gas lines are in good repair and do not leak. For flammable gasses, keep away from sparks.

7) Maintenance

7.1 Routine preventative maintenance must be performed and documented to assure optimum instrument performance. Refer to the current revision of SOP HS-EQ004 for preventative maintenance schedules.

7.2 Adequate acidification (pH ≤2) must be verified to assure inorganic carbonates are removed prior to analysis. Refer to Section 14.2 for specific instructions.

8) Interferences

8.1 Inorganic Carbonates (carbonate and bicarbonate) interfere with the TOC determination. This procedure eliminates inorganic carbonates in sample preparation (acidification and purging). Failure to acidify adequately will result in the incomplete conversion of carbonates to CO_2, which may bias the TOC result high

8.2 This procedure is applicable only to homogeneous samples that can be injected into the apparatus reproducibly by means of a microliter-type syringe or pipet. The openings of the syringe or pipet limit the maximum size of particle that may be included in the sample.

8.3 Removal of carbonate and bicarbonate by acidification and purging with purified gas results in the loss of volatile organic substances. The volatiles can also be lost during sample homogenization, particularly if the temperature is allowed to rise. Another important loss can occur if large carbon-containing particles fail to enter the needle used for injection.

8.4 Any contact with organic material may contaminate a sample. Avoid contaminated glassware, plastic containers and rubber tubing.

8.5 For Combustion method, the most major limitation is the magnitude and variability of the blank. The type of catalyst used in combustion chamber makes a significant impact.

9) Personnel Qualifications and Responsibilities

9.1 General Responsibilities - This method is restricted to use by or under the supervision of analysts experienced in the method.

9.2 Analyst - It is the responsibility of the analyst(s) to:

- 9.2.1 Each must read and understand this SOP and follow it as written. Any deviations or non-conformances must be documented and submitted to the QA Manager for approval.
- 9.2.2 Produce method compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP (HS-QS-009).
- 9.2.3 Complete the required initial demonstration of proficiency before performing this procedure without supervision.
- 9.2.4 Complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 9.2.5 The analysts must submit data for peer or supervisor review.

9.3 Section Supervisor - It is the responsibility of the section supervisor to:

- 9.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.
- 9.3.2 Ensure analysts have completed the required initial demonstration of proficiency before performing this procedure without supervision.
- 9.3.3 Ensure analysts complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 9.3.4 Ensure analysts produce method compliant data that meet all quality requirements using this procedure and the Data Reduction, Review and Validation SOP.

9.4 Project Manager - It is the responsibility of the Project Manager to ensure that all method requirements for a client requesting this procedure are understood by the laboratory prior to initiating this procedure for a given set of samples.

9.5 QA Manager: The QA Manager is responsible for

- 9.5.1 Approving deviations and non-conformances
- 9.5.2 Ensuring that this procedure is compliant with method and regulatory requirements,
- 9.5.3 Ensuring that the analytical method and SOP are followed as written through internal method and system audits.

10) Sample Collection, Handling, and Preservation

10.1 Sampling and storage of samples in amber glass vials is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is

permissible if it is established that the containers do not contribute contaminating organics to the samples.

10.2 Ship and store samples above freezing to 6˚C, and protected from sunlight and air. Acidify samples to pH ≤ 2 with H_2SO_4. The holding time for acidified samples is 28 days. Amber VOA vials provided by ALS contains H_2SO_4. Minimum of two vials must be sent for each sample.

11) Equipment and Supplies

11.1 Hamilton Gastight Syringes, or equivalent. Various sizes.

11.2 Volumetric flasks, Class A. Various sizes.

11.3 40-ml VOC vials with screw cap and Teflon™ liners.

11.4 Analytical Balance, capable of measuring to the nearest 0.0001g (0.1mg).

11.5 Shimadzu-TOC-V CSH Analyzer / ASI-V Auto Sampler/Furnace.

11.6 Air, Compressed

11.7 Top-loading balance, capable of weighing to 0.01-g.

11.8 Calibrated pipets, various volumes

11.9 Volumetric flasks, Class A, various sizes.

11.10 pH test strips – log in receipt log and assigned internal ID number for tracking.

11.11 Vortex mixer or equivalent.

11.12 Computer hardware and software: Shimadzu SSM Analyzer, with IR detection and operating software

12) Standards and Reagents

12.1 Note: All purchased standards must be stored in according to manufacturer specifications. Store all standard solutions (remaining stock, composite and calibration) below 6 ºC in glass containers having Teflon™ lined lids or in accord with the manufacturer's recommended conditions. All purchased stock standard solutions must be replaced after reaching the manufacturer's expiration date assigned to the standard. All laboratory prepared standard solutions must be replaced after six months or sooner if routine QC indicates a problem or if required by reference method. An assigned expiration date of a lab prepared standard cannot exceed the manufacturer's expiration date for any component used in the standard formulation. When analyzing or preparing samples, all standards, lot numbers must be associated with the run batch or prep batch. All standard container must be labeled for content and lot numbers. Internal prepared container must also include the GHS safety labeling info.

12.2 Deionized Reagent Water (DI Water) - Internally treated water meeting purity characteristics of Type I water (daily resistance ≥17 megohm-cm).

12.3 Sulfuric Acid H_2SO_4, Concentrated (98% Wt.), ACS Reagent Grade.

12.3.1 Manufacture established expiration date applies.

12.4 TOC Stock Standard, 1000-mg/L as carbon: Purchase a certified standard from an approved vendor [e.g. VWR (Ricca # 1847-16 or equivalent)].

12.4.1 A second source TOC standard is obtained from a different vendor. If the standard must be purchased from the same vendor, a different lot must be obtained.

12.4.2 The manufacturer established expiration date applies.

12.4.3 Document standard receipt and label within ALS tracking number, content, concentration, opened date and expiration date. GHS label for manufacturer's container is not needed, only internal prep containers.

12.5 TOC Calibration (ICAL) Standards: Prepare each calibration standard according to Table 12.5.6, diluting to volume with DI Water. For each calibration standard:

12.5.1 Begin with ~50 mL DI water in a 100-mL volumetric flask

12.5.2 Add the indicated volume of the appropriate standard and ~0.2-mL concentrated H_2SO_4.

12.5.3 Dilute to volume

12.5.4 Mix well.

12.5.5 Transfer the prepared standard to a 40-mL VOC vial fully (no headspace). Cap the vial promptly and label each vial with ID number.

12.5.6 Prepare fresh with each use.

Table 12.5.6 Calibration Standards for Total Organic Carbon

TOC ICAL STANDARD, mg/L	TOC Standard Concentration (mg/L)	TOC Standard Volume Added (mL)	Final Volume (mL)
1.0	1000-mg/L (Stock)	0.1	100
2.0	1000-mg/L (Stock)	0.2	100
5.0	1000-mg/L (Stock)	0.5	100
10.0	1000-mg/L (Stock)	1.0	100
25.0 (CCV)	1000-mg/L (Stock)	5.0	200
50.0*	1000-mg/L (Stock)	5.0	100

* For Shimadzu Instrument Only

12.6 TOC ICV/LCS/LCSD, 10.0 mg/L: Prepare from the second source standard in a 100-mL volumetric flask, according to table 12.5.6. Dilute to volume with DI Water. Mix the standard and transfer into a 40-ml VOC vial (fill and cap leaving no headspace). Prepare fresh daily.

12.6.1 Documents prep in the standard prep logbook, assigning standard ID to each standard prepared.

12.6.2 Transfer the prepared standard to a 40-mL VOC vial fully (no headspace). Cap the vial promptly and label each vial with standard ID for traceability.

10.7 TOC MS/MSD Spikes, 10-mg/L: Prepare by pipetting 0.2 mL of the 1000-mg/L TOC into a 20-ml aliquot of client sample. Mix the spiked sample and transfer into a 40-ml VOC vial. Prepare fresh daily.

12.6.1 Documents prep in the standard prep logbook, assigning standard ID to each standard prepared.

12.6.2 Transfer the prepared standard to a 40-mL VOC vial fully (no headspace). Cap

the vial promptly and label each vial with standard ID for traceability.

12.6.3 Prepare fresh at each use.

13) Method Calibration

13.1 Perform all support equipment calibration checks and documentations (balances, pipets, etc.) as required.

13.2 All the instrument to stabilize for at least 30 minutes prior to beginning analysis.

13.3 Procedures for instrument calibration are outlined in the operator's manual

13.4 The instrument is calibrating using blank and the standards (as per Table 10.6.6. The curve correlation coefficient, r, must be equal to or greater than 0.995.

13.5 The instrument must be recalibrated after major instrument maintenance, or when calibration verification samples fail to meet criteria (16.1, 18.2 and 16.3).

14) Sample Preparation/Analysis

14.1 Remove client samples from refrigerated storage.

14.2 Check the pH of each sample to verify the pH is 2 or lower after analysis. Note that even field acid preserved samples containing small amounts of sediment may slowly buffer the pH above 2 after field collection and preservation.

14.2.1 For any sample above 2, adjust second vial to 2 or below with drop wise additions of Concentrated H_2SO_4 and create a narrative in LIMS.

14.3 If sample is receive in container other than a VOA vial perform the following:

14.3.1 Vortex the sample for a minimum of 30 seconds.

14.3.2 Fill a 40-mL VOC vial with the homogenized sample, place the cap and label appropriately, indicating sample ID and dilution

14.4 Place the labeled vials onto the autosampler and create an analytical sequence in the instrument software, based on the current positioning of the vials on the autosampler. Include all vials in the sequence.

14.5 Initiate the instrument.

14.6 The TOC analyzer withdraws a 5.0-ml aqueous subsample and performs the following three steps:

14.6.1 Removal of inorganic carbon by purging the pre-acidified sample;

14.6.2 For combustion method, heat in the catalytic combustion tube to convert all carbon dioxide (CO_2).

14.6.3 The CO_2 formed can be measured directly by an infrared detector and then organic carbon is evolved for determination of TOC.

14.7 For analyses, three replicate injections from each sample vial are analyzed and the results are used to calculate an average for final reporting. Per method 5310B, acceptable replicates have 10% precision.

14.8 For SW-846 Method 9060A analysis, four replicate samples are analyzed and the results are used to calculate an average and range for final reporting.

14.9 A typical analytical sequence contains the following elements:

14.9.1 ICV (following ICAL)

14.9.2 CCV - use lot number in runlog to track standard.
14.9.3 CCB
14.9.4 Method Blank (MB)
14.9.5 Laboratory Control Sample (LCS) - use lot number in runlog to track standard.
14.9.6 Client sample
14.9.7 Client Matrix Spike (MS) - use lot number in runlog to track standard.
14.9.8 Client Matrix Spike Duplicate (MSD) – MS/MSD performed if sufficient sample volume provided.
14.9.9 Client samples (5)
14.9.10 CCV
14.9.11 CCB
14.9.12 Client Sample
14.9.13 Client Matrix Spike (MS)
14.9.14 Client Matrix Spike Duplicate (MSD)
14.9.15 Client Samples (7)
14.9.16 CCV
14.9.17 CCB

12.10 Verification of calibration is performed at the beginning of analysis, after every 10 samples, and at the end of the sequence. Reported data must be bracket by successful CCVs.

15) Troubleshooting

15.1 Prepare new standards, check instrument maintenance, prepare a new curve as needed, etc.

15.2 If a sample strongly effervesces after the addition of concentrated Sulfuric Acid (H_2SO_4), the addition indicates the need to remove high inorganic carbonates

16) Data Acquisition

16.1 Data is electronically recorded in each TOC analytical sequence. The TOC data is transferred into LIMS. LIMS assigns a batch ID to each batch entered.
16.1.1 Data is reported as the range of TOC recoveries and the mean average of replicates.

16.2 Once the data has been entered into LIMS and all QC validation steps have been completed, data is further reviewed by project management for reporting.

17) Calculation, and Data Reduction Requirements

17.1 TOC Calculations

$$\text{TOC, mg/L} = [\text{response, mg/L}] * \text{DF}$$

Where
DF = dilution factor, for analyst prepared sample dilutions

17.2 QC Calculations: LIMS calculates the percent recovery for various QC samples (LCS) according to the following equations:

17.2.1 % Recovery, %R (for MS and MSD Samples)

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SR = Sample Result (unspiked).
SA = Spike Amount Added (mg/L or mg/kg).

17.2.2 % Recovery, %R (for standards and LCS)

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SA = Spike Amount Added (mg/L or mg/kg).

17.2.3 RPD (for precision or duplicate evaluation)

$$RPD = \frac{|SR_1 - SR_2|}{½(SR_1 + SR_2)} \times 100$$

Where:
SR_1 = Sample result for duplicate 1.
SR_2 = Sample result for duplicate 2.

18) Quality Control, Acceptance Criteria and Corrective Action

18.1 Initial Calibration (ICAL)

18.1.1 Frequency: Analyze a new curve after major maintenance or if a failing CCV corrective action initiates the need for a new curve. A second source ICV must verify the new curve, and be analyzed at the beginning of each analytical batch of 10 or less samples thereafter.

18.1.2 Criteria: The new ICAL curve must have a correlation coefficient equal to or greater than 0.995.

18.1.3 Corrective Action: If correlation coefficient or ICV are outside their range, perform corrective action to determine the source of the error. (Prepare new standards, check instrument maintenance, prepare a new curve as needed, etc.).

18.2 Initial Calibration Verification (ICV)

18.2.1 Frequency: Analyzed as a source independent of the calibration source immediately after each ICAL.

18.2.2 Criteria: Recovery must be within 10% of the true value

18.2.3 Corrective action: Determine the source of the error, perform corrective action and reanalyze the ICV. Note, a new ICAL may be required.

18.3 Continuing Calibration (CCV)

18.3.1 Frequency: Analyze one CCV daily at the beginning of each sequence, once every 10 samples and at the end of a sequence.

18.3.2 Criteria: The CCV results must be within 10% of the true value.

18.3.3 Corrective Action: If the acceptance criteria are not met, discontinue analysis. Determine the source of error, perform the appropriate corrective action and re-analyze the CCV and all client samples that were bracketed by the failing CCV.

18.4 Method Blank (MBLK)

18.4.1 Frequency:

18.4.1.1 Waste Water

Methods SM 5310B / EPA 415.1- one MB with each batch of 10 or less field samples.

18.4.1.2 Hazardous Waste

Methods SW9060A- one MB with each batch of 20 or less field samples

18.4.2 Criteria: <1/2 LOQ.

18.4.3 Corrective Action: If the acceptance criterion is not met, determine the source of error, perform the appropriate corrective action and re-analyze the MBLK and all associated client samples.

18.5 Laboratory Control Standard (LCS)

18.5.1 Frequency:

18.5.1.1 Waste Water

Methods SM 5310B / EPA 415 - one LCS with each batch of 10 or less field samples. Perform a LCS/LCSD at the beginning of each batch.

18.5.1.2 Hazardous Waste

Method SW9060A - one LCS with each batch of 20 or less field samples.

18.5.1.3 Note: An LCSD is required only when there is not sufficient sample volume to analyze an MS/MSD within the batch.

18.5.2 Criteria: The LCS results must be within 20%.

18.5.3 Corrective Action: If the acceptance criterion is not met, determine the source of error, perform the appropriate corrective action and re-analyze the LCS and all associated client samples.

18.6 Matrix Spike Sample

18.6.1 Frequency: Matrix spikes must be analyzed on a frequency below.

18.6.1.1 Waste Water

Methods SM 5310B / EPA 415 - one MS with each batch of 10 or less field samples.

16.6.1.2 Hazardous Waste

Method SW9060A - one MS with each batch of 20 or less field samples

18.6.2 Criteria: Advisory Acceptance limits are 80 to 120 % for waters.

18.6.3 Corrective Action: If the spike results are outside the acceptance limits for recovery, first determine if the cause is a system error; if so, correct the problem and repeat the MS. If system error is not a factor, the data may only

be reported if the associated LCS is acceptable. The sample MS results are flagged indicating matrix interference.

18.7 Matrix Spike Duplicate Sample

18.7.1 Frequency: A Matrix Spike Duplicate must be analyzed on a frequency below.

18.7.1.1 Waste Water
Methods SM 5310B / EPA 415 - one MSD with each batch of 10 or less field samples.

16.6.1.2 Hazardous Waste
Method SW9060A - one MSD with each batch of 20 or less field samples

18.7.2 Criteria: Advisory Acceptance limits are 80 to 120 % recovery for waters and <20% for the MSD RPD.

18.7.3 Corrective Action: If the spike results are outside the acceptance limits for recovery, evaluate the MSD RPD. If the RPD is <20% and the LCS fall within the acceptance criteria, a matrix interference is suspected. If the MSD RPD >20%, further evaluate for error. If a systemic error is found, repeat the analysis of the samples and QC samples in the batch.

18.8 Initial Demonstration of Capability

18.8.1 Frequency: Analyze 4 LCS replicates during initial method development, or training of new analysts. Renew demonstrations annually.

18.8.2 Criteria: All 4 LCS replicates must meet the acceptance criteria of the LCS as listed in 18.5

18.8.3 Corrective Action: Identify the source of the error, perform corrective action and reanalyze the LCS replicates.

18.9 TIC Removal Efficiency Check

18.9.1 Frequency: Perform annually or after major instrument repair.

18.9.2 Criteria: Results must be within 15% of the true value.

18.9.3 Corrective Action: Identify the source of the error, perform appropriate instrument maintenance or other corrective action, and reanalyze the check sample.

19) Data Records Management

19.1 All data is stored electronically and/or hard copy for 5 years or for 10 years in the state of Louisiana.

17.2 All analytical sequence IDs and standard preparation information must be recorded in the TOC Run logbook. Hardcopy computer printouts of analytical sequences and raw data must be retained and initialed by the analyst (electronic initials are acceptable). To simplify standard tracking, analyst must attempt to use one lot of reagents and standards with each batch.

19.3 Complete all pertinent sections in the respective logbooks. If not-applicable then line out the section. “Z” out or “X” out all large sections of the worksheet that are not used. Make all corrections with single line through, date and initial. Make NO obliterations when manually recording data.

19.4 Logbooks are controlled. Never remove a page from a logbook. Completed logbooks are returned to the QA department when filled and no longer needed in the work area.

19.5 The effective date this SOP is the date in the header or last signature date, whichever is most recent.

20) Contingencies for Handling Out of Control or Unacceptable Data

20.1 When method required QC exceedances occur, in every case where sample data quality are affected, the source of the QC exceedance must be determined, corrected and sample reanalysis carried out when possible.

20.2 When affected sample analysis can not be repeated due to limitations (i.e. sample availability, or if reanalysis can only be performed after expiration of a sample hold time), the reporting of data associated with exceeded QC data must be appropriately flagged and narrated. This documentation is necessary to define for the data user the effect of the error has upon the data quality of the results reported (e.g. E flag data indicate the result to be only an estimate).

20.3 All analysts must report sufficient comments in laboratory data review checklist for exceeded QC associated with sample results so that project management can further narrate and ensure data qualifiers (flags) are properly assigned to the reported data.

20.4 NCARs must be issued for QC system exceedances. Matrix interferences are reported using the analyte reporting comment section in LIMS or using the Laboratory Data review checklist.

21) Method Performance

21.1 Method performance is determined by passing quality control standards, passing performance evaluation samples, MDL, LODs and LOQs.

22) Training

22.1 Training to perform the procedures for this method should take the following into consideration:

22.1.1 Review literature (see references section). Read and understand this SOP. Also review the applicable SDS for all reagents and standards used. Following the reviews, observe the procedure performed by an experienced analyst at least three times.

22.1.2 The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

22.1.3 Perform initial Demonstration of Capability (IDOC) study in this case 4 LCS. Summaries of the IDOC are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IDOC studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

22.2 Training is documented following *SOP CE-QA003*).

22.3 When the analyst training is documented by the supervisor on internal training documentation forms (HS-QAFORM010 and HS-QAFORM038) the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

23) Summary of Changes

Table 23.1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
6.6	09/24/2020	G. Moulton	Sec 1: Added Identification of the method.
6.6	09/24/2020	G. Moulton	Sec 2: Added Applicable matrices and indicate modification.
6.6	09/24/2020	G. Moulton	Sec 3.3: modification of method documented.
6.6	09/24/2020	G. Moulton	Sec 6: Changed to say Safety.
6.6	09/24/2020	G. Moulton	Sec 7: Changed to say maintenance
6.6	09/24/2020	G. Moulton	Sec 21: Modified method performance.
6.6	09/24/2020	G. Moulton	Sec 22: Added training
6.6	09/24/2020	G. Moulton	Sec 25: changed to say Tables, diagram, flowcharts and validation Data.
6.6	09/24/2020	G. Moulton	Updated table number.
6.5	8/12/2019	E. Howard	Removed extraneous reference to 5310C. Removed references to Low level analysis. Clarified in multiple sections that samples are pre-acidified. Removed sections related to TIC determination. Corrected typographical errors not altering the procedure.
6.5 Sec. 9	8/12/2019	E. Howard	Updated equipment and Supplies
6.5 Sec 10.4	8/12/2019	E. Howard	Removed Phosphoric acid. Not applicable to water method.
6.5 Sec 10.6	8/12/2019	E. Howard	Removed TOC intermediate standard (related to low level analysis which is no longer performed.
6.5 Table 10.7.6	8/12/2019	E. Howard	Updated to reflect current curve preparation.
6.5 Sec 12.2.1	8/12/2019	E. Howard	Added that samples receiving additional acidification in the lab require a narrative.
6.5 Sec 12.6	8/12/2019	E. Howard	Clarified the steps performed by the analyzer.
6.5 Sec 12.7	8/12/2019	E. Howard	Added 5310B precision requirement.
6.4	10/15/2018	G. Moulton	Updated new cover and new QA manager.
6.4	10/15/2018	G. Moulton	Modified sec, 17.1 data storage.

6.4	10/15/2018	G. Moulton	Modified sec 21.1.2, 21.1.4 and 21.1.5
06.3	11/30/2017	T. Yen	New Format and Signature Page – New Lab Director and Inorganics Manager.
06.3 – Section 4.5	11/30/2017	T. Yen	Job Safety Assessment added to SOP.
06.3 – Section 10	11/30/2017	T. Yen	Standard prep update – labeling all prepare standard container and adding GHD safety label if standard stored more than one day.
06.3 – Section 16 and 22.2	11/30/2017	T. Yen	CCV values set to ±10% of true value.
06.3 – Section 16 and 22.2	11/30/2017	T. Yen	QA LCS/MSD/MSD for SM5310/EPA 410.4 set to 10% frequency. QA LCS/MSD/MSD for SW9060A set to 20% frequency.
06.3 – Section 21.1	11/30/2017	T. Yen	Update reference.
06.2	11/15/2013	T. Yen	Persulfate oxidation reference and procedures removed from SOP.
06.2 – Section 17.2	11/15/2013	T. Yen	To simplify standard tracking, analyst must attempt to use single lots in sequence or batch.
06.2 – Section 17.5	11/15/2013	T. Yen	SOP effective date defined.
06.2 – Section 21	11/15/2013	T. Yen	References updated.
06.1	03/30/2012	J. Cady	Combustion Method addition
06.0	06/30/2011	J. Cady	Major document revision.

24) References and Related Documents

24.1 Referenced Documents

24.1.1 Method 9060A, Total Organic Carbon (Rev 1, Aug 2002), Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Third Edition, Proposed Update IIIB, October 2002.

24.1.2 SM 5310 B TOC. High-Temperature Combustion Method. Standard Methods for the Examination of Water and Wastewater, 22nd Edition, APHA/AWWA/WEF, 2012.

24.1.3 EPA Method 415.1, Total Organic Carbon, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020 (revised March 1983).

24.1.4 Current TNI Standards.

24.1.5 Current Department of Defense Quality Systems Manual.

25) Tables, Diagrams, Flowcharts and Validation Data

Table 25.1 Total Organic Carbon for Waters

Total Organic Carbon for Waters – LOD, LOQ MDLs are determined annually at a minimum, and are subject to change.		
Analyte – waters	LOD mg/L	LOQ mg/L
Total Organic Carbon	1.0	1.8

Table 25.2 Summary of Calibration and QC for TOC, SM5310B /EPA 415.1 /SW 9060A

Summary of Calibration and QC for TOC, SM5310B / EPA 415.1 / SW 9060A			
QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Calibration: 5 calibration standards and a blank.	After major maintenance or after failing CCV	r≥ 0.995	Correct problem, then rerun a new curve.
Initial Calibration Verification (ICV, as second source)	Analyze immediately after each initial calibration and at the beginning of each analytical batch	ICV within ±10% of expected value.	Correct problem then repeat ICV or prepare new curve and new ICV.
Continuing Calibration: CCV is prepared from the primary standard	Daily, before samples, then every 10 samples and at end of sequence.	CCV within ±10% of expected value.	Correct problem then repeat CCV or prepare new curve and new CCV. Reanalyze any affected samples since last passing CCV.
Laboratory Control Sample: LCS is prepared from the second source standard	Methods SM 5310B / EPA 415 - one per each batch of 10 or less field samples. Method 9060A - one per each batch of 20 or less field samples.	Analyte within ±20% of expected value.	Correct problem then repeat LCS analysis. Reanalyze any affected samples in the batch.
Method blank (MB).	Methods SM 5310B / EPA 415 - one per each batch of 10 or less field samples. Method 9060A - one	TOC not detected above the 1/2LOQ.	Correct problem, then re-analyze MB and all affected samples processed with the contaminated blank.

Summary of Calibration and QC for TOC, SM5310B / EPA 415.1 / SW 9060A			
QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
	per each batch of 20 or less field samples.		
MS / MSD	Methods SM 5310B / EPA 415 - one per each batch of 10 or less field samples. Method 9060A - one per each batch of 20 or less field samples.	Analyte within ±20% of expected value. RPD <20%	Describe in Laboratory Review Checklist.
Initial Demonstration of ability to generate acceptable accuracy and precision using four replicate LCS.	Once per analyst initially and annually thereafter.	Analyte within ±20% of expected value. RPD <20%	Recalculate results; locate and fix problem with system, then rerun demon-Stratton.

AMMONIA NITROGEN SM 4500-NH3 B/F

DOCUMENT ID: HS-WC026, REV 5.4

Approved By: Hoai. Van
Technical and Laboratory Director, Hoai Van

Date: 7/23/2020

Prepared By: Erica H Marinez
Quality Assurance Manager, Erica Marinez

Date: 07/23/2020

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1) Identification of the Method, Applicable Matrices, Scope and Applicability

1.1 1.1 Method SM4500NH3 B/F covers the determination of ammonia in water (ground, surface, and saline waters, soils, domestic and industrial wastes.

1.2 The applicable range is 0.025-1.00 mg/L NH_3 as N. Higher concentrations can be determined by sample dilution.

1.3 This method describes the use of Simple-distillation procedure.

2) Summary of Procedure

2.1 Ammonia in neutral to acidic aqueous solutions exists primarily as the ammonium (NH4+) cation. When the pH is raised above about 8.0-8.5, the chemical equilibrium shifts because the excess hydrogen on the ammonium cation reacts with the hydroxyl anion to yield ammonia gas (NH4+ + OH– → H2O + NH3 ↑). While the ammonia gas remains water-soluble, it may be stripped from solution by boiling and/or sparging. This allows for separation of the ammonia from potential ionic species that may act as interferents. Boric acid in aqueous solution readily absorbs the gaseous ammonia. To initiate the distillation, the sample is placed into a gas-tight distillation flask assembly, buffered to a pH of 9.5 with borate buffer, and then heated to boiling with the steam directed through a condenser to bubble through a solution of boric acid. The borate buffer is used in order to decrease hydrolysis of cyanates and organic nitrogen compounds.

2.2 The distillate is captured in a 0.04 N sulfuric acid solution. The sulfuric acid solution containing the sulfuric acid complex is determined calorimetrically. The ammonia distills within the first 25 ml of collection based on a 50-ml initial volume.

2.3 Alkaline phenol and hypochlorite react with ammonia (in the distillate) to form indophenol blue that is proportional to the ammonia concentration. The blue color formed is intensified with sodium nitroprusside and measured colorimetrically at 640-nm.

3) Definitions

3.1 Demonstration of Capability: The analysis of QC samples in series to verify the ability to produce data of acceptable precision and bias.

3.2 Exception Report: Appropriate comments reported with the associated sample batch that addresses sample anomalies such as demonstrated sample matrix effects.

3.3 Laboratory Control Sample (LCS): A sample matrix, free from the analytes of interest, spiked with known amounts of analytes or a material containing known and verified amounts of analytes.

3.4 Limit of Detection (LOD): an estimate of the minimum amount of a substance that an analytical process can reliably detect. The LOD is determined annually through the execution of a Method Detection Limit Study, and verified quarterly through the analysis of a Detectability Check Sample (DCS).

3.5 Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met.

3.6 Matrix Spike (MS): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available.

3.7 Matrix Spike Duplicate (MSD): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of recovery for each analyte.

3.8 Matrix: The substrate (e.g., water, soil, etc.) which may contain the analyte of interest.

3.9 Method Blank (MBLK): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analysis.

3.10 Method Detection Limit (MDL) study: a procedure described in 40CFR Part 136, Appendix B, that describes how to produce an MDL, a reporting element of certain EPA methods. The MDL study is one approach to determine the LOD.

3.11 NCAR: Nonconformance Corrective Action Report (refer to SOP HSQS003, current revision).

3.12 Organic Free Water: Deionized (DI) reagent water meeting purity of analyte free. For additional purification, the DI water is passed through an activated carbon filter.

3.13 Preparation Batch: A defined set of one to 20 client samples of the same matrix, meeting the batch definition criteria, and prepared for analysis within 24 hours. The preparation batch must also contain the required determinative method defined batch QC samples (e.g. method blank, laboratory control samples, matrix spikes, duplicates, etc.).

3.14 Batch: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** is composed of one (1) to twenty (20) environmental sample of the same quality systems matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be twenty-four (24) hours. An **analytical batch** is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.

3.15 NCAR: Nonconformance Corrective Action Report (refer to SOP HS-QS-003).

3.16 Exception Report – Appropriate comments reported with the associated sample batch that addresses sample anomalies such as demonstrated sample matrix effects.

4) Safety

4.1 Lab Safety: Due to various hazards in the laboratory, safety glasses and laboratory coats or aprons must be worn at all times while in the laboratory. In addition, gloves and a face shield should be worn when dealing with toxic, caustic, and/or flammable chemicals.

4.2 Chemical Hygiene: The toxicity or carcinogenicity of each reagent used has not been precisely defined; however, each chemical used should be treated as a potential health hazard. Exposure to laboratory reagents should be reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets (MSDS) is available to all personnel involved in these analyses.

4.3 Waste Management: The principal wastes generated by this procedure are the method-required chemicals and standards. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required. Laboratory procedures in SOP HS-SAF-001, Waste Disposal Procedures, must be followed.

4.4 Pollution Prevention: The materials used in this method pose little threat to the environment when recycled and managed properly. The quantities of chemicals purchased should be based on the expected usage during its shelf life. Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards or reagents to be disposed.

4.5 Job Safety Assessment

HAZARD ASSESSMENT		
Job Task #1:	**Hazards**	**Preventative Measures**
Sample handling.	Injury due to lifting and placing samples on storage locations and cuts from broken sample containers.	Use proper lift technique and cart to move coolers and stools/stepladder when working reaching above shoulder height in sample storage cooler. When transporting samples always use sample carrier or properly inspected cart. Wear proper PPE when handling sample container and have spill kits available.
Job Task #2:	**Hazards**	**Preventative Measures**
Sample Testing and/or standard and reagent/solvent use.	Exposure to possible hazardous chemicals.	Wear gloves, safety glasses and lab coat. Work in fume hood and avoid skin contact with solvents/acids/reagents. Know location of safety shower, first aid kits, spill kits and fire extinguisher when handling flammable material.
Job Task #3:	**Hazards**	**Preventative Measures**

Glassware cleaning,	Cuts from broken or chip glassware.	Wear proper gloves, safety glasses and lab coat or apron.
Job Task #4:	**Hazards**	**Preventative Measures**
Sample Distillation	Burn hazard from hot surface	Wear proper gloves, safety glasses and lab coat or apron and allow sample to cool own before handling

5) Maintenance

5.1 Routine preventative maintenance must be performed and documented to assure optimum instrument performance. Refer to the current revision of SOP HS-EQ004 for preventative maintenance schedules.

6) Interferences and Pollution Prevention

6.1 Distillation separates ammonia from potential interferences that may be present in wastewaters, etc.

6.2 Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent even at the pH of 9.5 at which distillation is carried out. Volatile alkaline compounds, such as certain ketones, aldehydes, and alcohols, may cause an off-color in the distillate. Boiling the sample at a low pH (approximately 2 to 3) prior to distillation may eliminate some of these compounds (e.g., formaldehyde). However, this shall not be done routinely nor without direct supervisory approval.

6.3 A number of aromatic and aliphatic amines, as well as other compounds, both organic and inorganic, will cause turbidity that may interfere. Steam distillation reduces the amount of the aromatic and aliphatic amines but may not entirely eliminate them.

6.4 Residual chlorine rapidly converts ammonia into chloramines, and this process accelerates at the boiling temperature used to distill the sample. Therefore, residual chlorine must be removed by pretreatment of the sample with sodium thiosulfate prior to distillation.

6.5 Glycine, urea, glutamic acid, cyanates and acetamides hydrolyze slowly in sample solutions to produce additional ammonia.

6.6 Samples MUST be kept acidic until distillation commences. Allowing the sample to stand at an alkaline pH will result in variable losses of ammonia.

6.7 Care should be taken not to contaminate or pollute the samples to be analyzed.

6.8 Use a new scoop for each sample.

6.9 Work under the hood as much as possible especially when handling that have fumes or odors.

7) Personnel Qualifications and Responsibilities

7.1 General Responsibilities - This method is restricted to use by or under the supervision of analysts experienced in the method.

7.2 Analyst - It is the responsibility of the analyst(s) to:

- 7.2.1 Each must read and understand this SOP and follow it as written. Any deviations or non-conformances must be documented and submitted to the QA Manager for approval.
- 7.2.2 Produce method compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP (HS-QS-009).
- 7.2.3 Complete the required initial demonstration of proficiency before performing this procedure without supervision.
- 7.2.4 Complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 7.2.5 The analysts must submit data for peer or supervisor review.

7.3 Section Supervisor - It is the responsibility of the section supervisor to:

- 7.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.
- 7.3.2 Ensure analysts have completed the required initial demonstration of proficiency before performing this procedure without supervision.
- 7.3.3 Ensure analysts complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 7.3.4 Ensure analysts produce method compliant data that meet all quality requirements using this procedure and the Data Reduction, Review and Validation SOP.

7.4 Project Manager - It is the responsibility of the Project Manager to ensure that all method requirements for a client requesting this procedure are understood by the laboratory prior to initiating this procedure for a given set of samples.

7.5 QA Manager: The QA Manager is responsible for

- 7.5.1 Approving deviations and non-conformances
- 7.5.2 Ensuring that this procedure is compliant with method and regulatory requirements,
- 7.5.3 Ensuring that the analytical method and SOP are followed as written through internal method and system audits.

8) Sample Collection, Handling, and Preservation

8.1 Aqueous samples are collected in either plastic or glass. The minimum aqueous sample required is 100 ml. Aqueous samples and extracts of soils must be preserved to a pH <2 and stored at >0 to 6°C until ready for distillation and analysis. The maximum holding time prior to analysis of the aqueous samples and soil extracts is 28 days. Residual chlorine checks must be performed on aqueous samples submitted

from a wastewater treatment process. Groundwater and untreated waters would not require checks.

8.2 Soil samples are collected in plastic or glass 4 oz. wide-mouth jars. The minimum sample required is 20g. Although storage requirements for soils are not defined, use aqueous sample storage requirements and hold times.

9) Equipment and Supplies

9.1 Direct simple distillation apparatus: The distillation glassware includes flasks, traps, and tubes.

9.2 Shimadzu model UV-2450 PC UV-Vis Scanning Spectrophotometer, for use at 640 nm, providing a light path of 1.0 cm. Operating software for the UV-VIS

9.3 Quartz cuvettes, matched, 1-cm path length

9.4 Oxford pipettes or equivalent, 5-mL and 10-mL, calibrated quarterly.

9.5 Assorted Eppendorf pipettes or equivalent, 0.25 to 1.00-ml, calibrated quarterly.

9.6 Assorted Class A volumetric flasks; 25-ml, 50-mL, 100-mL, 250-ml, 500-mL

9.7 100-mL and 25-mL graduated cylinders, Class A.

9.8 Teflon boiling Chip.

9.9 Computer hardware and software:NA

10) Standards and Reagents

10.1 Note: Store all purchased standards according to manufacturer specifications. Store all standard solutions (remaining stock, composite, calibration and surrogate) below 6 °C in glass containers having Teflon™ lined lids. All purchased stock standard solutions must be replaced after reaching the manufacturer's expiration date assigned to the standard. All laboratory prepared standard solutions must be replaced after six months or sooner if routine QC indicates a problem. An assigned expiration date of a lab prepared standard cannot exceed the manufacturer's expiration date for any component used in the standard formulation. Document all preparations in reagent/standard prep logbook and label storage bottles with content, concentration and expiration date. When analyzing standards, lot numbers must be associated with the calibration curve, run batch or prep batch.

10.2 Sodium Hydroxide (NaOH), 6 N solution: Dissolve 240 g of NaOH pellets in approximately 700 ml of DI water, and bring to 1000-ml or dissolve 480g of 50% NaOH into ~400 mL water and dilute to 1000-ml. Prepare fresh every 12 months.

10.2.1 Sodium Hydroxide (NaOH), 1.0 N solution: dilute 167 mL of 6 N NaOH into approximately 700 ml of DI water in a volumetric flask, and bring to final volume of 1000 mL.

10.3 Sulfuric Acid (H_2SO_4), 0.1N : Carefully add 28 mL of concentrated H_2SO_4 to 500 mL of DI water and dilute to a final volume of 1000 mL. Prepare fresh every 12 months.

10.4 Sodium Tetraborate Solution, 0.025 M solution: Dissolve 1.25 g of $Na_2B_4O_7$ [anhydrous] or 2.375 g of $Na_2B_4O_7 \cdot 10\ H_2O$ and dilute to 250 mL using DI water. Prepare monthly and document prep in logbook.

10.5 Borate Buffer Solution: Add 44 mL of 0.10 N NaOH to 250 mL of 0.025 M Sodium Tetraborate Solution and dilute to 500 mL using DI water. Prepare monthly and document prep in logbook.

10.6 HACH DPD powder or equivalent.

10.7 Dechlorinating Agent (Sodium Thiosulfate Solution): Dissolve 3.5 g of $Na_2S_2O_3 \cdot 5\ H_2O$ in approximately 800 mL of DI water and bring to final volume of 1L. Prepare fresh weekly. . Note: 1.0 mL of this solution will remove 1 mg/L residual chlorine in a 500 ml sample.

10.8 Phenol Solution: Mix 11.1mL of liquified phenol (89%) with 95%v/v ethyl alcohol to a final volume of 100 mL. See safety section for handling precautions. Prepare weekly.

10.9 Sodium nitroprusside (0.5%): Dissolve 0.5 g of sodium nitroprusside (CAS RN 14402-89-2) in 100 mL of reagent water. Store this solution in an amber bottle for up to 1 month.

10.10 Alkaline Citrate: Dissolve 200-g trisodium citrate and 10-g of sodium hydroxide in deionized water and bring to final volume of 1.0 L. Store in amber glass for up to 1 month.

10.11 Sodium Hypochlorite, commercial solution (~5%): purchase 1quart container of bleach. Adhere to the manufacturer's expiration date.

10.12 Oxidizing Solution: mix 50 mL of alkaline citrate solution with 12.5-ml of Sodium Hypochlorite. Prepare fresh daily.

10.13 Ammonia Nitrogen Calibration Stock Standard, 1000 mg/L as N: Purchase commercially available standard or prepare by dissolving 3.819 g of anhydrous NH_4Cl (dried at 100˚C) in water and dilute to 1000 ml. 1.00 mL = 1.00 mg N. Use for the calibration curve and CCV preparations.

10.13.1 Working Ammonia Standard, 10.0-mg/L: Dilute 1mL of the 1000 mg/L Stock Ammonia Standard to a final concentration of 100 mL. Preserve with 0.5 mL of H_2SO_4 (1+1). Prepare monthly and store at 4˚C.

10.13.2 Calibration standards are prepared fresh daily with each new curve or CCV. Prepare 25-ml of each standard.

Table 10.14.2	Blank	S1	S2	S3	S4	S5	S6
NH_3 as N – mg/L	0.0	0.025	0.05	0.10	0.20	0.50 ICV/CCV	1.00
Vol of 10 mg/L NH_3 as N, in µL	-	62.5	125	250	500	1250	2500
Final Volume, mL	25	25	25	25	25	25	25

10.14 Second Source Stock NH_3 as N, 1000 mg/L: Purchase or prepare a second source stock ammonia standard solution from a different source reagent.

10.14.1 Initial Calibration Verification (ICV) Standard: dilute the second source 1000 mg/L Stock NH_3 as N Standard to the ICV concentration in Table 10.14.2.

11.15 Continuing Calibration Verification (CCV) Standard: dilute the calibration source 1000 mg/L Stock NH_3 as N to the CCV concentration in Table 10.14.2.

11.16 LCS/MS/MSD for Water (0.20 mg/L): Add 1.0 mL of 10.0 mg/L Working NH_3 as N Standard to a 25 mL of a method blank or sample that has been prepared for distillation.

10.17 LCS/MS/MSD for Solids (10.0 mg/Kg): Add 1.0 mL of 10.0-mg/L Working NH_3 as N Standard onto a 1.0 gram solid method blank or solid sample that has been prepared for distillation. Next 25 mL of reagent water is added to the spiked solid prior to the distillation.

10.18 Method Blanks: for waters, distill 25 mL of reagent water; for soils, distill 50 ml of DI water that contains a 1.0 g portion of Ottawa Sand.

11) Calibration and Standardization

11.1 Perform Support Equipment Calibration Checks:

11.1.1 Balance Calibration Checks must be performed prior to balance use as per SOP HS-EQ-001, current revision.

11.1.2 Quarterly Pipet Calibration checks must be current for the micro-pipets when they are used to measure portions of DI water or standard solutions required in this procedure. Quarterly pipet calibration checks are performed according to SOP HS-EQ-003, current revision. For DoD samples, verification of pipettes must be done on the day the samples are being performed.

11.2 Initial Calibration (ICAL) is performed using a reagent blank and 6 standards in the range of 0.025 to 0.1.00 mg/L. The range must bracket the raw analytical results. A calibration blank (CCB) is run to demonstrate instrument readings are below the lowest standard in the ICAL curve. The ICAL standards do not require distillation.

11.3 Initial Calibration Verification (ICV) is prepared from the second source stock at 0.20 mg/L. This is prepared in the same manner as a calibration standard. The ICV does not require distillation.

11.4 Continuing Calibration Verification (CCV) is prepared from the ICAL source stock at 0.20 mg/L. The CCV does not require distillation.

11.5 Perform and document all required support equipment calibration checks (balances, pipettes, etc.).

12) Sample Preparation/Analysis

12.1 Pre-distillation: evaluate whether samples contain residual chlorine using DPD powder (Sec 10.6). Eliminate chlorine if present using sufficient dechlorinating reagent.

12.2 Distillation: Wastewater samples must be prepared using the distillation procedure. When the distillation is performed, following QC samples must be included: the method blank, LCS, Matrix Spike, Matrix Spike Duplicate and a sample duplicate. The ICV, ICB, CCV and CCB are not distilled. Document distillation in the prep log.

12.3 Distillation for Aqueous Samples:

12.3.1 Aqueous samples may be distilled on an "as received" basis except that they should be warmed to ambient temperature after being taken from refrigeration and checked for residual chlorine using DPD powder.

12.3.2 If residual chlorine is present, remove by the addition of 0.025 N Sodium Thiosulfate (Sec 10.7).

12.3.2.1 Add scoop of boiling chips to distillation tube.

12.3.3 For preparation of LCS, MS and MSD, add 1.0 mL of the 10 mg/L Stock

Ammonia (as N) standard (see section 10) to the 50 mL reagent water sample. DO NOT allow the sample to stand, as ammonia will begin evolving as soon as the solution is alkaline. It must be attached immediately to the distillation unit.

12.3.4 Add 25 mL of sample to the distillation tube. Add 1.25 mL of borate buffer solution to the distillation tube and adjust the sample to pH 9.5 with dropwise additions of 6.0N NaOH. Add 10 ml of 0.1 normal H2SO4 into trap solution add 1 N NAOH and bring the volume up to 25 mls with DI water (= 0.04N H2SO4 solution).

12.4 Distillation of Soil Samples:

12.4.1 Ammonia tends to leach poorly from soils; therefore soils must be distilled. Do NOT distill a water leachate unless a client specifies the approach.

12.4.2 Soil samples should be warmed to ambient temperature after being taken from refrigeration and should be composited or mixed to assure homogeneity.

12.4.3 Weigh 1 ±0.2 grams of soil and add it to a 50 mL distillation tube.

12.4.4 Add 25 mL of reagent water to the 50 mL distillation tube. Swirl the tube to mix the soil. If the soil sample clumps, use a glass or metal stir rod or spatula to break up clumps.

12.4.5 For preparation of LCS, MS and MSD, add 1.0 mL of the 10 mg/L Stock Ammonia (as N) standard (see section 10) to the 1.0 g soil. After the spike addition, immediately mix with 50 mL of DI water and close the system to the atmosphere.

12.4.6 Add 1.25 mL of borate buffer solution to the distillation tube and adjust the sample to pH 9.5 with NaOH. Add 10 ml of 0.1 normal H2SO4 into trapping solution Add Scoop of boiling chip.

12.4.7 Do NOT allow the sample to stand, as ammonia will begin evolving as soon as the solution is alkaline. It must be attached immediately to the distillation unit.

12.5 Sample Colorimetric Analysis

12.5.1 Add 1 normal NAOH to 10-ml distilled sample portion and bring up to 25 ml volume in the certified digestion cups, add, with through mixing after each addition, 1-ml of phenol solution, 1-ml Sodium nitroprusside solution and 2.5-ml of the oxidizing solution.

12.5.2 Cover the flask with a paraffin wrap and allow the color to develop in dark for at least 2 hours. The color is stable for 24-hours.

12.5.3 Measure the absorbance at 640-nm.

12.6 Analyze the samples and check the calibration by analysis of calibration verification (second source standard) at beginning, after each ten sample analyses, and at the end of the analysis. Analyze a blank at the end of the batch.

12.7 If any sample is greater than the highest standard, prepare a sample dilution and re-analyze. A soil distillate is analyzed and reported as mg/kg of original sample.

13) Troubleshooting

13.1 Accurate Borate solution pH adjustment is necessary for the distillation step. Prepare new standards, check instrument maintenance (check wavelength, clean cuvettes, and prepare a new curve as needed.

14) Data Acquisition

14.1 Use the manufacturer's instructions for operation for the UV-Vis instrument when generating the calibration curve, reading unknown samples, and storing the data files. The ICAL correlation coefficient must be equal to or greater than 0.995.

14.2 All data must be manually entered from the instrument record into LIMS for reporting the Ammonia Nitrogen. Record the instrument results in the colorimetric logbook. Maintain a copy of the instrument raw data and save the data electronically onto a file on the Shimadzu computer. LIMS assigns a batch ID to each batch entered. When sample dilutions are made, enter the dilution factors correctly into -LIMS for converting the raw data for reporting final results.

14.3 Once the data has been entered into LIMS and all QC validation steps have been completed, data is further reviewed by project management for reporting.

14.4 Typical Analytical Sequence:
- 14.4.1 Initial Calibration curve and a blank
- 14.4.2 Initial Calibration Verification standard
- 14.4.3 Initial Calibration Blank
- 14.4.4 Method Detection Limit Check Sample
- 14.4.5 Laboratory Control Sample
- 14.4.6 Client sample
- 14.4.7 Matrix spike
- 14.4.8 Matrix spike duplicate
- 14.4.9 Client samples (5)
- 14.4.10 Continuing Calibration Verification Standard
- 14.4.11 Continuing Calibration Blank

15) Calculation, and Data Reduction Requirements

15.1 Quantification Calculations

15.2 Aqueous Calculation: Quantitate the concentration of NH3-N (in mg/L) from the aqueous scrubber using the following equation:

$$NH3\text{-}N\ (mg/L) = [A \times B \times DF] / C$$

Where:
A = mg/L NH3-N read from standard curve.
B = mL of scrubber solution used for preparation of colorimetric analysis (normally 25 mL).
C = 25 mL.
DF = Dilution factor (based on any dilution of the scrubber solution before taking the color aliquot). If the scrubber solution is analyzed without pre-dilution, DF = 1.

15.3 QC Calculations: LIMS calculates the percent recovery for various QC samples (LCS) according to the following equations:
15.3.1 % Recovery, %R (for MS and MSD Samples)

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SR = Sample Result (unspiked).
SA = Spike Amount Added (mg/L or mg/kg).

15.3.2 % Recovery, %R (for standards and LCS)

$$\%R = \frac{(SSR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SA = Spike Amount Added (mg/L or mg/kg).

15.3.3 RPD (for precision or duplicate evaluation)

$$RPD = \frac{|SR_1 - SR_2|}{½(SR_1 + SR_2)} \times 100$$

Where:
SR_1 = Sample result for duplicate 1.
SR_2 = Sample result for duplicate 2.

16) Quality Control, Acceptance Criteria and Corrective Action

16.1 Initial Demonstration of Capability
- 16.1.1 Purpose: Verify the ability to produce data of acceptable precision and bias for a specific instrument type, matrix, method, and analyst.
- 16.1.2 Frequency: Initially during method development, and any time there is a significant change in instrument type, personnel, methodology, or matrix
- 16.1.3 Acceptance Criteria: Four consecutive LCS analysis meeting stated LCS criteria.
- 16.1.4 Corrective Action: Identify and correct the source of error. Reanalyze the demonstration.

16.2 Continuing Demonstration of Capability
- 16.2.1 Purpose: Verify the ability to produce data of acceptable precision and bias for a specific instrument type, matrix, method, and analyst.
- 16.2.2 Frequency: Annual to re-qualify analyst for analysts.
- 16.2.3 Acceptance Criteria: Four consecutive LCS analysis meeting stated LCS criteria or successful PT study.

16.3 Initial Calibration:
- 16.3.1 Frequency: perform quarterly at a minimum, or earlier if calibration verification fails (ICV or CCV). These standards are used to verify that the

instrument response is linear, and the curve is used to calculate the concentration of the samples.

16.3.2 Criteria: The correlation coefficient must be equal to or greater than 0.995.

16.3.3 Initial Calibration Curve linearity Exceedance Corrective Action: check standard sources and prepare new standards.

16.4 Initial Calibration Verification (ICV):

16.4.1 Frequency: Verify each new curve with a second source standard

16.4.2 Criteria: Agreement must be 90-110% of the true value.

16.4.3 Calibration Verification exceedance: prepare new standards and a new curve

16.5 Calibration Verification (CCV):

16.5.1 Frequency: Verify the curve prior to running samples, every ten samples thereafter and at the end of the run with the same source as the initial calibration standard

16.5.2 Criteria: Agreement must be 90-110% of the true value.

16.5.3 Calibration Verification exceedance: prepare new standards and a new curve, re-analyze all samples since the last passing CCV. The CCV may fail high if the bracketed samples are non-detect.

16.6 Continuing Calibration Blanks (ICB and CCB) and Method Blanks (MB)

16.6.1 Frequency: Verify that the system is free of contamination after each new curve (ICB) and prior to running samples, every ten samples thereafter (CCB) and at the end of the run (CCB). The method blank is distilled with each batch of 20 (RCRA) or 10 (wastewater QC).

16.6.2 Criteria: The blank results should not be more than ½ LOQ, or no more than 5% of sample concentration, or 5% of regulatory limits, whichever is greater. If above the limit, it is an indication of instrument drift and the baseline must be reset and the samples since the previous acceptable blank must be re-analyzed. If a method blank indicates contamination (>1/2 LOQ), all samples having detections must be re-distilled unless the MB is no more than 5% of sample concentration, or 5% of a regulatory limit, whichever is greater.

16.7 Laboratory Control Standard (LCS)

16.7.1 Frequency - The LCS is a mid-point standard that is prepared separately from the initial calibration. Each batch of 20 samples must include a LCS.

16.7.2 Criteria - The LCS results must be within the range 80 to 120 percent. The LCSD RPD limit is 20% for aqueous sample and 25% for solid samples.

16.7.3 LCS Exceedance Corrective Action: If the LCS outside the acceptance range, perform corrective action to solve the source of the error, and re-distill and re-analyze the sample batch. If the LCS fails high and the samples are non-detect, the data can be reported, but it must be narrated.

16.8 Matrix Spike Sample / Matrix Spike Duplicate

16.8.1 Frequency - Matrix spikes will be analyzed on a frequency of one spike for each 20 or less samples prepared in the batch.

16.8.2 Criteria: Acceptance limits employ the LCS limits for soil and water matrices. The MSD RPD limit is 20% for aqueous sample and 25% for solid samples.

16.8.3 MS exceedance Corrective Actions: If the spike results are outside the acceptance limits for recovery, evaluate the data against the LCS recovery to determine if a matrix effect is present or whether due to a possible a system error. Describe in the lab review checklist as necessary. Note that the LCS

must fall within the acceptance criteria. The sample MS results are flagged by LIMS when MS limit exceedance occurs.

16.9 Duplicate Sample

16.9.1 Frequency: Duplicates will be analyzed on a frequency of one duplicate for each 20 or less samples prepared in the batch.

16.9.2 Criteria: RPD Acceptance limits for the water matrix is 20% and soil matrix is 25 %.

16.9.3 Duplicate Sample RPD Exceedance Corrective Action: If the duplicate results are outside the acceptance limits for relative percent deviation, first determine if the cause is a system error; if so, correct the problem and repeat the duplicate. If not, the LCS must fall within the acceptance criteria in order for the data to be accepted. The sample duplicate results are flagged by LIMS when a limit exceedance occurs.

16.10 Limit of Detection:

16.10.1 Frequency: These are performed once per quarter. This data can be found in LIMS. Study must be performed according to the SOP HS-QS-006.

16.10.2 Criteria: LOD recovery 1-200%, LOQ 50-150%.

16.10.3 Corrective Action: LODs/LOQs are reanalyzed if the recoveries are not within range.

17) Data Records Management

17.1 All data is stored electronically and/or hard copy for 5 years or for 10 years in the state of Louisiana.

17.2 All analytical sequence IDs and standard preparation information must be recorded in the Run logbook. Hardcopy computer printouts of analytical sequences and raw data must be retained and initialed by the analyst (electronic initials are acceptable). To simplify standard and reagent tracking, analyst must attempt to use single lots of reagents and standards.

17.3 Complete all pertinent sections in the respective logbooks. If not-applicable then line out the section. "Z" out or "X" out all large sections of the worksheet that are not used. Make all corrections with single line through, date and initial. Make NO obliterations when manually recording data.

17.4 Logbooks are controlled. Never remove a page from a logbook. Completed logbooks are returned to the QA department when filled and no longer needed in the work area.

17.5 SOP effective date is the date noted in the header or last signature date, whichever is most recent.

18) Contingencies for Handling Out of Control Data

18.1 When method required QC exceedances occur, in every case where sample data quality are affected, the source of the QC exceedance must be determined, corrected and sample reanalysis carried out when possible.

18.2 When affected sample analysis cannot be repeated due to limitations (i.e. sample availability, or if reanalysis can only be performed after expiration of a sample hold time), the reporting of data associated with exceeded QC data must be appropriately

flagged and narrated. This documentation is necessary to define for the data user the effect of the error has upon the data quality of the results reported (e.g. E flag data indicate the result to be only an estimate).

18.3 All analysts must report sufficient comments in laboratory data review checklist for exceeded QC associated with sample results so that project management can further narrate and ensure data qualifiers (flags) are properly assigned to the reported data.

18.4 NCARs must be issued for QC system exceedances. Matrix interferences are reported using the analyte reporting comment section in LIMS or using the Laboratory Data review checklist.

19) Method Performance

Method performance is determined by the successful performance of performance evaluation samples, laboratory control standards, and MDLs.

20) Training

20.1 Training to perform the procedures for this method should take the following into consideration:

20.1.1 Review literature (see references section). Read and understand this SOP. Also review the applicable SDS for all reagents and standards used. Following the reviews, observe the procedure performed by an experienced analyst at least three times.

20.1.2 The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

20.1.3 Perform initial Demonstration of Capability (IDOC) study in this case two sets of duplicates. Summaries of the IDOC are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IDOC studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

20.2 Training is documented following *SOP CE-QA003*).

20.3 When the analyst training is documented by the supervisor on internal training documentation forms (HS-QAFORM010 and HS-QAFORM038) the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

21) Waste Management

21.1 The laboratory's waste management practices are conducted consistent with all applicable rules and regulations See waste management policy SHWD-001.

22) Summary of Changes

Table 22.1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
5.4	7/23/2020	G. Moulton	Sec1: Included Identification of the Method, Applicable matrices with scope and application.
5.4	7/23/2020	G. Moulton	Sec 2: Boric acid is removed from summary of the method as the collecting solution and replaced with 0.04N sulfuric acid.
5.4	7/23/2020	G. Moulton	Sec 16.10: Updated LOD/LOQ requirements.
5.4	7/23/2020	G. Moulton	Sec 10.5 modify 1L to 500 ml.
5.4	7/23/2020	G. Moulton	11.1.2 – included DoD requirement for pipette verification.
	7/23/2020	G. Moulton	Sec. 12.3.4: Modified to indicate addition of 1N NAOH and 0.04N H2SO4.
5.4	7/23/2020	G. Moulton	Removed original 12.5 to 12.5.4. Not needed.
5.4	7/23/2020	G. Moulton	Added 6.7-6.9 – pollution prevention measures.
5.4	7/23/2020	G. Moulton	Added Training as sec 20.
5.4	7/23/2020	G. Moulton	Added Waste Management as sec 21.
5.4	7/23/2020	G. Moulton	Added HACH DPD powder to sec 10.6 as an alternative for chlorine check.
5.4	7/23/2020	G. Moulton	Changed Appendix to say. Tables, diagrams, flowcharts and validation data
5.3	08/14/2019	G. Moulton	16.10.1 added quarterly requirement for DoD LODs.
5.3	08/14/2019	G. Moulton	Slight Modification to sec. 13.3 and 12.5
5.3	08/14/2019	G. Moulton	Included sec 19.1 method performance.
5.3	08/14/2019	G. Moulton	Renamed table to 10.14.2 and re numbered the standards for the calibration curve.
5.2	06/21/2019	G. Moulton	12.3.4: 25 ml sample, 1.25 ml, added also (10 ml 0.1 N H2SO4 into solution)
5.2	06/21/2019	G. Moulton	Sec. 12.4.4- Added 25 ml of reagent water.
5.2	06/21/2019	G. Moulton	Removed sec 12.5.2
5.2	06/21/2019	G. Moulton	12.5.4 – set timer to 1 hour, 130˚
5.2	06/21/2019	G. Moulton	12.5.5 – 25 ml of distillate
5.2	06/21/2019	G. Moulton	Add 1 N NAOH dropwise.
5.1	10/22/2018	G. Moulton	Updated new cover and new QA manager.
5.1	10/22/2018	G. Moulton	Modified sec, 17.1 data storage.
5.1	10/22/2018	G. Moulton	Modified 21.1, 21.3 and 21.4
05.0	08/31/2015	T. Yen	SOP Format Change, New Lab Director, Inorganic Manager and QA Manager.

05.0 – Section 4.5	08/31/2015	T. Yen	Job Safety Assessment (JSA) added.
05.0 – Section 10.	08/31/2015	T. Yen	Reagent update.
5.0 – Section 16	08/31/2015	T. Yen	Initial demonstration and continuing demonstration added.
05.0 – Section 17.2	08/31/2015	T. Yen	Use of single lots of standard/reagent to simplify standard tracking.
05.0 – Section 17.5	08/31/2015	T. Yen	SOP effective date defined.
05.0 – Section 21	08/31/2015	T. Yen	Reference updated.
04.1	08/01/2012	J. Cady	Minor revision. Format/font change.
04.0	08/05/2011	J. Cady	Major document revision.

23) References and Related Documents

23.1 Referenced Documents

23.1.1 Method 4500-NH3-B/F, Ammonia Nitrogen, Standard Methods for the Examination of Water and Wastewater, 22nd Edition, 2012.

23.2 Micro-Block™ Instruction Manual, Rev4.02, Environmental Express, Mt. Pleasant , SC 29464

23.3 Current TNI Standards.

23.4 Current Department of Defense Quality Systems Manual.

24) Tables, Diagrams, Flowcharts and Validation Data

Table 24.1 Ammonia Nitrogen LODs and LOQs

Ammonia Nitrogen LODs and LOQs					
Analyte – water matrix	LOD mg/L	LOQ mg/L	Analyte - soil matrix	LOD mg/Kg	LOQ mg/Kg
Ammonia Nitrogen	0.01	0.025	Ammonia Nitrogen	0.25	1.3

Table 24.2 Ammonia Nitrogen LCS Recovery Limits

Ammonia Nitrogen LCS Recovery Limits									
Analyte - Aqueous	SPK- mg/L	Low %	High %	RPD %	Analyte - Soil	SPK mg/Kg	Low %	High %	RPD %
Ammonia Nitrogen	0.20	80	120	20	Ammonia Nitrogen	10.0	80	120	25

Table 24.3 Summary of Calibration and QC Procedures for Ammonia Nitrogen

Summary of Calibration and QC Procedures for Ammonia Nitrogen – SM 4500 NH3 B/D			
QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Calibration: 5 standards minimally, verify with second source ICV	Every three months minimally	r ≥0.995 , ICV within ±10% of expected value.	Correct problem then repeat LCS analysis.
Continuing Calibration: CCV	Daily, before samples, then every 10 samples, and at end of sequence.	CCV within ±10% of expected value.	Correct problem then repeat CCV or prepare new curve and new CCV.
LCS, can use the second source for method control verification	Once per each batch of 20 or less samples, perform prior to running samples.	QC acceptance criteria, Table 24.2.	Correct problem then repeat LCS analysis.
Method blank.	One per batch of 20 or less.	NH3N not detected above the 1/2 LOQ.	Correct problem, and then re-analyze method blank and all samples processed with the contaminated blank.
MS/MSD	One MS per every 20 field samples per matrix.	QC acceptance criteria, Table 22.2. RPD <20% waters; RPD <25% soils	Describe in Laboratory Review Checklist.
Duplicate	One duplicate per every 20 field samples per matrix.	RPD <20% waters; RPD <25% soils	Describe in Laboratory Review Checklist.
Initial Demonstration of ability to generate acceptable accuracy and precision using four replicate LCS.	Once per analyst.	QC acceptance criteria, Table 24.2.	Recalculate results; locate and fix problem with system, then rerun demonstration
Continuing Demonstration of capability to generate acceptable accuracy and precision using four replicate LCS or acceptable PT.	Annually per analyst	QC acceptance criteria, Table 24.2.	Recalculate results; locate and fix problem with system, then rerun demon-Stratton.

AMMONIA NITROGEN BY ION SELECTIVE ELECTRODE (ISE), SM 4500-NH3 B/D AND EPA 350.3

DOCUMENT ID: HS-WC027, REV 3.2

Approved By: Hoai. Van
Technical and Laboratory Director, Hoai Van

Date: 10/15/18

Prepared By: Erica M Howard
Quality Assurance Manager, Erica Howard

Date: 10/15/2018

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1) Scope and Applicability

1.1 This method covers the determination of ammonia in water (ground, surface, saline) and wastewater (domestic, industrial) using an ammonia ion selective electrode (ISE).

1.2 The applicable range is 0.2-100 mg/L NH_3 as N. Higher concentrations can be determined by sample dilution.

1.3 This method also references the use of midi-distillation equipment for sample preparation and the use of the ammonia ion selective electrode (ISE) for analysis. Distillation is usually not necessary, but may be chosen on a project specific need.

2) Summary of Procedure

2.1 Ammonia in neutral to acidic aqueous solutions exists primarily as the ammonium (NH_4^+) cation. When the pH is raised above about 8.0-8.5, the chemical equilibrium shifts because the excess hydrogen on the ammonium cation reacts with the hydroxyl anion to yield ammonia gas ($NH_4^+ + OH^- \uparrow\ H_2O + NH_3 \rightarrow$). While the ammonia gas remains water-soluble, it may be stripped from solution by boiling and/or sparging. This allows for separation of the ammonia from potential ionic species that may act as interferents. Boric acid in aqueous solution readily absorbs the gaseous ammonia. To initiate the distillation, the sample is placed into a gas-tight distillation flask assembly, buffered to a pH of 9.5 with borate buffer, and then heated to boiling with the steam directed through a condenser to bubble through a solution of boric acid. The borate buffer is used in order to decrease hydrolysis of cyanates and organic nitrogen compounds.

2.2 The distillate is captured in a boric acid solution. The boric acid solution containing the ammonia-boric acid complex is determined colorimetrically. The ammonia distills within the first 25 ml of collection based on a 50-ml initial volume (see SOP HS-WC-026).

2.3 Analysis is performed using an Ammonia – selective electrode. The working range for the electrode is 0.2 to 50-mg/L Ammonia nitrogen.

3) Definitions

3.1 DI = Deionized reagent water, meeting purity characteristics of Type I laboratory distilled water (daily resistance of >17 MΩ-cm).

3.2 Batch: environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours.

3.3 Laboratory Control Sample (LCS): A known clean matrix spiked with all target analytes. This is used to evaluate and document laboratory method performance.

3.4 Matrix: The substrate (e.g., water, soil, etc.) which contains the analyte of interest.

3.5 Matrix Spike (MS): An aliquot of sample spiked with a known concentration of target analytes. The spiking occurs prior to sample preparation and analysis. A matrix spike is used to document the bias of a method in a given sample matrix.

3.6 Matrix Spike Duplicate (MSD): A duplicate sample is spiked with identical concentrations of target analytes. The spiking occurs prior to sample preparation and analysis. The MS/MSD pair are used to document the precision and bias of a method in

a given sample matrix.

3.7 Method Blank: An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

3.8 Limit of Detection (LOD): an estimate of the minimum amount of a substance that an analytical process can reliably detect. An LOD is analyte- and matrix-specific and may be laboratory-dependent. For this procedure, data are not reported below the lowest calibration standard. Therefore, the LOD is set to be equal to the LOQ.

3.9 Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence. This defined concentration can be no lower than the concentration of the lowest calibration standard adjusted for sample preparation factors and can only be used if acceptable quality control criteria are met.

3.10 Method Detection Limit (MDL) study: a procedure described in 40CFR Part 136, Appendix B, that describes how to produce an MDL, a reporting element of certain EPA method. An MDL study is one approach to determine the LOD.

3.11 NCAR: Nonconformance Corrective Action Report (refer to SOP HS-QS-003).

3.12 Exception Report – Appropriate comments reported with the associated sample batch that address sample anomalies such as demonstrated sample matrix effects

4) Health and Safety Warnings

4.1 Lab Safety: Due to various hazards in the laboratory, safety glasses and laboratory coats or aprons must be worn at all times while in the laboratory. In addition, gloves and a face shield should be worn when dealing with toxic, caustic, and/or flammable chemicals.

4.2 Chemical Hygiene: The toxicity or carcinogenicity of each reagent used has not been precisely defined; however, each chemical used should be treated as a potential health hazard. Exposure to laboratory reagents should be reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets (MSDS) is available to all personnel involved in these analyses.

4.3 Waste Management: The principal wastes generated by this procedure are the method-required chemicals and standards. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required. Laboratory procedures in SOP HS-SAF-001, Waste Disposal Procedures, must be followed.

4.4 Pollution Prevention: The materials used in this method pose little threat to the environment when recycled and managed properly. The quantities of chemicals purchased should be based on the expected usage during its shelf life. Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards or reagents to be disposed.

5) Cautions

5.1 Routine preventative maintenance must be performed and documented to assure optimum instrument performance. Refer to the current revision of SOP HS-EQ004 for preventative maintenance schedules.

6) Interferences

6.1 Distillation is unnecessary for waters when using the ISE method. Soils are distilled.

6.2 Amines are a positive interference.

6.3 Residual chlorine rapidly converts ammonia into chloramines, and this process accelerates at the boiling temperature used to distill the sample. Therefore, residual chlorine must be removed by pretreatment of the sample with sodium thiosulfate upon sample collection.

7) Personnel Qualifications and Responsibilities

7.1 General Responsibilities - This method is restricted to use by or under the supervision of analysts experienced in the method.

7.2 Analyst - It is the responsibility of the analyst(s) to:

- 7.2.1 Each must read and understand this SOP and follow it as written. Any deviations or nonconformances must be documented and submitted to the QA Manager for approval.
- 7.2.2 Produce method compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP (HS-QS-009).
- 7.2.3 Complete the required initial demonstration of proficiency before performing this procedure without supervision.
- 7.2.4 Complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 7.2.5 The analysts must submit data for peer or supervisor review.

7.3 Section Supervisor - It is the responsibility of the section supervisor to:

- 7.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.
- 7.3.2 Ensure analysts have completed the required initial demonstration of proficiency before performing this procedure without supervision.
- 7.3.3 Ensure analysts complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 7.3.4 Ensure analysts produce method compliant data that meet all quality requirements using this procedure and the Data Reduction, Review and Validation SOP.

7.4 Project Manager - It is the responsibility of the Project Manager to ensure that all method requirements for a client requesting this procedure are understood by the laboratory prior to initiating this procedure for a given set of samples.

7.5 QA Manager: The QA Manager is responsible for

- 7.5.1 Approving deviations and nonconformances
- 7.5.2 Ensuring that this procedure is compliant with method and regulatory requirements,
- 7.5.3 Ensuring that the analytical method and SOP are followed as written through internal method and system audits.

8) Sample Collection, Handling, and Preservation

8.1 Aqueous samples are collected in either plastic or glass. The minimum aqueous sample required is 100 ml. Aqueous samples and extracts of soils must be preserved to a pH <2 and stored above 0 to 6˚C until ready for analysis. The maximum holding time prior to analysis of the aqueous samples and soil extracts is 28 days. Residual chlorine checks must be performed on aqueous samples submitted from a wastewater treatment process. Groundwater and untreated waters would not require checks.

8.2 Soil samples are collected in plastic or glass 4 oz. wide-mouth jars. The minimum sample required is 20g. Although storage requirements for soils are not defined, use aqueous sample storage requirements and hold times.

9) Equipment and Supplies

9.1 Direct midi-distillation apparatus: see SOP HS-WC-026.

9.2 Ammonia – selective electrode, Fisher Ammonia Probe, Cat # 14002-794, or equivalent

9.3 Fisher Accumet AR 50 or 60, pH/mV/ion/Conductivity Meter or equivalent.

9.4 Temperature compensation probe, Fisher ATC Probe, Cat # 13-620-19, or equivalent

9.5 Oxford pipettes, 5-mL and 10-mL, calibration verified ± 2%.

9.6 Assorted Eppendorf pipettes, 0.25 to 1.00-ml, calibration verified ± 2%.

9.7 Assorted Class A volumetric flasks; 25-ml, 50-mL, 100-mL, 250-ml, 500-mL

9.8 100-mL and 25-mL Pyrex graduated cylinders.

9.9 Analytical balance, capable of reading ±0.0001-g

10) Standards and Reagents

10.1 Distillation Reagents: See SOP WC-026

10.2 Residual Chlorine Test Paper: EM Science, EM- 17923-1 or equivalent.

10.3 Dechlorinating Agent (Sodium Thiosulfate Solution): purchase 0.025N Sodium Thiosulfate. Note: 1.0-ml will remove 1 mg/L residual chlorine in a 500 ml sample.

10.4 Ammonia Nitrogen Calibration Stock Standard, 1000 mg/L as N: Purchase commercially available certified standard (1.00-ml = 1.00-mg N): Ricca Cat # 5455-16 or equivalent.

10.4.1 Working Ammonia CCV Standard, 10.0-mg/L: Dilute 5-ml of the 1000 mg/L Stock Ammonia Standard to a final concentration of 500-ml. Preserve with 0.5-ml of H2SO4 (1+1). Prepare monthly and store >0 to 6˚C.

10.4.2 Calibration standards are prepared fresh daily when a new curve is generated using the following table.

Table 10.4.2	Blank	S1	S2	S3	S4	S4
NH_3 as N – mg/L by ISE	0.0 CCB	0.2	1.0	5.0	10.0	50.0
Vol of 10.0 mg/L NH_3 as N (CCV)	-	2.0	10.0	-	-	-
Vol of 1000.0 mg/L NH_3 as N	-	-	-	0.50	1.00	5.00
Final Volume, ml	100	100	100	100	100	100

10.5 Second Source Stock NH_3 as N, 1000 mg/L: Purchase second source certified stock ammonia standard. .

10.5.1 Initial Calibration Verification (ICV) Standard: dilute the second source 1000 mg/L Stock NH_3 as N in the same manner as the CCV (§ 10.4.1).

10.6 LCS/MS/MSD for Water (10 mg/L): Add 0.5-ml of 1000 mg/L Stock NH_3 as N Standard to a 50 ml of a method blank or sample that has been prepared for analysis (or distillation).

10.7 LCS/MS/MSD for Solids (10.0 mg/Kg): Add 0.5-ml of 1000-mg/L Working NH_3 as N Standard onto a 1.0 gram solid method blank or solid sample that has been prepared for distillation. 50 ml of a reagent water is added to the spiked solid prior to the distillation.

10.8 Method Blanks: for waters, distill 50 ml of DI water; for soils, distill 50 ml of DI water that has been added to 1.0 g of Ottawa Sand.

11) Method Calibration

11.1 Support Equipment Calibration Checks:

11.1.1 Daily Balance Calibration Checks must be performed daily prior to balance use as per SOP HS-EQ-001, current revision, when applicable.

11.1.2 Quarterly Pipet Calibration checks must be current for the auto pipets when they are used to prepare dilutions or standard solutions required in this procedure. Quarterly pipet calibration checks are performed according to SOP HS-EQ-003, current revision.

11.1.3 All support equipment are assigned unique identifiers. These identifiers must be noted on the applicable test procedure data bench logs when used.

11.2 Initial Calibration (ICAL) is performed using 5 standards (0.1, 1.0, 5.0, 10.0 and 50.0 mg/L). The range must bracket the raw analytical results. A calibration blank (CCB) is run to demonstrate instrument readings are below the lowest standard in the ICAL curve. The ICAL standards do not require distillation.

11.3 Initial Calibration Verification check (ICV) is prepared from the second source stock at 10.0-mg/L. This is prepared in the same manner as a calibration standard. The ICV does not require distillation.

11.4 Calibration Verification check (CCV) is prepared from the ICAL source stock at 10.0-mg/L. The CCV does not require distillation.

11.5 Record initial calibration curve slope in the Ammonia (ISE) Logbook. The slope must be in the 55 to 59-mV range.

12) Sample Preparation/Analysis

12.1 Pre-distillation (only if required by the project): evaluate whether samples contain residual chlorine using Chlorine Test paper. Eliminate chlorine if present using sufficient dechlorinating reagent.

12.2 Distillation: When the distillation is performed, following QC samples must be included: the method blank, LCS, matrix spike and sample duplicate. The ICV, ICB, CCV and CCB are not distilled.

12.3 Distillation for Aqueous or Soil Samples (see SOP HS-WC-026):

12.4 Sample ISE Analysis: Transfer a 50-ml sample portion into a 100-ml beaker, add 1 mL of 50% NaOH to the sample while stirring. Allow the probe to stabilize and measure the ammonia nitrogen with the ISE. Document the reading in the logbook.

12.5 If any sample is greater than the highest standard (50 ppm), prepare a sample dilution and re-analyze. A soil distillate is analyzed and reported as mg/kg of original sample.

13) Troubleshooting

13.1 Maintain the ISE according to the manufacture's instructions.

14) Data Acquisition

14.1 Use the manufacturer's instructions for generating the ISE calibration curve, reading unknown samples. The ISE Calibration slope must fall within in the 55 to 59-mV range.

14.2 All data must be manually entered from the instrument record into the e-LIMS for reporting the Ammonia Nitrogen. Record the instrument results in the ISE logbook. LIMS assigns a batch ID to each batch entered. When sample dilutions are made, enter the dilution factors to correctly into e-LIMS for converting the raw data for reporting final results. Record all volumes use to calculate dilution factors.

14.3 Once the data has been entered into LIMS and all QC validation steps have been completed, data is further reviewed by project management for reporting.

14.4 Typical Analytical Sequence:
- 14.4.1 Initial Calibration curve and a blank
- 14.4.2 Initial Calibration Verification standard
- 14.4.3 Initial Calibration Blank
- 14.4.4 Laboratory Control Sample
- 14.4.5 Client sample
- 14.4.6 Matrix spike
- 14.4.7 Matrix spike duplicate or sample duplicate
- 14.4.8 Client samples (5)
- 14.4.9 Continuing Calibration Verification Standard

15) Calculation, and Data Reduction Requirements

15.1 Quantification Calculations

15.2 Aqueous Calculation: Quantitate the concentration of NH3-N (in mg/L) from the aqueous scrubber using the following equation:

15.2.1 NH3-N (mg/L) = [A x DF]

Where:
A = mg/L NH3-N read from ISE standard curve.
DF = Dilution factor (based on any dilution of the sample before taking the ISE aliquot). If the sample is analyzed without pre-dilution, DF = 1.

15.3 QC Calculations: e-LIMS calculates the percent recovery for various QC samples (LCS) according to the following equations:

15.3.1 % Recovery, %R (for MS and MSD Samples)

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SR = Sample Result (unspiked).
SA = Spike Amount Added (mg/L or mg/kg).

15.3.2 % Recovery, %R (for standards and LCS)

$$\%R = \frac{(SSR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SA = Spike Amount Added (mg/L or mg/kg).

15.3.3 RPD (for precision or duplicate evaluation)

$$RPD = \frac{|SR_1 - SR_2|}{½(SR_1 + SR_2)} \times 100$$

Where:
SR_1 = Sample result for duplicate 1.
SR_2 = Sample result for duplicate 2.

16) Quality Control, Data Assessment and Corrective Action

16.1 Initial Calibration :

16.1.1 Frequency: perform quarterly at a minimum, or earlier if calibration verification fails (ICV or CCV). These standards are used to verify that the instrument response is linear, and the curve is used to calculate the concentration of the samples.

16.1.2 Criteria: initial calibration curve slope for the Ammonia (ISE) must be in the 55 to 59-mV range.

16.1.3 Initial Calibration Curve linearity Exceedance Corrective Action: check standard sources and prepare new standards.

16.2 Initial Calibration Verification (ICV):

16.2.1 Frequency: Verify each new curve with a second source standard

16.2.2 Criteria: Agreement must be 90-110% of the true value.

16.2.3 Calibration Verification exceedance: prepare new standards and a new curve

16.3 Calibration Verification (CCV):

16.3.1 Frequency: Verify the curve prior to running samples, every ten samples thereafter and at the end of the run with the same source as the initial calibration standard

16.3.2 Criteria: Agreement must be 90-110% of the true value.

16.3.3 Calibration Verification exceedance: prepare new standards and a new curve, re-analyze all samples since the last passing CCV. Samples associated with a CCV that demonstrates a high bias can be reported if the sample is non-detect.

16.4 Continuing Calibration Blanks (ICB and CCB) and Method Blanks (MB)

16.4.1 Frequency: Verify that the system is free of contamination after each new curve (ICB) and prior to running samples, every ten samples thereafter (CCB) and at the end of the run (CCB). The method blank is distilled with each batch of 20 (RCRA) or 10 (wastewater QC).

16.4.2 Criteria: The blank results should be less than the LOQ, or no more than 5% of sample concentration, or 5% of regulatory limits, whichever is greater. If above the limit, it is an indication of instrument drift and the baseline must be reset and the samples since the previous acceptable blank must be re-analyzed. If a method blank indicates contamination (>LOQ), all samples having detections must be re-analyzed unless the MB is no more than 5% of

sample concentration, or 5% of a regulatory limit, whichever is greater.

16.5 Laboratory Control Standard (LCS)

16.5.1 Frequency - The LCS is a 10.0-ppm standard that is prepared separately from the initial calibration. Each batch of 20 samples must include a LCS.

16.5.2 Criteria - The LCS results must be within the range 80 to 120 percent. The LCSD RPD limit is 20%.

16.5.3 LCS Exceedance Corrective Action: If the LCS outside the acceptance range, perform corrective action to solve the source of the error, and re-prepare and re-analyze the sample batch. If the LCS fails high and the samples are non-detect, the data can be reported, but it must be narrated.

16.6 Matrix Spike Sample

16.6.1 Frequency - Matrix spikes will be analyzed on a frequency of one spike for each 20 samples analyzed. If fewer than 20 samples are in a batch, one spike will be analyzed.

16.6.2 Criteria: Acceptance limits employ the LCS limits for soil and water matrices. The MSD RPD limit is 20%.

16.6.3 MS exceedance Corrective Actions: If the spike results are outside the acceptance limits for recovery, evaluate the data against the LCS recovery to determine if a matrix effect is present or whether due to a possible a system error. Describe in the lab review checklist as necessary. Note that the LCS must fall within the acceptance criteria. The sample MS results are flagged by LIMS when MS limit exceedance occurs.

16.7 Duplicate Sample (or as the MSD)

16.7.1 Frequency: Duplicates will be analyzed on a frequency of one duplicate for each 20 samples analyzed. If fewer than 20 samples are in a batch, one duplicate will be analyzed.

16.7.2 Criteria: Acceptance limits for the water matrix and soil matrix are 20 % RPD.

16.7.3 Duplicate Sample RPD Exceedance Corrective Action: If the duplicate results are outside the acceptance limits for relative percent deviation, first determine if the cause is a system error; if so, correct the problem and repeat the duplicate. If not, the LCS must fall within the acceptance criteria in order for the data to be accepted. The sample duplicate results are flagged by LIMS when a limit exceedance occurs.

17) Data Records Management

17.1 All data is stored electronically and/or hard copy for 5 years or for 10 years in the state of Louisiana.

17.2 All analytical sequence IDs and standard preparation information must be recorded in the Run logbook. Hardcopy computer printouts of analytical sequences and raw data must be retained and initialed by the analyst (electronic initials are acceptable).

17.3 Complete all pertinent sections in the respective logbooks. If not-applicable then line out the section. “Z” out or “X” out all large sections of the worksheet that are not used. Make all corrections with single line through, date and initial. Make NO obliterations when manually recording data.

17.4 Logbooks are controlled. Never remove a page from a logbook. Completed logbooks are returned to the QA department when filled and no longer needed in the work area.

18) Contingencies for Handling Out of Control Data

18.1 When method required QC exceedances occur, in every case where sample data quality

are affected, the source of the QC exceedance must be determined, corrected and sample reanalysis carried out when possible.

18.2 When affected sample analysis can not be repeated due to limitations (i.e. sample availability, or if reanalysis can only be performed after expiration of a sample hold time), the reporting of data associated with exceeded QC data must be appropriately flagged and narrated. This documentation is necessary to define for the data user the effect of the error has upon the data quality of the results reported (e.g. E flag data indicate the result to be only an estimate).

18.3 All analysts must report sufficient comments in laboratory data review checklist for exceeded QC associated with sample results so that project management can further narrate and ensure data qualifiers (flags) are properly assigned to the reported data.

18.4 NCARs must be issued for QC system exceedances. Matrix interferences are reported using the analyte reporting comment section in e-LIMS or using the Laboratory Data review checklist.

19) Method Performance

19.1 See Section 6 of Reference 20.1 and Section 8 of Reference 20.2

20) Summary of Changes

Table 20.1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
3.2	10/15/2018	G. Moulton	Updated new cover and new QA manager.
3.2	10/15/2018	G. Moulton	Modified sec 17.1 data storage.
03.1	09/01/2012	J. Cady	Minor revision. Format/font change.
03.0	09/30/2011	J. Cady	Major document revision.

21) References and Related Documents

21.1 Referenced Documents

21.1.1 Method 4500-NH3-B/D, Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005.

21.1.2 Method 350.3, Nitrogen, Ammonia (Potentiometric, Ion Selective Electrode), U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA/600/4-79/020, Issued 1974

22) Appendix

Table 22.1 Ammonia Nitrogen by ISE, LODs and LOQs, at time of SOP revision

Table 22.1 - Ammonia Nitrogen by ISE, LODs and LOQs, at time of SOP revision. LODs are determined annually at a minimum, and are subject to change.					
Analyte – water matrix	LOD mg/L	LOQ mg/L	Analyte - soil matrix	LOD mg/Kg	LOQ mg/Kg
Ammonia Nitrogen	0.2	0.2	Ammonia Nitrogen	10	10

Table 22.2 Ammonia Nitrogen LCS Recovery Limits

Table 22.2 - Ammonia Nitrogen LCS Recovery Limits

Analyte - Aqueous	SPK-mg/L	Low %	High %	RPD %	Analyte - Soil	SPK mg/Kg	Low %	High %	RPD %
Ammonia Nitrogen	10	80	120	20	Ammonia Nitrogen	500	80	120	20

Table 22.3 Summary of Calibration and QC Procedures for Ammonia Nitrogen

Table 22.3 Summary of Calibration and QC Procedures for Ammonia Nitrogen – SM 4500 NH3 B/D, EPA 350.3			
QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Calibration: 4 standards minimally	Prior to running samples	Slope in range of 55 to 59 mV	Correct problem then repeat LCS analysis.
Second Source Initial Calibration Verification (ICV)	After each new initial calibration, and after each new ICAL stock standard preparation	ICV within ±10% of expected value.	Correct problem, prepare new curve and new ICV.
Continuing Calibration: CCV	Daily, before samples, then every 10 samples, and at end of sequence.	CCV within ±10% of expected value.	Correct problem then repeat CCV or prepare new curve and new CCV.
LCS, can use the second source for method control verification	Once per each batch of 20 or less samples.	QC acceptance criteria, Table 21.2.	Correct problem then repeat LCS analysis.
Method blank.	One per batch of 20 or less.	NH3N not detected above the LOQ.	Correct problem, and then re-analyze method blank and all samples processed with the contaminated blank.
MS	One MS per every 20 or less field samples per matrix.	QC acceptance criteria, Table 21.2.	Describe in Laboratory Review Checklist.
Duplicate or MSD	One duplicate per every 20 or less field samples per matrix.	RPD <20% waters; RPD <25% soils	Describe in Laboratory Review Checklist.
Initial Demonstration of ability to generate acceptable accuracy and precision using four replicate LCS.	Once per analyst.	QC acceptance criteria, Table 21.2.	Recalculate results; locate and fix problem with system, then rerun demonstration

TOTAL KJELDAHL NITROGEN BY METHODS EPA 351.3 AND SM 4500-NH3 B/D

DOCUMENT ID: HS-WC033, REV 2.2

Approved By: Hoai. Van
Technical and Laboratory Director, Hoai Van

Date: 10/15/18

Prepared By: Erica M Howard
Quality Assurance Manager, Erica Howard

Date: 10/15/2018

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1) Scope and Applicability

1.1 This method covers the determination of Total Kjeldahl Nitrogen in water (ground, surface, saline), wastewater (domestic, industrial), or solid material (soil, sediment) by use of an initial sample block digestion step and then followed by the analysis of the digestate for ammonia nitrogen using the ion selective electrode (ISE).

1.2 The procedure converts nitrogen components of biological origin such as amino acids, proteins and peptides to ammonia, but may not convert the nitrogenous compounds of some industrial wastes such as amines, nitro compounds, hydrazones, oximes, semicarbazones and some refractory tertiary amines.

1.3 The applicable range for water is 0.2-50 mg/L TKN. Higher concentrations can be determined by sample dilution.

1.4 The applicable range for solid water is 10-2500 mg/Kg TKN. Higher concentrations can be determined by digestate dilution.

1.5 This method also references the use of block digestion / midi-distillation equipment for sample preparation and references the current revision of SOP HS-WC027, Ammonia Nitrogen by ISE, for sample analysis

2) Summary of Procedure

2.1 A 25 mL sample is combined with a digestion solution containing potassium sulfate, copper sulfate, and sulfuric acid.

2.2 The sample is then digested on a heating block for 1.5 hours.

2.3 Following digestion, the sample is cooled to room temperature and 25 mL DI water is added to the digestate followed by vortex mixing.

2.4 3 mL of 10N NaOH is added to the solution which is allowed to cool to room temperature before being diluted to 50 mL with DI water.

2.5 The digestate is then analyzed according to SOP HS-WC027, Ammonia Nitrogen by ISE.

3) Definitions

3.1 DI = Deionized reagent water, meeting purity characteristics of Type I laboratory distilled water (daily resistance of >17 MΩ-cm).

3.2 Batch: environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours.

3.3 Laboratory Control Sample (LCS): A known clean matrix spiked with all target analytes. This is used to evaluate and document laboratory method performance.

3.4 Matrix: The substrate (e.g., water, soil, etc.) which may contain the analyte of interest.

3.5 Matrix Spike (MS): An aliquot of sample spiked with a known concentration of target analytes. The spiking occurs prior to sample preparation and analysis. A matrix spike is used to document the bias of a method in a given sample matrix.

3.6 Matrix Spike Duplicate (MSD): A duplicate sample is spiked with identical concentrations of target analytes. The spiking occurs prior to sample preparation and analysis. The MS/MSD pair are used to document the precision and bias of a method in a given sample matrix.

3.7 Method Blank: An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

3.8 Limit of Detection (LOD): an estimate of the minimum amount of a substance that an analytical process can reliably detect. An LOD is analyte- and matrix-specific and may be laboratory-dependent.

3.9 Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence. This defined concentration can be no lower than the concentration of the lowest calibration standard adjusted for sample preparation factors and can only be used if acceptable quality control criteria are met.

3.10 Method Detection Limit (MDL) study: a procedure described in 40CFR Part 136, Appendix B, that describes how to produce an MDL, a reporting element of certain EPA method. An MDL study is one approach to determine the LOD.

3.11 NCAR: Nonconformance Corrective Action Report (see SOP HS-QS-003, current revision).

3.12 Exception Report – Appropriate comments reported with the associated sample batch that addresses sample anomalies such as demonstrated sample matrix effects.

4) Health and Safety Warnings

4.1 Lab Safety: Due to various hazards in the laboratory, safety glasses and laboratory coats or aprons must be worn at all times while in the laboratory. In addition, gloves and a face shield should be worn when dealing with toxic, caustic, and/or flammable chemicals.

4.2 Chemical Hygiene: The toxicity or carcinogenicity of each reagent used has not been precisely defined; however, each chemical used should be treated as a potential health hazard. Exposure to laboratory reagents should be reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets (MSDS) is available to all personnel involved in these analyses.

4.3 Waste Management: The principal wastes generated by this procedure are the method-required chemicals and standards. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required. Laboratory procedures in SOP HS-SAF-001, Waste Disposal Procedures, must be followed.

4.4 Pollution Prevention: The materials used in this method pose little threat to the environment when recycled and managed properly. The quantities of chemicals purchased should be based on the expected usage during its shelf life. Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards or reagents to be disposed.

5) Cautions

5.1 Routine preventative maintenance must be performed and documented to assure optimum instrument performance. Refer to the current revision of SOP HS-EQ004 for preventative maintenance schedules.

5.2 The digestion block must be located inside a ventilated acid-resistant fume hood. It is recommended that the microprocessor be located outside the fume hood.

5.3 The digestion with H_2SO_4 is very strong, at a very high temperature. Great care must be taken when performing this procedure. Always add acid to water unless otherwise directed. Personal Protective Equipment must be worn, including gloves and a face mask. If acids are spilled on the skin, immediately wash with copious amounts of water.

5.4 Neutralize any acid spills with sodium carbonate (Na_2CO_3) or sodium bicarbonate ($NaHCO_3$).

Digests must be cool before dilution water is added to avoid a violent reaction during which the acid can shoot out of the flask.

6) Interferences

6.1 Distillation is unnecessary for waters when using the ISE method. Soils are distilled.

6.2 Amines are a positive interference.

6.3 Residual chlorine rapidly converts ammonia into chloramines, and this process accelerates at the boiling temperature used to distill the sample. Therefore, residual chlorine must be removed by pretreatment of the sample with sodium thiosulfate upon sample collection.

6.4 High nitrate concentrations (10X or more than the TKN level) result in low TKN values. The reaction between nitrate and ammonia can be prevented by the use of an anion exchange resin (chloride form) to remove the nitrate prior to the TKN analysis.

7) Personnel Qualifications and Responsibilities

7.1 General Responsibilities - This method is restricted to use by or under the supervision of analysts experienced in the method.

7.2 Analyst - It is the responsibility of the analyst(s) to:

- 7.2.1 Each must read and understand this SOP and follow it as written. Any deviations or nonconformances must be documented and submitted to the QA Manager for approval.
- 7.2.2 Produce method compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP (HS-QS-009).
- 7.2.3 Complete the required initial demonstration of proficiency before performing this procedure without supervision.
- 7.2.4 Complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 7.2.5 The analysts must submit data for peer or supervisor review.

7.3 Section Supervisor - It is the responsibility of the section supervisor to:

- 7.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.
- 7.3.2 Ensure analysts have completed the required initial demonstration of proficiency before performing this procedure without supervision.
- 7.3.3 Ensure analysts complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 7.3.4 Ensure analysts produce method compliant data that meet all quality requirements using this procedure and the Data Reduction, Review and Validation SOP.

7.4 Project Manager - It is the responsibility of the Project Manager to ensure that all

method requirements for a client requesting this procedure are understood by the laboratory prior to initiating this procedure for a given set of samples.

7.5 QA Manager: The QA Manager is responsible for
- 7.5.1 Approving deviations and nonconformances
- 7.5.2 Ensuring that this procedure is compliant with method and regulatory requirements,
- 7.5.3 Ensuring that the analytical method and SOP are followed as written through internal method and system audits.

8) Sample Collection, Handling, and Preservation

8.1 Aqueous samples are collected in either plastic or glass. The minimum aqueous sample required is 100 ml. Aqueous samples and extracts of soils must be preserved to a pH <2 and stored at 4 C until ready for distillation and analysis. The maximum holding time prior to analysis of the aqueous samples and soil extracts is 28 days.

8.2 Residual chlorine checks must be performed on aqueous samples submitted from a wastewater treatment process. Groundwater and untreated waters would not require checks.

8.3 Soil samples are collected in plastic or glass 4 oz. wide-mouth jars. The minimum sample required is 20g. Although storage requirements for soils are not defined, use aqueous sample storage requirements and hold times.

9) Equipment and Supplies

9.1 Microprocessor – A.I. Scientific AIM600 Digestion System

9.2 Ammonia – selective electrode

9.3 Oxford pipettes, 5-mL and 10-mL, calibration verified ± 2%.

9.4 100-mL and 25-mL Pyrex graduated cylinders.

9.5 Analytical Balance, capable of reading ±0.0002-g

9.6 Heating Block – Environmental Express – TKN-50

9.7 Vortex Mixer

9.8 Teflon Boiling Stones

10) Standards and Reagents

10.1 DI Water

10.2 Digestion Reagent: Purchase from Aqua Solutions (Cat#2780-1L) or prepare:
- 10.2.1 Dissolve 134 g K_2SO_4 and 7.3 g $CuSO_4$ in ~700 mL of DI water. Carefully add 134 mL conc H_2SO_4.
- 10.2.2 Allow the solution to cool to room temperature.
- 10.2.3 Dilute to volume with DI water to 1L.
- 10.2.4 Mix well.
- 10.2.5 Store at a temperature close to 20°C to prevent crystallization.
- 10.2.6 Prepare fresh every 6 months.

10.3 Ammonia Nitrogen Calibration Stock Standard, 1000 mg/L as N: Purchase commercially available standard or prepare by dissolving 3.819 g of anhydrous NH_4Cl (dried at 100°C) in water and dilute to 1000 ml. 1.00-ml = 1.00-mg N. Use for the calibration curve and CCV preparations.
- 10.3.1 Working Ammonia Standard, 10.0-mg/L: Dilute 5-ml of the 1000 mg/L Stock

Ammonia Standard to a final concentration of 500-ml. Preserve with 0.5-ml of H2SO4 (1+1). Prepare monthly and store at 4˚C.

10.3.2 Calibration standards are prepared fresh daily with each new curve or CCV. Prepare 100 ml of each standard.

Table 10.3.2	Blank	S1	S2	S3	S4 CCV/ ICV	S4
NH_3 as N – mg/L by ISE	0.0 CCB	0.5	1.0	5.0	10.0	50
Vol of 10.0 mg/L NH_3 as N (CCV)	-	5.0	10.0	-	-	-
Vol of 1000.0 mg/L NH_3 as N	-	-	-	0.50	1.00	5.00
Final Volume, ml	100	100	100	100	100	100

10.4 Second Source Stock NH_3 as N, 1000 mg/L: Purchase or prepare a second source stock ammonia standard solution from a different source reagent.

10.4.1 Initial Calibration Verification (ICV) Standard: dilute the second source 1000 mg/L Stock NH_3 as N Standard to the ICV concentration in Table 10.3.2. Prepare fresh daily.

10.5 Continuing Calibration Verification (CCV) Standard: dilute the calibration source 1000 mg/L Stock NH_3 as N to the CCV concentration in Table 10.3.2. Prepare fresh daily.

10.6 LCS/MS/MSD for Water (10 mg/L): Add 0.5-ml of 1000 mg/L Stock NH_3 as N Standard to a 50 ml of a method blank or sample that has been prepared for distillation.

10.7 LCS/MS/MSD for Solids (10.0 mg/Kg): Add 0.5-ml of 1000-mg/L Working NH_3 as N Standard onto a 0.5 gram solid method blank or solid sample that has been prepared for distillation. 50 ml of a reagent water is added to the spiked solid prior to the distillation.

10.8 Method Blanks: for waters, distill 50 ml of DI water; for soils, distill 50 ml of DI water that has been added to 1.0 g of Ottawa Sand.

11) Method Calibration

11.1 Support Equipment Calibration Checks:

11.1.1 Daily Balance Calibration Checks must be performed daily prior to balance use as per SOP HS-EQ-001, current revision.

11.1.2 Quarterly Pipet Calibration checks must be current for the volumes used to prepare standard solutions or sample aliquoting. Quarterly pipet calibration checks are performed according to SOP HS-EQ-003, current revision.

11.1.3 All support equipment are assigned unique identifiers. These identifiers must be noted on the applicable test procedure data bench logs when used.

11.2 Calibration standards should be carried through the same digestion procedure as the samples. If samples have been preserved with H_2SO_4, standards should be prepared in the same manner.

11.3 Refer to the current revision of SOP HS-WC027, Ammonia Nitrogen by ISE, for detailed instructions regarding meter calibration.

12) Sample Preparation/Analysis

12.1 Check each sample with a test strip for high Nitrate. If interference is suspected, samples should be diluted.

12.2 Check for Residual Chlorine per 8.2 using a subsample and adding DPD powder and looking for a pink color. Treat with Sodium Thiosulfate. Check to ensure that there is no Residual Chlorine remaining before proceeding.

12.3 Shake sample and transfer 25 mL using a Class A Graduated Cylinder of well-mixed sample into a 100 mL digestion tube.

12.4 Pipet 5 mL of the digestion solution to the sample in the digestion tube.

12.5 Mix the sample and reagents using a vortex mixer and add 5 Teflon boiling stones.

12.6 Place the tubes into the digestion block and start the program assigned to this method using the microprocessor

12.6.1 Microprocessor Program:

12.6.1.1 Step to 200°C

12.6.1.2 Hold for 60 minutes

12.6.1.3 Ramp 2°C/min to 380°C

12.6.1.4 Hold for 30 minutes

12.6.1.5 End

12.7 After the audio alarm has sounded, indicating the end of the program, allow the samples to cool to room temperature by placing the tube rack on the cooling stand. CAUTION: Salting may occur!

12.8 Pipet 10 mL DI water and mix with the vortex mixer.

12.9 Make the digestate alkaline by carefully pipetting 3 mL of 10N Sodium Hydroxide solution. Cool to room temperature using the cooling stand.

12.10 Dilute to 50 mL in a Class A Graduated Cylinder with DI water and transfer to a 100 mL disposable beaker.

12.11 Analyze for ammonia. Refer to the current revision of SOP HS-WC027, Ammonia Nitrogen by ISE.

13) Troubleshooting

13.1 Refer to the manufacture's instructions for troubleshooting and maintenance.

14) Data Acquisition

14.1 Use the manufacturer's instructions for generating the ISE calibration curve, reading unknown samples. The ISE Calibration slope must fall within in the 54 to 60-mV range.

14.2 All data must be manually entered from the instrument record into the e-LIMS for reporting the Ammonia Nitrogen. Record the instrument results in the ISE logbook. LIMS assigns a batch ID to each batch entered. When sample dilutions are made, enter the dilution factors to correctly into e-LIMS for converting the raw data for reporting final results. Record all volumes use to calculate dilution factors.

14.3 Once the data has been entered into LIMS and all QC validation steps have been completed, data is further reviewed by project management for reporting.

14.4 Typical Analytical Sequence:

14.4.1 Initial Calibration curve and a blank

14.4.2 Initial Calibration Verification standard

14.4.3 Initial Calibration Blank
14.4.4 Laboratory Control Sample
14.4.5 Client sample
14.4.6 Matrix spike
14.4.7 Matrix spike duplicate or sample duplicate
14.4.8 Client samples (5)
14.4.9 Continuing Calibration Verification Standard

15) Calculation, and Data Reduction Requirements

15.1 Aqueous Calculation: Quantitate the concentration of NH3-N (in mg/L) from the aqueous scrubber using the following equation:

15.1.1 TKN (mg/L) = [A x DF]

Where:
A = mg/L NH3-N read from ISE standard curve.
DF = Dilution factor (based on any dilution of the sample before taking the ISE aliquot). If the sample is analyzed without pre-dilution, DF = 1.

15.2 Calculation of Total Organic Nitrogen: Calculate the difference between TKN results and the sum of all other nitrogen forms.

$$N_{TON}[\text{mg/L}] = N_{TKN}[\text{mg/L}] - N_{NH_3}[\text{mg/L}] - N_{NO_3}[\text{mg/L}] - N_{NO_2}[\text{mg/L}]$$

Where
N_{xxx} = is the concentration of the indicated form of nitrogen

15.3 QC Calculations: e-LIMS calculates the percent recovery for various QC samples (LCS) according to the following equations:

15.4

15.4.1 % Recovery, %R (for MS and MSD Samples)

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SR = Sample Result (unspiked).
SA = Spike Amount Added (mg/L or mg/kg).

15.4.2 % Recovery, %R (for standards and LCS)

$$\%R = \frac{(SSR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SA = Spike Amount Added (mg/L or mg/kg).

15.4.3 RPD (for precision or duplicate evaluation)

$$RPD = \frac{|SR_1 - SR_2|}{½(SR_1 + SR_2)} \times 100$$

Where:

SR_1 = Sample result for duplicate 1.
SR_2 = Sample result for duplicate 2.

16) Quality Control, Data Assessment and Corrective Action

16.1 Initial Calibration :

16.1.1 Frequency: perform quarterly at a minimum, or earlier if calibration verification fails (ICV or CCV). These standards are used to verify that the instrument response is linear, and the curve is used to calculate the concentration of the samples.

16.1.2 Criteria: initial calibration curve slope for the Ammonia (ISE) must be in the 54 to 60-mV range.

16.1.3 Initial Calibration Curve linearity Exceedance Corrective Action: check standard sources and prepare new standards.

16.2 Initial Calibration Verification (ICV):

16.2.1 Frequency: Verify each new curve with a second source standard

16.2.2 Criteria: Agreement must be 90-110% of the true value.

16.2.3 Calibration Verification exceedance: prepare new standards and a new curve

16.3 Calibration Verification (CCV):

16.3.1 Frequency: Verify the curve prior to running samples, every ten samples thereafter and at the end of the run with the same source as the initial calibration standard

16.3.2 Criteria: Agreement must be 90-110% of the true value.

16.3.3 Calibration Verification exceedance: prepare new standards and a new curve, re-analyze all samples since the last passing CCV. The CCV may fail high if the bracketed samples are non-detect.

16.4 Continuing Calibration Blanks (ICB and CCB) and Method Blanks (MB)

16.4.1 Frequency: Verify that the system is free of contamination after each new curve (ICB) and prior to running samples, every ten samples thereafter (CCB) and at the end of the run (CCB). The method blank is distilled with each batch of 20 (RCRA) or 10 (wastewater QC).

16.4.2 Criteria: The blank results should be less than the LOQ, or no more than 5% of sample concentration, or 5% of regulatory limits, whichever is greater. If above the limit, it is an indication of instrument drift and the baseline must be reset and the samples since the previous acceptable blank must be re-analyzed. If a method blank indicates contamination (>LOQ), all samples having detections must be re-analyzed unless the MB is no more than 5% of sample concentration, or 5% of a regulatory limit, whichever is greater.

16.5 Laboratory Control Standard (LCS)

16.5.1 Frequency - The LCS is a 10.0-ppm standard that is prepared separately from the initial calibration. Each batch of 20 samples must include a LCS.

16.5.2 Criteria - The LCS results must be within the range 80 to 120 percent. The LCSD RPD limit is 20%.

16.5.3 LCS Exceedance Corrective Action: If the LCS outside the acceptance range, perform corrective action to solve the source of the error, and re-prepare and re-analyze the sample batch. If the LCS fails high and the samples are non-detect, the data can be reported, but it must be narrated.

16.6 Matrix Spike Sample

16.6.1 Frequency - Matrix spikes will be analyzed on a frequency of one spike for each 20 samples analyzed. If fewer than 20 samples are in a batch, one spike will be analyzed.

16.6.2 Criteria: Acceptance limits employ the LCS limits for soil and water matrices. The MSD RPD limit is 20%.

16.6.3 MS exceedance Corrective Actions: If the spike results are outside the acceptance limits for recovery, evaluate the data against the LCS recovery to determine if a matrix effect is present or whether due to a possible a system error. Describe in the lab review checklist as necessary. Note that the LCS must fall within the acceptance criteria. The sample MS results are flagged by LIMS when MS limit exceedance occurs.

16.7 Duplicate Sample (or as the MSD)

16.7.1 Frequency: Duplicates will be analyzed on a frequency of one duplicate for each 20 samples analyzed. If fewer than 20 samples are in a batch, one duplicate will be analyzed.

16.7.2 Criteria: Acceptance limits for the water matrix and soil matrix are 20 % RPD.

16.7.3 Duplicate Sample RPD Exceedance Corrective Action: If the duplicate results are outside the acceptance limits for relative percent deviation, first determine if the cause is a system error; if so, correct the problem and repeat the duplicate. If not, the LCS must fall within the acceptance criteria in order for the data to be accepted. The sample duplicate results are flagged by LIMS when a limit exceedance occurs.

16.8 Limit of Detection:

16.8.1 Frequency: An annual method detection limit study must be performed according to the SOP HS-QS-006.

16.8.2 Criteria: Refer to the LOD / LOQ SOP.

17) Data Records Management

17.1 All data is stored electronically and/or hard copy for 5 years or for 10 years in the state of Louisiana.

17.2 All analytical sequence IDs and standard preparation information must be recorded in the Run logbook. Hardcopy computer printouts of analytical sequences and raw data must be retained and initialed by the analyst (electronic initials are acceptable).

17.3 Complete all pertinent sections in the respective logbooks. If not-applicable then line out the section. “Z” out or “X” out all large sections of the worksheet that are not used. Make all corrections with single line through, date and initial. Make NO obliterations when manually recording data.

17.4 Logbooks are controlled. Never remove a page from a logbook. Completed logbooks are returned to the QA department when filled and no longer needed in the work area.

18) Contingencies for Handling Out of Control Data

18.1 When method required QC exceedances occur, in every case where sample data quality are affected, the source of the QC exceedance must be determined, corrected and sample reanalysis carried out when possible.

18.2 When affected sample analysis can not be repeated due to limitations (i.e. sample availability, or if reanalysis can only be performed after expiration of a sample hold time), the reporting of data associated with exceeded QC data must be appropriately flagged and narrated. This documentation is necessary to define for the data user the effect of the error has upon the data quality of the results reported (e.g. E flag data indicate the result to be only an estimate).

18.3 All analysts must report sufficient comments in laboratory data review checklist for exceeded QC associated with sample results so that project management can further

narrate and ensure data qualifiers (flags) are properly assigned to the reported data.

18.4 NCARs must be issued for QC system exceedances. Matrix interferences are reported using the analyte reporting comment section in e-LIMS or using the Laboratory Data review checklist.

19) Method Performance

19.1 Method performance is determined by the following:

19.1.1 Analysis of proper quality control samples with each batch of samples

19.1.2 MDL performed per 40 CFR part 136 Appendix B.

19.1.3 PT samples every six months.

20) Summary of Changes

Table 20.1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
2.2	10/15/2018	G. Moulton	Updated new cover and new QA manager.
2.2	10/15/2018	G. Moulton	Modified sec 17.1 data storage.
2.2	10/15/2018	G. Moulton	Modified sec 19.1 method performance
02.1	09/01/2012	J. Cady	Minor revision. Format/font change.
02.0	09/30/2011	J. Cady	Major document revision.

21) References and Related Documents

21.1 Referenced Documents

21.1.1 U.S. Environmental Protection Agency, Method 351.2 Determination of Total Kjeldahl Nitrogen by Semi-Automated Colorimetry, Methods for Chemical Analysis of Water and Wastes, EPA/600/4-79/020, Revision 2, 1993.

21.1.2 U.S. Environmental Protection Agency, Method 351.3 Nitrogen, TKN, (Colorimetric, Potentiometric, Titrimetric), Methods for Chemical Analysis of Water and Wastes, EPA/600/4-79/020, Revised 1978.

21.1.3 APHA/AWWA/WEF, Ammonia by ISE – Section 4500 NH3 – D, Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005.

21.1.4 APHA/AWWA/WEF, Block Digestion – Section 4500 Norg – D, Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005.

21.1.5 "Sample Preparation For Total Kjeldahl Nitrogen (TKN) Analysis." Technical Note. Environmental Express.

21.1.6 Application Note, "Total Kjeldahl Nitrogen and Total Phosphorus in Water and Waste Water." A.I. Scientific, 2002.

22) Appendix

Table 22.1 Total Kjeldahl Nitrogen by ISE, LODs and LOQs, at time of SOP revision.

Table 22.1 - Total Kjeldahl Nitrogen by ISE, LODs and LOQs, at time of SOP revision. LODs are determined annually at a minimum, and are subject to change.					
Analyte – water matrix	LOD mg/L	LOQ mg/L	Analyte - soil matrix	LOD mg/Kg	LOQ mg/Kg
Nitrogen, Total Kjeldahl	1	1	Nitrogen, Total Kjeldahl	10	10

Table 22.2 Total Kjeldhal Nitrogen LCS Recovery Limits

Table 22.2 - Total Kjeldhal Nitrogen LCS Recovery Limits

Analyte - Aqueous	SPK-mg/L	Low %	High %	RPD %	Analyte - Soil	SPK mg/Kg	Low %	High %	RPD %
Nitrogen, Total Kjeldahl	10	80	120	20	Nitrogen, Total Kjeldahl	500	80	120	20

Table 22.3 Calibration and QC Procedures for Kjeldhal Nitrogen

Table 22.3 Calibration and QC Procedures for Kjeldhal Nitrogen – EPA 351.2 / SM 4500 NH3 B/D			
QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Calibration: 5 standards minimally	At method set up, and after the installation of a fresh probe	Subtracting the 5.0 mg/L Standard mV reading from the 50 mg/L Standard mV reading, the range should be between 54 to 60 mV; ICV within ±10% of expected value.	Correct problem then repeat LCS analysis.
Second Source Initial Calibration Verification (ICV)	To be analyzed after each calibration.	ICV within ±10% of expected value.	Correct problem then repeat calibration prepare new curve and new CCV.
Continuing Calibration: CCV	Daily, before samples, then every 10 samples, and at end of sequence.	CCV within ±10% of expected value.	Correct problem then repeat CCV or prepare new curve and new CCV.
LCS, can use the second source for method control verification	Once per each batch of 20 or less samples.	QC acceptance criteria, Table 22.2.	Correct problem then repeat LCS analysis.
Method blank.	One per batch of 20 or less.	TKN not detected above the LOQ.	Correct problem, and then re-analyze method blank and all samples processed with the contaminated blank.
MS	One MS per every 20 or less field samples per matrix.	QC acceptance criteria, Table 22.2.	Describe in Laboratory Review Checklist.
Duplicate or MSD	One duplicate per every 20 or less field samples per matrix.	RPD <20% waters; RPD <30% soils	Describe in Laboratory Review Checklist.
Initial Demonstration of ability to generate acceptable	Once per analyst.	QC acceptance criteria, Table 21.2.	Recalculate results; locate and fix problem with system, then rerun demonstration

Table 22.3 Calibration and QC Procedures for Kjeldhal Nitrogen – EPA 351.2 / SM 4500 NH3 B/D			
QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
accuracy and precision using four replicate LCS.			

SULFIDE BY METHYLENE BLUE METHOD SM-4500-S^2 D

DOCUMENT ID: HS-WC035, REV 3.4

Approved By: _____ Date: 3/5/2020
Technical and Laboratory Director, Hoai Van

Prepared By: _____ Date: 03/05/2020
Quality Assurance Manager, Erica Marinez

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1) Identification of the Method

1.1 This SOP will be followed to perform the analysis of sulfide by Method SM4500-S^2 D.

2) Applicable Matrices

2.1 Method SM4500-S^2 D is applicable to the analysis of total sulfide in water, waste water, and sediment samples.

3) Limits of Quantitation and Detection

3.1 The Reporting limit of sulfide by method SM4500-S^{2}D is 0.2 mg/L. Limits of Detection (LOD) and limit of Quantitation (LOQ) are performed quarterly and can be found in ALS LIMS.

4) Scope and Applicability

4.1 This procedure is not appropriate for the analysis of dissolved sulfide, which must be isolated immediately upon sampling. This procedure is appropriate for the analysis of total sulfide.

5) Summary of the Method

5.1 Samples are pretreated prior to analysis for potential interferences and preservation.

5.2 Hydrogen Sulfide and acid-soluble metal sulfides react with N, N-dimethyl-p-phenylenediamine sulfate to form methylene blue. The intensity of the blue color is proportional to the concentration of sulfide in the sample.

5.3 The test results are measured at 665 nm.

6) Definitions

6.1 Demonstration of Capability: The analysis of QC samples in series to verify the ability to produce data of acceptable precision and bias.

6.2 Exception Report: Appropriate comments reported with the associated sample batch that addresses sample anomalies such as demonstrated sample matrix effects.

6.3 Laboratory Control Sample (LCS): A sample matrix, free from the analytes of interest, spiked with known amounts of analytes or a material containing known and verified amounts of analytes.

6.4 Limit of Detection (LOD): an estimate of the minimum amount of a substance that an analytical process can reliably detect. The LOD is determined annually through the execution of a Method Detection Limit Study, and verified quarterly through the analysis of a Detectability Check Sample (DCS).

6.5 Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met.

6.6 Matrix Spike (MS): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available.

6.7 Matrix Spike Duplicate (MSD): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of recovery for each analyte.

6.8 Matrix: The substrate (e.g., water, soil, etc.) which may contain the analyte of interest.

6.9 Method Blank (MBLK): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analysis.

6.10 Method Detection Limit (MDL) study: a procedure described in 40CFR Part 136, Appendix B, that describes how to produce an MDL, a reporting element of certain EPA methods. The MDL study is one approach to determine the LOD.

6.11 NCAR: Nonconformance Corrective Action Report (refer to SOP HSQS003, current revision).

6.12 Organic Free Water: Deionized (DI) reagent water meeting purity of free of compound of interest. For additional purification, the DI water is passed through an activated carbon filter.

6.13 Preparation Batch: A defined set of one to 20 client samples of the same matrix, meeting the batch definition criteria, and prepared for analysis within 24 hours. The preparation batch must also contain the required determinative method defined batch QC samples (e.g. method blank, laboratory control samples, matrix spikes, duplicates, etc.).

6.14 Surrogate: An analyte added to a sample, which is unlikely to be found in any sample at significant concentration, and which is added directly to a sample aliquot in known amounts before any sample processing procedures are conducted. It is measured with the same procedures used to measure other sample components. The purpose of the surrogate analyte is to monitor method performance with each sample.

6.15 Surrogate Spike: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environmental samples and is added to them for quality control purposes.

3.16 Batch: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** is composed of one (1) to twenty (20) environmental sample of the same quality systems matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be twenty-four (24) hours. An **analytical batch** is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.

6.16 Laboratory Duplicates: Two sample aliquots, taken in the laboratory from the same container, and analyzed separately with identical procedures. Duplicate Analyses indicate precision associated with the lab procedures, removing any associated variables attributed by sample collection, preservation, or storage procedures.

6.17 Hydrogen Sulfide = Sulfide (34/32) = Sulfide (1.0625)

7) Health and Safety Warnings

7.1 Lab Safety: Due to various hazards in the laboratory, safety glasses and laboratory coats or aprons must be worn at all times while in the laboratory. In addition, gloves and a face shield should be worn when dealing with toxic, caustic, and/or flammable chemicals.

7.2 Chemical Hygiene: The toxicity or carcinogenicity of each reagent used has not been precisely defined; however, each chemical used should be treated as a potential health hazard. Exposure to laboratory reagents should be reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets (MSDS) is available to all personnel involved in these analyses.

7.3 Job Safety Assessment

HAZARD ASSESSMENT		
Job Task #1:	**Hazards**	**Preventative Measures**
Glassware Washing.	Possible cuts from broken glassware.	Wear proper protective equipment such as Kevlar kit gloves.
Job Task #1:	**Hazards**	**Preventative Measures**
Sample Testing and/or standard and reagent/solvent use.	Exposure to possible hazardous chemicals.	Wear gloves, safety glasses and lab coat. Work in fume hood and avoid skin contact with solvents/acids/reagents. Know location of safety shower, first aid kits, spill kits and fire extinguisher when handling flammable material.

8) Cautions

8.1 Routine preventative maintenance must be performed and documented to assure optimum instrument performance. Refer to the current revision of SOP HS-EQ004 for preventative maintenance schedules.

9) Interferences

9.1 Strong reducing agents interfere in this method by preventing the formation of the blue color resulting in a false negative. Such reducing agents include sulfite, thiosulfate, and hydrosulfite. Proper pretreatment reduces the effect of this

interference.

9.2 High concentrations of sulfide may prevent the formation of the blue color resulting in a false negative. Sample dilution reduces the effect of this interference.

9.3 Sample color and turbidity may interfere with photometric readings.

9.4 High iron if present, oxidation may be fairly rapid.

10) Personnel Qualifications and Responsibilities

10.1 General Responsibilities - This method is restricted to use by or under the supervision of analysts experienced in the method.

10.2 Analyst - It is the responsibility of the analyst(s) to:

- 10.2.1 Each must read and understand this SOP and follow it as written. Any deviations or non-conformances must be documented and submitted to the QA Manager for approval.
- 10.2.2 Produce method compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP (HS-QS-009).
- 10.2.3 Complete the required initial demonstration of proficiency before performing this procedure without supervision.
- 10.2.4 Complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 10.2.5 The analysts must submit data for peer or supervisor review.

10.3 Section Supervisor - It is the responsibility of the section supervisor to:

- 10.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.
- 10.3.2 Ensure analysts have completed the required initial demonstration of proficiency before performing this procedure without supervision.
- 10.3.3 Ensure analysts complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 10.3.4 Ensure analysts produce method compliant data that meet all quality requirements using this procedure and the Data Reduction, Review and Validation SOP.

10.4 Project Manager - It is the responsibility of the Project Manager to ensure that all method requirements for a client requesting this procedure are understood by the laboratory prior to initiating this procedure for a given set of samples.

10.5 QA Manager: The QA Manager is responsible for

- 10.5.1 Approving deviations and non-conformances
- 10.5.2 Ensuring that this procedure is compliant with method and regulatory requirements,
- 10.5.3 Ensuring that the analytical method and SOP are followed as written through internal method and system audits.

11) Sample Collection, Preservation, Shipment and Storage

11.1 Samples collected for laboratory analysis must be preserved. Samples are collected in a pre-cleaned plastic bottle and preserved with zinc acetate solution.

11.2 Samples that are to be analyzed for total sulfide determination are preserved with zinc acetate and sodium hydroxide prior to filling it with sample. If zinc acetate was used, wait at least 10 minutes before making a visual color comparison.

- 11.2.1 Use 0.2mL of 2M zinc acetate per 100 mL of sample.
- 11.2.2 The final pH should be at least 9.
- 11.2.3 Add additional NaOH if necessary.
- 11.2.4 Fill the bottle completely and stopper.

11.3 Samples are stored to just above 0°C to 6°C for 2 weeks.

12) Equipment and Supplies

12.1 Spectrophotometer for measurement at 664nm, with cells providing light paths of 1cm.

- 12.1.1 Shimadzu UV-VIS Spectrometer.

12.2 Assorted Class A volumetric pipets; various sizes.

12.3 100-mL and 25-mL PMP graduated cylinders, Class A or glass Class A.

12.4 125 or 250-ml Erlenmeyer flasks or Beakers.

12.5 pH meter, calibrated daily before use.

12.6 Buffers for pH meter, 2, 4, 7, 10, 12 and on second source for confirmation (pH 6).

12.7 Top-loading balance - capable of weighing 0.01 g, serviced yearly and verify daily prior to use.

12.8 Reagents and Standards Analytical balance, Mettler AE163, or equivalent, capable of measurements to 0.0001-g, serviced yearly and verify daily prior to use.

12.9 Oxford pipettes or equivalent, 5-mL and 10-mL.

12.10 Eppendorf pipette or equivalent, 0.010, 0.25, 0.5 and 1.0-mL pipettes.

12.11 Timer or Stopwatch.

12.12 Certified Weights for balances.

12.13 Cuvettes, 1cm path length for Shimatzu.

12.14 Centrafuge tube, 50 mL.

12.15 Amber bottle of various sizes all the Teflon lined caps.

12.16 Test tubes.

13) Computer Hardware and Software

13.1 N/A

14) Standards and Reagents

14.1 Note: All purchased stock standard solutions must be replaced after reaching the manufacturer's expiration date assigned to the standard and store in accord with manufacturer's instructions. All laboratory prepared standard solutions must be replaced after six months or sooner if routine QC indicates a problem or if required by reference method. An assigned expiration date of a lab prepared standard cannot exceed the manufacturer's expiration date for any component used in the standard formulation. When analyzing or preparing samples, all standards, lot numbers must be associated with the run batch or prep batch.

14.2 Deionized Water (DI)

14.3 Sodium Hydroxide Solution, NaOH, 6N –purchased or made by dissolving 240g NaOH pellets in 1 L of reagent water, assign one year expiration date.

14.4 Sulfuric Acid, concentrated.

14.5 Sulfuric Acid, 1:1 – made by mixing equal parts of sulfuric acid and reagent water. Note: This reaction is very exothermic and will generate great amount of heat, mixing container should be chilled with ice. NEVER ADD WATER TO ACID, ALWAYS ADD ACID TO WATER.

14.6 Zinc Acetate Solution:

14.6.1 Dissolve 220 g $Zn(C2H_3O_2)_2 \cdot 2H_2O$ in 870 mL Deionized Water, this make 1L solution.

14.6.2 Prepare fresh every 6 months.

14.7 $Na_2S \cdot 9H_2O$, stock solution (1000 mg/L): Dissolve 3.75 g of sodium sulfide in 500 ml DI water, or purchase a prepared solution. Prepare fresh every 3 months and document in preparation logbook.

14.8 $Na_2S \cdot 9H_2O$, intermediate solution (10 mg/L): Dilute1 mL of the Na2S·9H2O stock solution to100 mL of deionized water in volumetric flask. Prepare fresh every 3 months and document in preparation logbook.

14.9 Amine-sulfuric acid stock solution*:* Dissolve 27 g *N,N*dimethyl- *p*-phenylenediamine oxalate* in an iced mixture of 50 mL conc H2SO4 and 20 mL distilled water. Cool and dilute to 100 mL with distilled water. Use fresh oxalate because an old supply may be oxidized and discolored to a degree that results in interfering colors in the test. Store in a dark glass bottle. If available may be purchased commercially.

14.10 Amine-sulfuric acid reagent: Dilute 25 mL amine-sulfuric acid stock solution with 975 mL 1: 1 H2SO4. Store in a dark glass bottle. If available may be purchased commercially.

14.11 Ferric chloride solution: Dissolve 100 g FeCl3 •6H2O in 40 mL water. If available may be purchased commercially.

14.12 Diammonium hydrogen phosphate solution*:* Dissolve 400 g $(NH_4)2HPO_4$ in 800 mL distilled water. If available may be purchased commercially.

15) Calibration and Standardization

15.1 Perform all support equipment calibration checks (balances, pipets, etc.) as required.

15.1.1 Daily Balance Calibration Checks must be performed daily prior to balance use as per SOP HS-EQ001, current revision.

15.1.2 Quarterly Pipet Calibration checks must be current for the equipment used for dilutions or standard preparations required in this procedure. Quarterly pipet calibration checks are performed according to SOP HS-EQ-003, current revision.

15.2 Turn on the Shimadzu UV-VIS spectrophotometer and set the wavelength to 665 nm. Allow sufficient time for the instrument to warm up (at least 30 minutes).

15.3 Using the intermediate solution (10 mg/L) calibration standard, prepare the following calibration curve standards. Use the Eppendorf pipette to measure volumes of 1-mL or below. Use the Oxford pipette to measure volumes greater than 1-mL. Use DI for dilution to the final volume. Prepare calibration curve standards fresh each time a new curve is prepared. Prepare calibration standards as shown in table 14.3. A new calibration curve is required when batch QC fail to meet the criteria outlined in Table 26.1 Calibration must be generated every 3 months (90 days).

Table 15.3 Initial Calibration Standards for Sulfide Curve

Table 15.3 – Initial Calibration Standards for Sulfide Curve		
ICAL STDN Conc. - mg/L	mL of Standard	Final Volume
0	0	50 mL
0.050	0.25 mL	50 mL
0.100	0.50 mL	50 mL
0.200	1.0 mL	50 mL
0.500	2.5 mL	50 mL
0.800	4.0 mL	50 mL

15.4 CCV, 0.50 mg/L: prepare the continuing calibration verification standard to check the initial calibration curve by preparing a standard from the table above and the instructions in Section 10. Prepare the CCV fresh for each use.

15.5 ICV, 0.20 mg/L: prepare the initial calibration verification standard to check the initial calibration curve by preparing a standard from the table above and the instructions in Section 10. Prepare the ICV fresh for each calibration. Prepare this standard as a second source. If purchased, the vendor should not be same as the vendor of the CCV, unless vendor has a second source standard program.

15.6 LCS/MS/MSD – Spike sample add 1 mL of the 10 mg/L intermediate standard into measured volume of sample or DI water for LCS, 50 mL.

15.7 Blank – consists of 50 mL of reagent water.

15.8 Store hard copy curves in a three-ring binder, date and initial all curves.

16) Procedure/Sample Preparation/Analysis

16.1 Sample Pretreatment to Remove Interfering Substances:

16.1.1 To a 50 mL centrifuge tube, add 2 drops Zinc Acetate Solution and 1 drops 6*N* NaOH.

16.1.2 Fill the bottle with 50 mL of sample, or 50 mL of reagent water for blank and LCS and add 1 additional drops 6*N* NaOH. Spike sample by adding 1 mL of intermediate standard to each spike or LCS mixture

16.1.3 Stopper the bottle (with no air bubbles) and mix (side to side, vigorously)

16.1.4 **Note**: It may be necessary to vary the volumes of these reagents to obtain a precipitate that is not excessively bulky, and settles readily.

16.1.5 Add enough NaOH to reach a pH above 9.

16.1.6 Let precipitate settle for 30 minutes. This treated sample should be stable for several hours. Analysis must be completed same day as sample treatment.

16.1.7 Decant as much of the supernatant as possible without losing the precipitate.

16.1.8 Refill bottle with distilled water, shake to suspend precipitate, and quickly withdraw a sample. If interfering substances are present in high concentration, settle, de- cant, and refill a second time.

16.1.9 If sulfide concentration is known to be low, add only enough water to bring volume to one-half or one-fifth of original volume. Use this technique for analyzing samples of very low sulfide concentrations. After colorimetric determination of the sulfide concentration, multiply the result by the ratio of final to initial volume.

16.2 Sample Analysis

16.2.1 Color development: For each QC and Client Sample:

16.2.1.1 Transfer 7.5 mL aliquot of sample to two test tube for each sample, including blank, LCS and matrix spikes, labeling one A and the second aliquot B.

16.2.1.2 Add 0.5mL amine-sulfuric acid reagent and 3 drops of $FeCL_3$ solution to Tube A. Mix by inverting slowly. Presence of sulfide will be indicated by appearance of blue color in this tube.

16.2.1.3 To Tube B (background of sample) add 0.5mL of 1:1 sulfuric acid and 3 drops $FeCL_3$ solution. Stopper and invert to mix.

16.2.1.4 Note: The solution will turn pink initially and then turn blue if sulfide is present. Color development is usually completed in about 1 minute, but a longer time often is required for fading out the pink color.

16.2.1.5 Wait 5 minutes and add 1.6 mL of $(NH_4)2HPO_4$ solution to each test tube.

16.2.1.6 Wait 3 to 15 minutes, transfer an aliquot of sample to a cuvette and measure on the spectrophotometer.

16.2.1.7 Pour sample from Tube B into a cuvette and zero the instrument before reading concentration from Tube A.

17) Data Analysis

17.1 Data is manually recorded in controlled logbooks and manually entered into LIMS,

where LIMS assigns a batch ID to each batch entered.

17.2 Once the data has been entered into LIMS and all QC validation steps have been completed, data is further peer reviewed prior to project management reporting.

18) Calculation, and Data Reduction Requirements

18.1 QC Calculations: LIMS calculates the percent recovery for various QC samples (LCS) according to the following equations:

18.1.1 % Recovery, %R (for MS and MSD Samples)

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SR = Sample Result (unspiked).
SA = Spike Amount Added (mg/L or mg/kg).

18.1.2 % Recovery, %R (for standards and LCS)

$$\%R = \frac{(SSR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SA = Spike Amount Added (mg/L or mg/kg).

$$RPD = \frac{|SR_1 - SR_2|}{½(SR_1 + SR_2)} \times 100$$

18.1.3 RPD (for precision or duplicate evaluation)

Where:
SR_1 = Sample result for duplicate 1.
SR_2 = Sample result for duplicate 2.

18.2 Sulfide Calculations:

mg/L sulfide = concentration from instrument * dilution

18.3 Calculation for MS/MSD % recovery:

18.3.1 % Recovery = [(MS– sample) / (Spike added)] X 100

18.4 Calculation for duplicate RPD (for precision evaluation)

Where:
SR1 = Sample result for replicate 1

$$RPD = \frac{|SR_1 - SR_2|}{½(SR_1 + SR_2)} \times 100$$

19) Quality Control, Acceptance Criteria and Corrective Action

19.1 Initial Demonstration of Capability

- 19.1.1 Purpose: Verify the ability to produce data of acceptable precision and bias for a specific instrument type, matrix, method, and analyst.
- 19.1.2 Frequency: Initially during method development, and any time there is a significant change in instrument type, personnel, methodology, or matrix
- 19.1.3 Acceptance Criteria: Four spikes QC samples with true concentration between 1-4 times the reporting limit.
- 19.1.4 Corrective Action: If the recoveries do not meet criteria, Identify and correct the source of error. Reanalyze the demonstration.

19.2 Continuing Demonstration of Capability

- 19.2.1 Purpose: Verify the ability to produce data of acceptable precision and bias for a specific instrument type, matrix, method, and analyst.
- 19.2.2 Frequency: Annual to re-qualify analyst for analysts.
- 19.2.3 Acceptance Criteria: Four spikes QC samples with true concentration between 1-4 times the reporting limit or successful PT study.

19.3 Corrective Action: Identify and correct the source of error. Reanalyze the demonstration.

19.4 Limit of Detection Determination and Verification:

- 19.4.1 Frequency: Prior to sample analysis and verified quarterly. Verification must is performed on each instrument. The LOD is spiked at 2-3 times the detection limit for single compound analyses and 1-4 times the detection limit for multi-analyte standards.
- 19.4.2 Acceptance Criteria: The apparent signal to noise ratio at the LOD must be at least three and the results must meet all method requirements for analyte identification (e.g., ion abundance, second-column confirmation, or pattern recognition.) For data systems that do not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least three standard deviations greater than the mean method blank concentrations.
- 19.4.3 Corrective Action: Repeat the Detection Limit Determination and LOD Verification at a higher concentration or perform and pass two consecutive LOD verifications at a higher concentration and set the LOD at the higher concentration

19.5 Limit of Quantitation Establishment and Verification:

- 19.5.1 Frequency: Prior to sample analysis and verified quarterly.
- 19.5.2 Acceptance Criteria: Data must empirically demonstrate precision and bias at the LOQ.
- 19.5.3 Corrective Action: Identify and correct the source of error, reanalyze the LOQ. If failure persists re-evaluate the appropriateness of the LOQ.

19.6 Method Blanks

- 19.6.1 Frequency: Analyze one blank with each batch of 20 or less samples.
- 19.6.2 Criteria: The method blank must be less than the LOQ.
- 19.6.3 Corrective Action: If it is above the LOQ, there is an indication of contamination in the system. Correct the problem (check glassware and reagents, etc.) and analyze all affected samples that have detection above the LOQ.

19.7 Laboratory Control Standard/ Laboratory Control Standard

19.7.1 Frequency: Analyze one LCS and LCSD with each batch of 20 or less samples

19.7.2 Perform a LCS at the beginning of each batch.

19.7.3 Criteria: The LCS results must meet acceptance criteria limits of 80 to 120 %. If outside this range, discontinue analysis and perform corrective action to solve the source of the error.

19.8 Duplicate Sample

19.8.1 Frequency: Duplicate must be analyzed on a frequency of one spike for each 20 or less samples in the batch analyzed. Perform on a matrix specific basis.

19.8.2 Criteria: RPD limit is ±20 % for water matrices.

19.8.3 Corrective Action: If the spike results are outside the acceptance limits for recovery, first determine if the cause is a system error; if so, correct the problem and repeat the Duplicate. If not, the LCS/LCSD must fall within the acceptance criteria in order for the data to be accepted. The sample results should be flagged for matrix interference.

20) Data Records Management

20.1 All data is stored electronically and/or hard copy for five (5) years, or ten (10) years for data to be submitted to the state of Louisiana. Operational software is maintained for the same duration.

20.2 All analytical sequence IDs and standard preparation information must be recorded in the logbook. Hardcopy computer printouts of analytical sequences and raw data must be retained and initialed by the analyst (electronic initials are acceptable). To simplify standard and reagent tracking, analyst must attempt to use single lots of reagents and standards.

20.3 Complete all pertinent sections in the respective logbooks. If not-applicable then line out the section. "Z" out or "X" out all large sections of the worksheet that are not used. Make all corrections with single line through, date and initial. Make NO obliterations when manually recording data.

20.4 Logbooks are controlled. Never remove a page from a logbook. Completed logbooks are returned to the QA department when filled and no longer needed in the work area.

20.5 SOP effective date is the date noted in the header.

21) Contingencies for Handling Out of Control or Unacceptable Data

21.1 When method required QC exceedances occur, in every case where sample data quality are affected, the source of the QC exceedance must be determined, corrected and sample reanalysis carried out when possible.

21.2 When affected sample analysis cannot be repeated due to limitations (i.e. sample availability, or if reanalysis can only be performed after expiration of a sample hold time), the reporting of data associated with exceeded QC data must be appropriately flagged and narrated. This documentation is necessary to define for the data user the effect of the error has upon the data quality of the results reported (e.g. E flag data indicate the result to be only an estimate).

21.3 All analysts must report sufficient comments in laboratory data review checklist for

exceeded QC associated with sample results so that project management can further narrate and ensure data qualifiers (flags) are properly assigned to the reported data.

21.4 NCARs must be issued for QC system exceedances. Matrix interferences are reported using the analyte reporting comment section in LIMS or using the Laboratory Data review checklist.

22) Method Performance

22.1 Method performance is determined by:

22.1.1 The performance of PT samples to determine if the laboratory is providing correct results.

22.1.2 The performance of batch Laboratory Control and other QC samples.

23) Training

23.1 Training to perform the procedures for this method should take the following into consideration:

23.1.1 Review literature (see references section). Read and understand this SOP. Also review the applicable SDS for all reagents and standards used. Following the reviews, observe the procedure as performed by an experienced analyst at least three times.

23.1.2 The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

23.1.3 Perform initial Demonstration of Capability (IDOC) study as described above for water samples. Summaries of the IDOC are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IDOC studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

23.2 Training is documented following *SOP CE-QA003*).

23.3 When the analyst training is documented by the supervisor on internal training documentation forms (HS-QAFORM010 and HS-QAFORM038) the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

24) Waste Management

24.1 The principal wastes generated by this procedure are the method-required chemicals and standards. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage

discharge permits and regulations is required. Laboratory procedures in SOP HS-SAF-001, Waste Disposal Procedures, must be followed.

25) Pollution Prevention

25.1 The materials used in this method pose little threat to the environment when recycled and managed properly. The quantities of chemicals purchased should be based on the expected usage during its shelf life. Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards or reagents to be disposed.

26) Troubleshooting and Maintenance

26.1 In the event that the outcome of the procedure is not what it should be, the analyst should make fresh reagents, clean the spectrophotometer, ensure it is on the correct wavelength and redo the analysis.

26.2 All support equipment used for this analysis should be properly cleaned after use and kept in good condition.

27) Summary of Changes

Table 27.1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
3.4 Sec 22-	03/05/2020	G. Moulton	Added a section on Training
3.4 Sec 26	03/05/2020	G. Moulton	Added a section on Trouble shooting and maintenance
3.4 Sec 13	03/05/2020	G. Moulton	Added a section on Computer hardware and software.
3.4 Sec 14.3	03/05/2020	G. Moulton	Corrected table ID from 144.3 to 14.3
3.3	05/09/2019	G. Moulton	Section 15.2.1.1 changed volume of sample to 7.5 mls.
3.2	12/01/2018	G. Moulton	Updated to new ALS Cover and new quality manager.
3.2	12/01/2018	G. Moulton	Modified sec 25.1.4 and 25.1.5
3.2	12/01/2018	G. Moulton	Modified sec 19.1 data storage, sec 21, method performance.
3.2	12/01/2018	G. Moulton	Modified 18.1.3, 18.1.4 IDOC criteria. 18.2.3 DOC criteria.
3.2	12/01/2018	G. Moulton	Included appropriate headers for sec 1, 2, 3, 4, 11, 16, 26
3.1	2/28/2018	T. Yen	New Signature page
3.1 – Sect 4.5	2/28/2018	T. Yen	Job Safety Assessment

3.1 – Sect 12.2	2/28/2018	T. Yen	Sample volume change to 7.5 ml.
3.1 – Tables	2/28/2018	T. Yen	Table 22.1 LC/LCSD set to ±15% Table 22.2 LCS/DUP/MDL frequency set to 10% (1 in every 10 samples)
3.0	09/30/2014	T. Yen	SOP Format Change and New Lab Director, Inorganic Manager and QA Manager. SOP resurrected for recertification after 1 ½ years of not performing this method.
03.0 – Section 9	09/30/2014	T. Yen	Equipment List Updated
03.0 – Sections 16.1 -16.4	09/30/2014	T. Yen	Initial and Continuing Demonstration of Capability, MDL and LOD added.
03.0 – Section 17.2	09/30/2014	T. Yen	Use of single lots of standard/reagent to simplify standard tracking.
03.0 – Section 17.5	09/30/2014	T. Yen	SOP effective date defined.
03.0 – Section 21	08/31/2014	T. Yen	References updated.
02.1	08/01/2012	J. Cady	Minor revision. Format/font change.
02.0	08/05/2011	J. Cady	Major document revision.

28) References and Related Documents

28.1 Referenced Documents

28.1.1 APHA/AWWA/WEF, Method 4500 S-2 D, Sulfide by Methylene Blue, Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005.

28.1.2 APHA/AWWA/WEF, Method 4500 S-2 C, Sample Pretreatment to Remove Interfering Substances or to Concentrate the Sulfide, Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005.

28.1.3 U.S. Environmental Protection Agency, Method 376.2, Sulfide, (Colorimetric, Methylene Blue), Methods for Chemical Analysis of Water and Wastes, EPA/600/4-79/020, 1978.

28.1.4 Current TNI Standards.

28.1.5 Current Department of Defense Quality Systems Manual.

29) Tables, Diagrams, Flowcharts and Validation Data

Table 29.1 Summary of QC Procedures for Sulfide SM4500S^2-D

Table 26.1 Summary of QC Procedures for Sulfide by titrimetric method, SW9034			
QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Calibration: 5 standards minimally, verify with second source ICV	every three months minimally	r $\geq$ 0.995	Correct problem and generate new curve
ICV	Immediately following calibration curve.	Analyte within ±20% of expected value.	Correct problem then repeat ICV. IF second ICV fails generate new curve with fresh standards.
CCV	Before analysis, after every ten reading AND end of sequence.	Analyte within ±20% of expected value. Sample must be bracketed by acceptable CCVs.	Correct problem then repeat CCV and reanalyze samples. IF second ICV fails generate new curve with fresh standards.
LCS/LCSD, known amount of sulfide standard	Once per each batch of 10 or less samples, perform prior to running samples.	Analyte within 80 to 120 % of expected value.	Correct problem and repeat samples.
Sample Dup	One dup per every 10 field samples per matrix.	QC RPD acceptance criteria 20%	Narrative if confirmed to be matrix interference. IF problem was identified as analytical error, reanalyze the batch.
Method blank.	One per batch of 10 or less.	$S^=$ not detected above the LOQ.	Correct problem, and then re-analyze method blank and all samples processed with the contaminated blank.
Matrix Spike	One MS per every 10 field samples per matrix.	QC RPD acceptance criteria 20%	Narrative if confirmed to be matrix interference. IF problem was identified as analytical error, reanalyze the batch.
Initial Demonstration of ability to generate acceptable accuracy and precision using four replicate LCS.	Once per analyst.	QC acceptance criteria 80 to 120 % of expected value.	Recalculate results; locate and fix problem with system, then rerun demonstration

QUALITY ASSURANCE MANUAL

ALS Environmental – Simi Valley
2655 Park Center Drive, Suite A
Simi Valley, CA 93065
(805) 526-7161
www.alsglobal.com

QUALITY ASSURANCE MANUAL

Doc ID:	ALSMV-QAM	Rev. Number:	35.0	Effective Date:	2/1/2021

Approved By: _____ Date: 1/27/2021
Laboratory Director – Randy Gates

Approved By: _____ Date: 1/27/21
QA Manager – Nick Nash

Approved By: _____ Date: 1/27/21
Technical Manager (Volatiles GC/MS) – David Mirakian

Approved By: _____ Date: 1/27/21
Technical Manager (Volatiles GC & Semi-Volatiles) – Wade Henton

Archival Date:	_____	Doc Control ID#:	Uncontrolled	Editor:	_____

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1.0 Scope

The purpose of this Quality Assurance Manual is to outline the quality system for the Simi Valley location of ALS Environmental (ALS Group USA Corp. dba ALS Environmental). ALS Environmental is a professional analytical services laboratory which performs chemical and microbiological analyses on a wide variety of sample matrices, including drinking water, groundwater, surface water, wastewater, soil, sludge, sediment, tissue, industrial and hazardous waste, air, and other material. Refer to Appendix J for a list of analytical capabilities specific to the Simi Valley location and corresponding accreditation status.

Quality Control (QC) procedures are used to continually assess performance of the laboratory and quality systems. ALS Environmental maintains control of analytical results by adhering to written standard operating procedures (SOPs), using analytical control parameters with all analyses, and by observing sample custody requirements. All analytical results are calculated and reported in units consistent with project specifications to allow comparability of data. Appendix H includes a list of data qualifiers and acronyms.

This QAM is applicable to the facility listed on the title page. The information in this QAM has been organized according to requirements found in the National Environmental Laboratory Accreditation Program (NELAP) Quality Systems Standards (2016), DoD Quality Systems Manual, Naval Sea Systems Command Laboratory Accreditation Program (NAVSEA-LAP), and *General Requirements for the Competence of Testing and Calibration Laboratories*, ISO/IEC ISO/IEC 17025:2017.

Quality Policy Statement

The policy at ALS is to use good professional practices, to maintain quality, to uphold the highest standard of service, and to operate in accordance with these requirements and those of regulatory agencies, accrediting authorities, and certifying organizations. We recognize that quality assurance requires a commitment to quality by everyone in the organization - individually, within each operating unit, and throughout the entire laboratory. Laboratory management is committed to ensuring the effectiveness of its quality systems and to ensure that all tests are carried out in accordance to customer requirements. Key elements of this commitment are set forth in the *SOP for Laboratory Ethics and Data Integrity* and in this Quality Assurance Manual (QAM). ALS Environmental is committed to operate in accordance with these requirements and those of regulatory agencies, accrediting authorities, and certifying organizations. The laboratory also strives for improvement through varying continuous improvement initiatives and projects. ALS management reviews its operations on an ongoing basis and seeks input from staff and clients to make improvements.

Quality Management Systems are established, implemented and maintained by management. Policies and procedures are established in order to meet requirements of accreditation bodies and applicable programs as well as client's quality objectives. The laboratory's management is committed to complying with the National Environmental Laboratory Accreditation Program (NELAP) Quality Systems Standards (2016 TNI standard), ISO/IEC 17025:2017, Naval Sea System Command Laboratory Accreditation Program (NAVSEA-LAP), and the Department of Defense (DoD) Quality Systems Manual for Environmental Laboratories. Systems are designed so that there will be sufficient Quality Assurance (QA) activities conducted in the laboratory to ensure that all analytical data generated and processed will be scientifically sound, legally defensible, of known and documented quality, and will accurately reflect the material being tested. Quality Systems are applicable to all fields of testing in which the laboratory is involved. All personnel involved with environmental testing and calibration activities must familiarize

themselves with the quality documentation and implement the policies and procedures in their work.

Quality Management System

The laboratory has developed a Quality Management System to ensure all products and services meet our client's needs. The system is implemented and maintained by the Quality Assurance Manager (QA Manager) with corporate oversight by the Corporate Quality Assurance Manager (CQAM). These systems are based upon the ISO/IEC 17025:2017 standard, upon which fundamental programs (TNI/NELAP, NAVSEA-LAP, and DoD QSM) are based. Implementation and documentation against these standards are communicated in corporate policy statements, this QAM, and SOPs. Actual procedures, actions and documentation are defined in both administrative and technical SOPs. Figure 1-1 shows the relationships of the quality systems and associated documentation. Quality systems include:

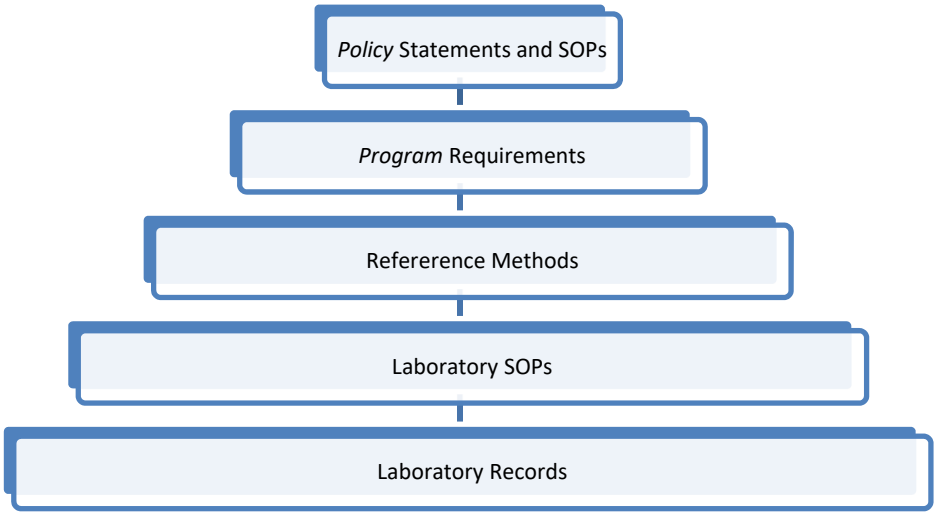
- Standard Operating Procedures
- Sample Management and Chain of Custody procedures
- Statistical Control Charting
- Standards Traceability
- Ethics Training
- Document Control
- Corrective Action Program
- Management Reviews
- Demonstration of Capability

The effectiveness of the quality system is assessed in several ways, including:

- Internal and External Audits covering all aspects of the organization
- Annual Management Reviews
- Analysis of Customer Feedback
- Internal and External Proficiency Testing

Figure 1-1

Relationships of Quality Management Systems and Documentation



Laboratory Data Integrity and Ethics Training

New employees complete a QA and Ethics orientation as part of the induction process. On an ongoing basis, all employees receive annual ethics refresher training. Topics covered are documented in writing and all training is documented. It is the responsibility of the QA Manager to ensure that the training is conducted as described.

Key topics covered are the organizational mission and its relationship to the critical need for honesty and full disclosure in all analytical reporting, how and when to report data integrity issues and record keeping. Training includes discussion regarding all data integrity procedures, data integrity training documentation, in-depth data monitoring and data integrity procedure documentation.

Data integrity training provides assurance that a highly ethical approach to testing is a key component of all laboratory planning, method implementation, and training. There are four elements to the laboratory's procedures for data integrity. These include:

1) Data integrity training (conducted initially and at least annually);
2) Signed data integrity documentation for all employees;
3) In-depth periodic monitoring of data integrity;
4) Data integrity procedure documentation (*SOP for Laboratory Ethics and Data Integrity*).

There is specific emphasis on the importance of proper written narration on the part of the analyst with respect to those cases where analytical data may be useful, but are in one sense or another partially deficient. A signature attestation sheet of data integrity training including their understanding of their obligations related to data integrity and as specified in the training is generated for attendees and maintained on file for review. Trainees are required to understand that any infractions of the laboratory data integrity

procedures will result in a detailed investigation that could lead to very serious consequences including immediate termination, or civil/criminal prosecution.

The training session includes many concepts and topics, numerous examples of improper actions (defined by DoD as deviations from contract-specified or method-specified analytical practices and may be intentional or unintentional), legal and liability implications (company and personal), causes, prevention, awareness, and reporting mechanisms.

2.0 Normative References

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

- ISO/IEC 17025:2017, *General requirements for the competence of testing and calibration laboratories*
- TNI 2016, VOLUME 1, *Management and Technical Requirements for Laboratories Performing Environmental Analysis*
- DoD/DOE QSM, *Department of Defense (DoD), Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories*
- Naval Sea Systems Command Laboratory Accreditation Program (LAP): S0005-AC-TED-010, Revision 4, March 1, 2020.

3.0 Terms and Definitions

- Impartiality - presence of objectivity
- Complaint - expression of dissatisfaction by any person or organization to a laboratory, relating to the activities or results of that laboratory, where a response is expected
- Inter-laboratory comparison - organization, performance and evaluation of measurements or tests on the same or similar items by two or more laboratories in accordance with predetermined conditions
- Intra-laboratory comparison - organization, performance and evaluation of measurements or tests on the same or similar items within the same laboratory in accordance with predetermined conditions
- Proficiency testing - evaluation of participant performance against pre-established criteria by means of inter-laboratory comparisons
- Laboratory - body that performs one or more of the following activities:
  - Testing;
  - Calibration;
  - Sampling, associated with subsequent testing or calibration
- Decision rule - rule that describes how measurement uncertainty is accounted for when stating conformity with a specified requirement
- Verification - provision of objective evidence that a given item fulfils specified requirements
- Validation - verification , where the specified requirements are adequate for an intended use

4.0 General Requirements

4.1 Impartiality

4.1.1 All employees are required to enter into the following agreements:

- **Code of Conduct Agreement**

  Provides a framework for decisions and actions in relation to conduct in employment. The agreement covers a wide range of topics including personal and professional behavior, conflicts of interest, gifts, confidentiality, legal compliance, security of information, among others. The code of conduct agreement is administered by the USA Human Resources department. This agreement is provided to the employee during the hiring and induction process and the agreement is reviewed and signed.

- **Confidentiality Agreement**

  Describes policies for identifying and protecting information owned by ALS and its customers, and for keeping this information in confidence. The confidentiality agreement is administered by the USA Human Resources department. This agreement is provided to the employee during the hiring and induction process and the agreement is reviewed and signed.

- **Ethics and Data Integrity Agreement**

  Provided to the employee as part of the hiring and induction process, and reviewed during periodic ethics refresher training. This is coordinated between the Human Resources and Quality Assurance (QA) departments. This agreement is provided to the employee during the hiring and induction process and the agreement is reviewed and signed. All employees are required to take annual ethics and data integrity refresher training.

In addition to the agreements, project managers act as a firewall to insulate the analysts from clients so that the lab personnel have no contact with clients. Lab IDs are assigned to samples and used throughout preparation and analysis to make the samples ambiguous to lab personnel. Together these agreements and procedures ensure freedom from undue internal and external commercial, financial, and other pressures or influences that could adversely affect the quality of work. They protect customers' confidential information and ALS' proprietary rights. They ensure avoidance of activities that could diminish confidence in the competence, impartiality, judgment or integrity of any ALS laboratory and staff.

4.1.2 It is the responsibility of all staff to comply with all procedures, be familiar with current management systems and policies, and to record all data as established by management. This and the peer review of all data will ensure that all testing is objective and conflicts of interest do not exist. As a commercial laboratory, the decision making using test results, opinions and interpretation of data is outside the scope of the laboratory activities.

4.2 Confidentiality

All employees signed confidentiality statement upon employment. These are maintained by Human Resources (HR).

Documents provided to the laboratory are held in strict confidence by project management staff. Documents pertaining to quality assurance and analytical requirements are reviewed with appropriate managers and staff through the project specific meetings and LIMS. Project related information provided by clients is securely

archived using procedures described in the ALS *SOP for Data and Record Archiving* (ADM-ARC).

The transmittal of final results is specified by clients and follows those requirements unless specific changes are made by the ALS Project Manager assigned to the client/project. Client communication procedures and documentation requirements are listed in ALS *SOP for Project Management* (ADM-PMGMT).

5.0 Structural Requirements

5.1 ALS Environmental – Simi Valley is legally identifiable as ALS Group USA, Corp., dba ALS Environmental. ALS Group USA Corp. is a component of ALS Limited, a publicly held Australian company. The ALS global website may be referred to for corporate ownership information (www.alsglobal.com). Organizational charts detailing the operational structure and reporting relationships in the laboratory are provided in Appendix B.

5.2 The support functions of this laboratory involved with testing and services are under the direction of the laboratory director. The laboratory director reports to the Regional Manager, Life Sciences, USA. There are other support functions such as human resources, accounting, safety oversight and computer systems that are provided to the laboratory by corporate entities but none of which is responsible for managing laboratory activities.

5.3 ALS Environmental employs methods and analytical procedures from a variety of external sources. Reference documents include but are not limited to: ASTM, NCASI, NIOSH, OSHA, SCAQMD, USEPA SW-846, USEPA 600/4-79-020, 600/R-93/100 (inorganic substances), 600/625/R-96/010b (air samples), EPA 40 CFR part 136 and associated Method Update Rules and Supplements, and *Standard Methods for the Examination of Water and Wastewater* for water and wastewater samples. Complete citations for these references can be found in Section 10. Other published procedures, such as state-specific methods, program-specific methods, or in-house methods may be used. Several factors are involved with the selection of analytical methods to be used in the laboratory. These include the method detection limit, the concentration of the analyte being measured, method selectivity, accuracy and precision of the method, the type of sample being analyzed, and the regulatory compliance objectives. The implementation of methods by ALS Environmental is described in SOPs specific to each method. A list of accredited methods is given in Appendix J.

This QAM is designed to be an overview of ALS operations. Detailed methodologies and practices are written in ALS Standard Operating Procedures (SOPs). Where appropriate, ALS SOPs are referenced in this document to direct the reader to more complete information.

5.4 ALS is committed to producing legally defensible analytical data of known and documented quality acceptable for its intended use and in compliance with applicable regulatory programs. This QAM is designed to satisfy the applicable requirements of various states, United States Environmental Protection Agency (USEPA), DoD QSM, NAVSEA-LAP, TNI Volume 1 2016 and ISO 17025:2017.

5.5 The ALS Environmental-Simi Valley staff, consisting of approximately 30 employees, includes chemists, technicians and support personnel. They represent diverse educational backgrounds, experience, and provide the comprehensive skills that the laboratory requires. As seasonal workload increases, temporary employees may be hired to perform specific tasks.

ALS Environmental is committed to providing an environment that encourages excellence. All employees share the responsibility for maintaining and improving the

quality of our analytical services. The responsibilities of key personnel within the laboratory are described below. Table 5-1 lists the ALS Environmental-Simi Valley personnel assigned to these key positions. Managerial staff members are provided the authority and resources needed to perform their duties. An organizational chart of the laboratory, as well as the resumes of key local level personnel, can be found in Appendix B.

- The role of the **Laboratory Director** is to provide technical, operational, and administrative leadership through planning, allocation and management of personnel and equipment resources. The Laboratory Director provides leadership and support for the QA program including ensuring compliance with ISO/IEC 17025:2017 and is responsible for overall laboratory efficiency and the financial performance of the Simi Valley facility.

  The Laboratory Director has the authority to stop work in response to quality problems. The Laboratory Director also provides resources for implementation of the QA program, reviews and approves this QA Manual, reviews and approves standard operating procedures (SOPs), and provides support for business development by identifying and developing new markets through continuing support of the management of existing client activities.

- The **Quality Assurance Manager** (QA Manager) has the authority and responsibility for implementing, maintaining, and improving the quality system. This includes coordination of QA activities within the laboratory, ensuring that all personnel understand their contributions to the quality system, ensuring communication takes place at all levels within the laboratory regarding the effectiveness of the quality system, evaluating the effectiveness of training; and monitor trends and continually improve the quality system. Audit and surveillance results, control charts, proficiency testing results, data analysis, corrective and preventive actions, customer feedback, and management reviews can all be used to support quality system implementation. The QA Manager is responsible for ensuring compliance with all applicable regulatory compliance quality standards (i.e. NELAP/TNI, ISO/IEC 17025:2017, NAVSEA-LAP, DoD QSM, etc.). The QA Manager works with laboratory staff to establish effective quality control and assessment plans and has the authority to stop work in response to quality problems. The QA Manager is responsible for maintaining the QA Manual and performing an annual review of it; reviewing and approving SOPs and ensuring the annual review of technical SOPs; maintaining QA records such as metrological records, archived logbooks, PT results, etc.; document control; conducting PT sample studies; approving nonconformity and corrective action reports; maintaining the laboratory's certifications and approvals; and performing internal QA audits.

  The QA Manager reports directly to the Laboratory Director and also reports indirectly to the Manager of Quality Assurance, USA. It is important to note that when evaluating data, the QA Manager does so in an objective manner and free of outside, or managerial, influence.

- The <u>Manager of Quality Assurance, USA</u> is responsible for the overall QA program at all the ALS Environmental Group laboratories. The Manager of Quality Assurance, USA is responsible for oversight of QA Managers regulatory compliance efforts (NELAP/TNI, ISO/IEC 17025:2017, NAVSEA-LAP, DoD QSM, etc) and may perform internal audits to evaluate compliance. The Manager of Quality Assurance, USA provides assistance to the laboratory QA staff and laboratory managers as necessary.

- In the case of absence of the Laboratory Director or QA Manager, deputies are assigned to act in that role. Default deputies for these positions are a Project Manager or Volatiles (GC/MS) Technical Manager (for the Laboratory Director) and the Laboratory Director (for the QA Manager).

  The following deputies are assigned in the case of absence of a Technical Manager. The Volatiles (GC/MS) Technical Manager will serve as the deputy for the Volatiles (GC)/Semi-Volatiles Technical Manager. The Volatile (GC)/Semi-Volatiles Technical Manger will serve as the deputy for the Volatile (GC/MS) Technical Manager.

- In the event that work is stopped in response to quality problems, only the Laboratory Director or QA Manager have the authority to resume work. Projects falling under the Naval Sea Systems Command Laboratory Accreditation Program (NAVSEA-LAP) require that the resumption of work after a work stoppage be approved in writing by the QA Manager.

- **Environmental Health and Safety Coordinator(s)** (EH&S) are responsible for the administration of the laboratory health and safety policies.

  This includes the formulation and implementation of safety policies, the supervision of new-employee safety training, the review of accidents, incidents and prevention plans, the monitoring of hazardous waste disposal and the conducting of departmental safety inspections. The EH&S Coordinator(s) are also designated as the Chemical Hygiene Officer(s). The EH&S Coordinator(s) have a dotted-line reporting responsibility to ALS North America EH&S Manager.

- The **Client Services Manager** is responsible for the Client Services Department defined for the laboratory (i.e. Project Managers, data reporting, etc.) and the sample management office/bottle preparation sections. The Client Services Department provides a complete interface with clients from initial project specifications to final deliverables. Sample management handles all activities associated with receiving, storage, and disposal of samples. The Client Services Manager has the authority to stop subcontractor work in response to quality problems.

- The **Project Manager** is assigned to clients to act as a liaison between the client and the laboratory. The Project Manager is responsible for ensuring that the analyses performed by the laboratory meet all project, contract, and regulatory-specific requirements. This entails coordinating with the ALS Environmental laboratory and administrative staff to ensure that client-specific needs are understood and that the services ALS Environmental provides are properly executed and satisfy the requirements of the client.

- The Analytical Laboratory is divided into operational units based upon specific disciplines. Each department is responsible for establishing, maintaining and documenting a QC program meeting department needs. Each **Department Manager and Supervisor** has the responsibility to ensure compliance with ISO/IEC 17025:2017, ensure that QC functions are carried out as planned, and to guarantee the production of high quality data. Department managers and bench-level supervisors have the responsibility to monitor the day-to-day operations to ensure that productivity and data quality objectives are met. Each department manager has the authority to stop work in response to quality problems in their area. Analysts have the responsibility to carry out testing according to prescribed methods, SOPs, and quality control guidelines particular to the laboratory in which he/she is working.

- The **Sample Management Office and Media Preparation Department** play key roles in the laboratory QA program by performing and/or assisting in the proper preparation and shipment of sampling media. In addition, personnel are responsible for the verification of sample receipt information, performing sample acceptance and log-in and distribution of documentation per laboratory defined procedures and the initial storage of samples in the proper environment and location and performing proper sample disposal. Responsibilities also include monitoring and recording of critical thermal preservation equipment temperatures and calibration of associated thermometers against NIST traceable thermometers.
- **Information Technology** (IT) staff is responsible for the administration of the Laboratory Information Management System (LIMS) and other necessary support services. Other functions of the IT staff include laboratory network maintenance, IT systems development and implementation, education of analytical staff in the use of scientific software, Electronic Data Deliverable (EDD) generation, and data back-up, archival and integrity operations.
- The **LIMS Manager** is responsible for LIMS development including all areas of software development such as design, coding, testing and distribution.
- The **Procurement Manager** is responsible for directing and coordinating activities of personnel engaged in buying materials and supplies.

Table 5-1

Simi Valley Personnel	Project Role
Randy Gates, B.S.	Laboratory Director
Sue Anderson, B.S.	Project Manager
Hayden Akers, B.S.	Project Manager
Nick Nash, A.S., B.S.	Quality Assurance Manager
Robert De La O	Systems Analyst / Information Technology
Wade Henton, B.S.	Volatiles (GC)/Semi-Volatiles Technical Manager
David Mirakian, B.S., M.S.	Volatiles (GC/MS) Technical Manager & Environmental Health and Safety Coordinator
Wida Ang, B.S., M.S.	Volatiles (GC/MS) Team Leader

Corporate Level Personnel	Project Role
Bob Di Rienzo, B.S.	Corp Quality Assurance Manager, USA
Hirenkumar Prajapati, B.S.	IT Manager USA
Albert Valle, A.A.S.	LIMS Manager USA
Steven Manak, B.S.	Procurement Group Leader

5.6 It is the responsibility of all technical and support staff to comply with all procedures and be familiar with current quality systems and policies as established by management. At ALS, improvement of the quality systems and preventive action is effected through an ongoing systems review by management using input from all staff. ALS actively seeks employee and client input for improvements through surveys and questionnaires. For clients, ALS surveys and gains feedback on services provided. This input to management is provided from the corporate level. To comply with these requirements all staff are responsible but not limited to the following:

- ✓ Follow project requirements as delineated by project managers to ensure analyses and commitments, including TAT, are performed as requested.
- ✓ Develop knowledge and understanding of the QAM requirements under which samples are handled and tested.
- ✓ Notify managers and Quality Assurance personnel when QA problems arise.
- ✓ Follow Quality Assurance requirements as outlined in the QAM and SOPs.
- ✓ Follow appropriate channels regarding modification of existing SOPs.
- ✓ Maintain accurate electronic and written records.
- ✓ Ensure that applicable data are included in each process in accordance with applicable SOPs.
- ✓ Record all nonconformance.
- ✓ Follow appropriate protocols when the handling and testing does not meet acceptance criteria.
- ✓ Apply integrity and professional judgment when dealing with analytical processes and laboratory operations.

5.7 Although verbal communication with employees is essential, written and visual communication through email and computer systems is the cornerstone of effective communication at ALS. Computer workstations throughout the lab provide access to LIMS, ALS Portals, Instruments used for testing, Policies and Procedures, and Email. All information essential for effective and consistent communication of analytical requirements, client requirements and details affecting quality are available through these computerized systems.

ALS management is committed to improvements of the management systems through compliance with its own policies and procedures. ALS management ensures improvements are made to the management systems and also ensures data integrity is maintained.

5.8 <u>Avoiding Conflict of Interest through Organizational Structure</u>

5.8.1 Through application of the policies and procedure outlined in this QA Manual and use of a defined organizational structure, the laboratory assures that it is impartial and that personnel are free from undue commercial, financial, or other undue pressures that might influence their technical judgment.

5.8.2 Policies are in place to prevent outside pressures or involvement in activities that may affect competence, impartiality, judgment, operational integrity, or the quality of the work performed at the laboratory.

5.8.3 Management and technical personnel have the authority and resources to carry out their duties and have procedures to identify and correct departures from the laboratory's management system.

5.8.4 Personnel understand the relevance and importance of their duties as related to the maintenance of the laboratory's management system. Ethics and data integrity procedure ensure that personnel do not engage in activities that diminish confidence in the laboratory's capabilities. Procedures and policies are also established to ensure confidentiality is maintained.

5.9 Technical Elements of the Quality Assurance Program

The laboratory's technical procedures are based upon procedures published by various agencies or organizations (See Section 10). The Quality Assurance Program provides laboratory organization, procedures, and policies by which the laboratory operates. The necessary certifications and approvals administered by external agencies are maintained by the QA department. This includes method approvals and audit administration. In addition, internal audits are performed to assess compliance with policies and procedures. SOPs are maintained for technical and administrative functions. A document control system is used for SOPs, as well as laboratory notebooks, and this QA Manual. A list of QA Program documents is provided in Appendix I and SOPs in Appendix G.

Acceptable calibration procedures are defined in the SOP for each test procedure. Calibration procedures for laboratory support equipment (gauges, thermometers, etc.) are also defined. Quality Control (QC) procedures are used to monitor the testing performed. Each analytical procedure has associated QC requirements to be achieved in order to demonstrate data quality. The use of method detection limit studies, control charting, technical training and preventive maintenance procedures further ensure the quality of data produced. Proficiency Testing (PT) samples are used as an external means of monitoring the quality and proficiency of the laboratory. PT samples are obtained from qualified vendors and are performed on a regular basis. In addition to method proficiency, documentation of analyst training is performed to ensure proficiency and competency of laboratory analysts and technicians. Sample handling and custody procedures are defined in SOPs. Procedures are also in place to monitor the sample storage areas. The technical elements of the QA program are discussed in further detail in later sections of this QA manual.

5.10 Professional Conduct

One of the most important aspects of the success of ALS Environmental is the emphasis placed on the integrity of the data provided and the services rendered. This success is reliant on both the professional conduct of all employees within ALS Environmental as well as established laboratory practices.

To promote quality, ALS Environmental requires certain standards of conduct and ethical performance among employees. The following examples of documented ALS Environmental policy are representative of these standards, and are not intended to be limiting or all-inclusive:

- Under no circumstances is the willful act of fraudulent manipulation of analytical data condoned. Such acts are to be reported immediately to senior management for appropriate corrective action.
- Unless specifically required in writing by a client, alteration, deviation or omission of written contractual requirements is not permitted. Such changes must be in writing and approved by senior management.
- Falsification of data in any form will not be tolerated. While much analytical data is subject to professional judgment and interpretation, outright falsification, whenever observed or discovered, will be documented, and appropriate remedies and punitive measures will be taken toward those individuals responsible.
- It is the responsibility of all ALS Environmental employees to safeguard sensitive company information, client data, records, and information; and matters of national

security concern should they arise. The nature of our business and the well-being of our company and of our clients is dependent upon protecting and maintaining proprietary company/client information. All information, data, and reports (except that in the public domain) collected or assembled on behalf of a client is treated as confidential. Information may not be given to third parties without the consent of the client. Unauthorized release of confidential information about the company or its clients is taken seriously and is subject to formal disciplinary action. All employees sign a confidentiality agreement upon hire to protect the company and client's confidentiality and proprietary rights.

5.11 Prevention and Detection of Improper, Unethical or Illegal Actions

It is the intention of ALS Environmental to proactively prevent and/or detect any improper, unethical or illegal action conducted within the laboratory.

This is performed by the implementation of a program designed for not only the detection but also prevention. Prevention consists of educating all laboratory personnel of their roles and duties as employees, company policies, inappropriate practices, and their corresponding implications as described here.

In addition to education, appropriate and inappropriate practices are included in SOPs such as manual integration, data review and specific method procedures. Internal audits are performed regularly over the course of a year. Requirements are described in the *SOP for Internal Audits* and details are listed in laboratory administrative SOPs. All aspects of this program are documented and retained on file according to the company policy on record retention.

The *SOP for Laboratory Ethics and Data Integrity* also contains information on the ALS Environmental ethics and data integrity program, including mechanisms for reporting and seeking advice on ethical decisions.

5.12 Management and Employee Commitment

ALS Environmental makes every attempt to ensure that employees are free from any commercial, financial, or other undue pressures that might affect their quality of work. Related policies are described in the *SOP for Laboratory Ethics and Data Integrity*. This includes:

- ALS Environmental Open Door Policy – Employees are encouraged to bring any work related problems or concerns to the attention of local management or their Human Resources representative. However, depending on the extent or sensitivity of the concern, employees are encouraged to directly contact any member of upper management.
- An anonymous and confidential reporting system available to all employees that is used to communicate misconduct and other concerns. The program shall help minimize negative morale, promote a positive work place, and encourage reporting suspected misconduct without retribution. Associated upper management is notified and the investigations are documented.
- Use of flexible work hours. Within reason and as approved by supervisors, employees are allowed flexible work hours in order to help ease schedule pressures which could impact decision-making and work quality.
- Operational and project scheduling assessments are continually made to ensure that project planning is performed and that adequate resources are available during anticipated periods of increased workloads. Procedures for subcontracting work are established, and within the ALS Environmental laboratory network additional capacity is typically available for subcontracting, if necessary.
- Gifts and Favors (Code of Conduct Agreement) – To avoid possible conflict of interest implications, employees do not receive unusual gifts or favors to, nor accept such

gifts or favors from, persons outside the Company who are, or may be, in any way concerned with the projects on which the Company is professionally engaged.

All employees are required to sign and adhere to the requirements set forth in the *Code of Conduct Agreement, Confidentiality Agreement,* and *Ethics and Data Integrity Agreement*.

6.0 Resources Requirements

6.1 General

6.1.1 ALS management has committed its full support to provide the personnel, facilities, equipment, and procedures required by this QAM.

6.2 Personnel

6.2.1 It is the responsibility of all staff to comply with all procedures, be familiar with current management systems and policies, and to record all data as established by management. This will ensure that all testing is objective and conflicts of interest do not exist. As a commercial laboratory, the decision making using test results is outside the scope of the laboratory activities. The ALS laboratory employs sufficient personnel to complete required analyses and support activities.

6.2.2 The ALS training program specified in the *SOP for Training Policy* and *SOP for ALS Environmental Induction Training for Quality Assurance* includes quality training, technical training, safety training, and other training as described in this QAM. ALS managers are responsible to ensure that all staff training is initiated, completed, verified, and documented.

The specific training and experience of laboratory personnel is documented in individual training files maintained in accordance with the *SOP for Training Policy* and *SOP for ALS Environmental Induction Training for Quality Assurance* and includes records of analytical proficiency.

Job Descriptions include requirements for education, qualification, training, technical knowledge, skills and experience.

Technical position descriptions are available for all employees, regardless of position or level of seniority. These documents are maintained by the Human Resources personnel and are available for review. In order to assess the technical capabilities and qualifications of a potential employee, all candidates for employment at ALS Environmental are evaluated, in part, against the appropriate technical description.

6.2.3 All ALS staff assigned to perform tasks affecting or relating to testing receives training relative to pertinent areas of responsibility, both prior to performing work on client samples and on an ongoing basis. Such training comes from internal and external sources.

Training begins the first day of employment at ALS Environmental when the company policies are presented and discussed. Safety and QA/QC requirements are integral parts of all technical SOPs and, consequently, are integral parts of all training processes at ALS Environmental. Safety training begins with reading the *Environmental Health and Safety Manual* and other safety related documents as applicable. Employees are also required to participate in periodic safety training performed by the Environmental, Health and Safety Coordinators.

Employees are responsible for complying with the requirements of the QA Manual and QA/QC requirements associated with their function(s). Quality Systems training begins with Quality Assurance orientation for new employees and reading the Quality Assurance Manual. New employees receive Ethics training and learn about ALS Environmental quality systems as part of the induction process. Each employee participates in annual Ethics Refresher training.

ALS Environmental also encourages its personnel to continue to learn and develop new skills that will enhance their performance and value to the Company. Ongoing training occurs for all employees through a variety of mechanisms. The corporate, company-wide training and development program, external and internal technical seminars and training courses, and laboratory-specific training exercises are all used to provide employees with professional growth opportunities.

All technical training is documented and records are maintained by the QA department. Training requirements and its documentation are described in the *SOP for Training Policy*. A training plan is developed whenever an employee starts a new procedure or new position. The training plan includes a description of the step-by-step process for training an employee and for initial demonstration of capability.

6.2.3.1 Initial Demonstration of Capability (IDOC)

Training in analytical procedures typically begins with the reading of the Standard Operating Procedure (SOP) for the method. Hands-on training begins with the observation of an experienced analyst performing the method, followed by the trainee performing the method under close supervision, and culminating with independent performance of the method on quality control samples. Successful completion of the applicable Demonstration of Capability analysis qualifies the analyst to perform the method independently. Demonstration of Capability is performed by one of the following:

- Successful completion of an Initial Precision and Recovery (IPR) study (required where mandated by the method).
- Analysis of 4 consecutive Laboratory Control Samples, with acceptable accuracy and precision.
- Where spiking is not possible but QC standards are used ("non-spiked" Laboratory Control Samples), analysis of 4 consecutive Laboratory Control Samples with acceptable accuracy and precision.
- Where one of the three above is not possible training is performed and supervisor approval is documented.

A flowchart identifying the Demonstration of Proficiency requirements is given in Figure 6-1. The flowchart identifies allowed approaches to assessing Demonstration of Capability when a 4-replicate study is not mandated by the method, when spiking is not an option, or when QC samples are not readily available.

6.2.3.2 Continuing Demonstration of Proficiency (CDP)

A periodic demonstration of proficiency is required to maintain continuing qualification. Continuing Demonstration of Proficiency is required each year, and may be performed one of the following ways:

- Successful performance on external (independent) single-blind sample analyses using the test method, or a similar test method using the same technology. I.e. PT sample or QC sample blind to the analyst.
- Performing Initial Demonstration of Capability as described above, with acceptable levels of precision and accuracy.
- Analysis of at least 4 consecutive LCSs with acceptable levels of accuracy and precision from in-control analytical batches.
- If the above cannot be performed, analysis of authentic samples with results statistically indistinguishable from those obtained by another trained analyst.
- For methods for which PT samples are not available and a spiked analysis (LFB, MDL, etc.) is not possible, analysis of field samples that have been analyzed by another analyst with statistically indistinguishable results.

6.2.3.3 Documentation of Training

Records are maintained to indicate the employee has the necessary training, education, and experience to perform their functions. Information of previously acquired skills and abilities for a new employee is maintained in Human Resources personnel files and ALS Environmental resumes. QA maintains a record of the various technical skills and training acquired while employed by ALS Environmental. Information includes the employee's name, a description of the skill including the appropriate method and SOP reference, the mechanism used to document proficiency, and the date the training was completed. General procedures for documenting technical training are described in the *SOP for Training Policy*.

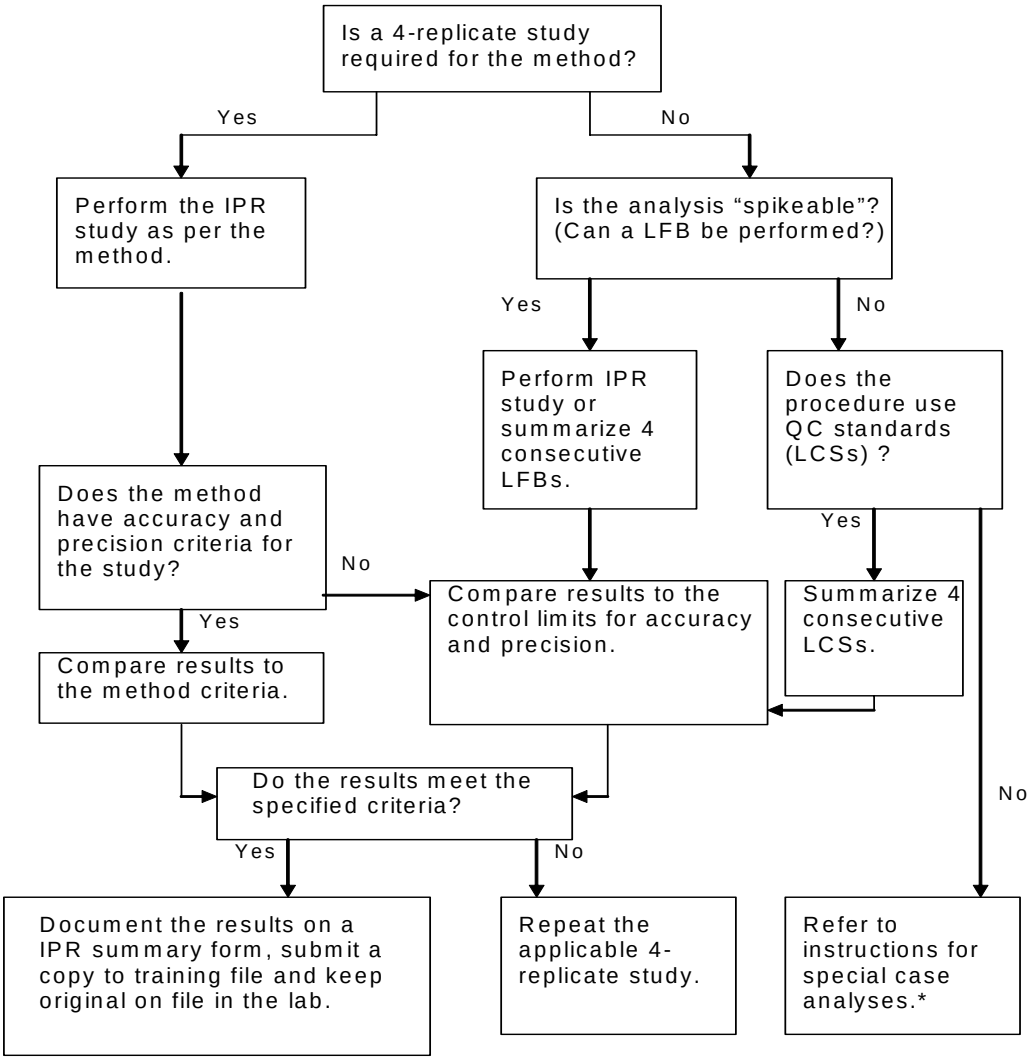
6.2.4 Laboratory personnel resources needed to carry out their duties. See 5.6

6.2.5 The laboratory *SOP for Training Policy*, includes the following and records are retained for:

- ✓ determining the competence requirements;
- ✓ selection of personnel;
- ✓ training of personnel;
- ✓ supervision of personnel;
- ✓ authorization of personnel;
- ✓ monitoring competence of personnel.

6.2.6 It is the responsibility of Technical and Support Management to authorize staff to perform specific laboratory activities. These tasks include testing methods, peer review and authorization to report results. Records are retained for the pertinent authorizations by the Quality Assurance department.

Figure 6-1
Initial Demonstration of Capability Requirements[a]



[a] For IDOC IPR or LFB studies, "second-source" reference materials are used, as per TNI/NELAP requirements
* Refer to the SOP for Training Policy for details. References for Quality Systems, External Documents, Manuals, Standards, and Analytical Procedures.

6.3 Facilities and Environmental Conditions

6.3.1 ALS management has committed its full support to provide the personnel, facilities, equipment, and procedures required by this QAM.

6.3.2 Records are maintained for the requirements and conditions necessary for method and regulatory compliance in the facility.

6.3.3 Records are retained for monitoring and control of environmental conditions to relevant method and regulatory specifications.

6.3.3.1 Temperature Control

Temperature Control Temperatures are monitored and recorded for all critical measurement temperature-regulating devices including freezers and refrigerators. Each piece of equipment is labeled with a unique identifier, the required temperature or range of use according to the needs of the analysis or application. Temperature record logs are kept which contain equipment identifier, daily-recorded temperatures (if in use, business days), acceptance criteria and the initials of the laboratory staff member who performed the checks for all temperature-regulating devices in daily use.

6.3.4 ALS Environmental-Simi Valley maintains approximately 20,000 square feet of laboratory and administrative workspace. Refer to Appendix D for facility floor plan. The laboratory has been designed and constructed to provide safeguards against cross-contamination of samples and is arranged according to work function, which enhances the efficiency of analytical operations. The ventilation system is designed to meet any needs of analyses performed in the separate work areas. ALS Environmental-Simi Valley minimizes laboratory contamination sources by employing janitorial staff to ensure good housekeeping. In addition, the segregated laboratory areas are designed for safe and efficient handling of a variety of sample types. These specialized areas (and access restrictions) include:

- Sample Management Office; Shipping and Receiving
- Records Archival
- Volatile Organics Laboratory (GC & GC/MS)
- Semi-Volatiles Laboratory (GC, GC/MS & HPLC)
- Ultra-Low Level Volatile Organics GC/MS
- General/Wet Chemistry Laboratory
- Canister Conditioning and Maintenance
- Flow Controller and Critical Orifice Calibration Station
- Sample Storage Walk-in Refrigerator
- Sample, Standards, and Media Storage
- Waste Disposal
- Laboratory Deionized Water System
- Laboratory Management, Client Service, Report Generation and Administration
- Information Technology (IT)

The designated areas for sample receiving, refrigerated sample storage, dedicated sample container preparation and shipping provide for the efficient and safe handling of a variety of sample types. The laboratory is equipped with state-of-the-art analytical and administrative support equipment. The equipment and instrumentation are appropriate for the procedures in use.

Laboratory security and access is important in maintaining the integrity of samples received at ALS Environmental-Simi Valley. Access to the building is

limited to the reception area and sample receiving doors, which are manned during business hours and locked at all other times. All non-employees are required to sign in at the main entrance. The laboratory is equipped with an alarm system which is monitored by a private security firm who provides nighttime and weekend security.

6.3.5 Environmental conditions are evaluated and recorded at the off-site storage facility as part of the annual audit schedule.

6.3.6 Water Purification Systems

Purified water is utilized for a number of laboratory functions including instrument and method blanks, trip blanks, washes and sample dilutions. The water purification system utilizes three mixed-ion beds, four filters, and resistively lights with constant water recirculation. It is designed to produce deionized water of ASTM Type II quality, with 16-18 megohm-cm resistance at 25˚C and is checked and recorded daily (prior to and if in use). Maintenance and repair on the system is conducted by an approved service supplier and all records including purification checks/verifications are maintained on file for review. For procedures on additional purification (i.e., boiling and/or purging) and purification checks/verifications, refer to the applicable method standard operating procedures.

6.4 Equipment

6.4.1 Appendix E lists the major equipment, illustrating the laboratory's overall capabilities and depth.

6.4.2 Laboratory support equipment (thermometers, weights, gauges) are verified on an annual basis by a vendor accredited to ISO/IEC 17025:2017. All analytical measurements generated at ALS Environmental are performed using materials and/or processes that are traceable to a reference material. Metrology equipment (analytical balances, thermometers, etc.) is calibrated using reference materials traceable to the National Institute of Standards and Technology (NIST). These primary reference materials are themselves recertified on an annual basis. Vendors used for metrology support are required to verify compliance to International Standards by supplying the laboratory with a copy of their scope of accreditation. Support equipment is calibrated or verified as described in the *SOP for Calibration and Use of Laboratory Support Equipment*

6.4.3 Preventive maintenance is a crucial element of the Quality Assurance program. Instruments at ALS Environmental (e.g., GC/MS systems, gas and liquid chromatographs, analytical balances, gas and liquid chromatographs, etc.) are maintained by in-house personnel. All equipment and instruments used at ALS Environmental are operated, maintained, and calibrated according to the manufacture's guidelines and recommendations, as well as to criteria set forth in the applicable analytical methodology. All routine and special maintenance activities pertaining to the instruments are recorded in instrument maintenance logbooks. The maintenance logbooks used at ALS Environmental contain extensive information about the instruments used at the laboratory.

An initial demonstration of analytical control is required on every instrument used at ALS Environmental before it may be used for sample analysis. Each instrument must be recalibrated following any instrument maintenance which may change or effect the sensitivity or linearity of the instrument or if the continuing calibration verification acceptance criteria have not been met as specified in the standard operating procedure. If an instrument is modified or repaired, a return to analytical control is required before subsequent sample analyses can occur. When an

instrument is acquired at the laboratory, the following information is noted in a bound maintenance notebook specifically associated with the new equipment:

- The equipment's serial number;
- Date the equipment was received;
- Date the equipment was placed into service;
- Condition of equipment when received (new, used, reconditioned, etc.); and
- Prior history of damage, malfunction, modification or repair (if known).

Preventive maintenance procedures, frequencies, etc. are available for each instrument used at ALS Environmental. They may be found in the various SOPs for routine methods performed on an instrument and may also be found in the operating or maintenance manuals provided with the equipment at the time of purchase. Procedures applicable to support equipment can be found in the *SOP for Calibration and Use of Laboratory Support Equipment.*

Responsibility for ensuring that routine maintenance is performed lies with the department supervisor or laboratory director. The supervisor may perform the maintenance or assign the maintenance task to a qualified bench level analyst who routinely operates the equipment. In the case of non-routine repair of capital equipment, the department supervisor is responsible for providing the repair, either by performing the repair themselves with manufacturer guidance or by acquiring on-site manufacturer repair. The laboratory maintains an adequate supply of expendable maintenance items (expected lifetime of part of less than 1 year.) These parts include items needed to perform the preventive maintenance procedures listed in Table 6-1.

When performing maintenance on an instrument (whether preventive or corrective), additional information about the problem, attempted repairs, etc. is also recorded in the notebook. Typical logbook entries include the following information:

- Details and symptoms of the problem;
- Repairs and/or maintenance performed;
- Description and/or part number of replaced parts;
- Source(s) of the replaced parts;
- Analyst's signature and date; and
- Demonstration of return to analytical control.

See Table 6-1 for a list of preventive maintenance activities and frequency for each instrument.

For further information regarding Instrumentation see the *SOP for Analytical Instrument Acquisition, Reassignment, Maintenance and Documentation*.

6.4.4 All instruments are calibrated or verified before use, using reference materials with traceability established. Specific calibration requirements are detailed in the method or SOP and support equipment SOP.

6.4.5 The instrument manuals are provided in electronic format usually in the software programs or on CDs. Software is controlled through licensing and is the responsibility of computer support to maintain licenses required.

6.4.6 Testing instruments are calibrated as per method, regulatory and verification procedures listed in method SOPs. Support equipment has verification and calibration frequencies specified in the *SOP for Calibration and Use of Laboratory Support Equipment*.

6.4.7 Operation and calibration are performed by personnel who have been properly trained in these procedures. Documentation of calibration information is

maintained in appropriate reference files. Brief descriptions of the calibration procedures for major laboratory equipment and instruments are described below. Refer to method SOPs and the *SOP for Calibration and Use of Laboratory Support Equipment* for specific calibration requirements. Calibration verification is performed according to the applicable analytical methodology. Documentation of calibration verification is maintained in appropriate reference files. Records are maintained to provide traceability of reference materials.

6.4.7.1 Temperature Measuring Devices

All thermometers are identified by a unique identifying number (i.e., serial number), and the calibration of these thermometers is checked annually (quarterly if digital) against a National Institute of Standards and Technology (NIST) certified thermometer. All corresponding correction factors are noted on the device as well as in the thermometer calibration logbook. The NIST calibrated thermometer is recertified by an approved vendor accredited to ISO/IEC 17025:2017 International Standard on an annual basis and certificates are retained on file for review. All temperature monitoring is conducted in accordance with the *SOP for Sample Receipt, Acceptance and Log-In* and thermometer calibration requirements are performed in accordance with the *SOP for Calibration and Use of the Laboratory Support Equipment.*

Specific thermometers include a temperature range per certain project requirements (complies with Department of Defense Quality Systems Manual for Environmental Laboratories); this range is recorded to document consistent compliance with required temperatures for refrigerators and freezers, where applicable.

6.4.7.2 Volumetric Dispensing Devices

The accuracy of pipettes used to make critical-volume measurements is verified on a quarterly basis. The indicated volume or range (where applicable) of the pipette is checked and an accuracy and precision verification performed. The calibrations are evaluated against the intended use (volume or range) of the pipette and if the calibration is not approved for the specified volume(s) it is tagged accordingly (i.e. “Do Not Use Below 5uL”). The results for all calibration verifications are recorded and maintained.

Note: Glass microliter syringes including gas-tight syringes are considered in the same manner as Class A glassware and are not held to the calibration/verification requirements as are other volumetric dispensing devices.

6.4.7.3 Analytical Weights and Balances

Analytical weights are calibrated/recertified and certificates issued annually by an approved vendor accredited to ISO/IEC 17025:2017 International Standard. The calibration of each balance is checked once each day (prior to use) in the expected range, utilizing the calibrated weights. Bound record books are kept which contain the identification of balance (serial number), recorded measurements and the initials of the

analyst who performed the check. All certificates for the weights are available for review.

6.4.7.4 Pressure/Vacuum Gauges

ALS Environmental-Simi Valley digital pressure/vacuum gauges are used in a number of critical measurements within the laboratory. The following is a list of the uses for this gauge type.

- Canister cleaning and conditioning.
- Measure the vacuum on canisters before they are sent to the client for sampling.
- Measure the initial/final vacuum/pressure of canisters prior to analysis.
- Measure pressure during the preparation of selected standards.

Digital pressure/vacuum gauges are calibrated and certificates issued once per year by an approved metrology organization. All calibrations are performed against standards traceable to the National Institute of Standards and Technology (NIST) or other recognized national metrology institutes. In addition, ALS Environmental-Simi Valley performs a calibration check for each gauge six months following the calibration date. The laboratory retains all corresponding calibration and verification documentation for review.

6.4.7.5 Instrument Calibration

The laboratory specifies the procedures and documentation for initial instrument calibration and continuing calibration verification in the applicable method standard operating procedures to ensure that data is of known quality and is appropriate for a specific regulation and/or client requirement. The procedural steps for calibration including, frequency, number of points, integration, calculations, acceptance criteria (appropriate to the calibration technique employed), corrective action, associated statistics, and data qualifications are included in applicable methods, method standard operating procedures and/or client project plans. The essential elements that define the procedures and required documentation for initial instrument calibrations are specified below.

- Sufficient raw data records are retained to permit reconstruction of all calibrations.
- If a reference or mandated method does not specify the number of calibration standards, the initial calibration range shall consist of a minimum of 5 contiguous calibration points for organics and a minimum of 3 contiguous calibration points for inorganics. The actual numbers of points utilized is specified in the corresponding method SOP.
- The concentrations should bracket the expected concentration range of samples.
- Initial instrument calibration procedures referenced in test methods (either directly or indirectly) are readily available to the analysts.
- All sample results are quantitated from the initial instrument calibration and are not quantitated from any continuing instrument calibration verification unless otherwise specified by regulation, method or program.

- The initial instrument calibration is verified with a standard obtained from a second manufacturer or lot and traceability to a national standard is maintained, where available.
- The acceptance criteria utilized is appropriate for the calibration technique employed.
- The lowest calibration standard in the initial calibration is at or below the lowest concentration for which quantitative data are to be reported and is referred to at this laboratory as the method reporting limit (MRL). Some programs and/or agencies refer to this limit as the practical quantitation limit (PQL) or Limit of Quantitation (LOQ).
- Any data reported below the MRL or above the highest calibration standard is considered to have an increased quantitative uncertainty and is appropriately qualified in the report.
- The lowest calibration standard is above the limit of detection or method detection limit (MDL).

6.4.7.6 Internal and External Calibrations

Internal standard calibration involves the comparison of instrument responses from the target compounds in the sample to the responses of specific standards added to the sample or sample extract prior to injection. The ratio of the peak area of the target compound in the sample or sample extract to the peak area of the internal standard in the sample or sample extract is compared to a similar ratio derived for each calibration standard. The ratio is termed the response factor (RF) or relative response factor (RRF) in some methods.

External standard calibration involves comparison of instrument responses from the sample to the responses from the target compounds in the calibration standards. Sample peak areas are compared to peak areas of the standards. The ratio of the detector responses to the amount (mass) of analyte in the calibration standard is defined as the calibration factor or in some cases it may be referred to as response factor.

6.4.7.7 Continuing Calibration Verification

The essential elements that define the procedures and required documentation for continuing instrument calibration verification are specified below.

- When an initial calibration is not performed on the day of analysis, continuing instrument calibration verification is analyzed with each batch.
- Calibration is verified for each reported compound, element or parameter; however, for analyses such as total petroleum hydrocarbons a representative chemical related substance or mixture may be used. The allowance for this exception is dependent on applicable regulatory, method, or client project plans.
- Generally, the instrument calibration verification is performed at the beginning, end, and every ten samples of each analytical batch (except, if an internal standard is used, only one verification needs to be performed at the beginning of the analytical batch); whenever it is suspected that the analytical system may be out of calibration; if the time period for calibration or most previous calibration

verification has expired; or for analytical systems that contain a specific calibration verification requirement. Specific requirements for the frequency of continuing calibration verification, for a particular method, is specified in the corresponding method standard operating procedure.

6.4.8 Calibration and verification period are designated in support equipment and analytical method SOPs. This equipment is labeled with calibration dates and any correction factors, if needed.

6.4.9 Equipment that has been subjected to overloading or mishandling, gives questionable results, or has been shown to be defective or outside specified requirements, is taken out of service and labeled accordingly until repaired. It shall be recalibrated and not returned to service until it has been verified to perform correctly. The laboratory shall examine the effect of the defect or deviation from specified requirements and shall initiate the nonconformance process.

6.4.10 Support equipment is verified per the *SOP for Calibration and Use of Laboratory Support Equipment* and calibration verification is required on analytical instruments as per method, program and SOP requirements.

6.4.11 Reference materials ordered by ALS have available documentation of purity, traceability and uncertainty. Support equipment which require correction factors are documented.

6.4.12 Passing verification criteria ensures that unintended adjustment of equipment is identified.

6.4.13 Records of instruments are retained and include specifications, manufacturer, serial numbers, identification, software version, location, status and the date of purchase. The majority of firmware has no impact on laboratory activities. There are some instruments in which the firmware is the software and can affect the laboratory operations. These instruments are usually small like pH meters. If an instrument does not have typical software to load and firmware is used to generate results, then the firmware version must be entered in the instruments record log and any updates to the firmware will be noted in the instrument maintenance log.

Records of calibration, maintenance, reference materials used, calibration checks or verifications are kept with analytical data.

Table 6-1

Equipment Maintenance Procedures

Instrument	Applicable Activity	Frequency	Performed
Gas Chromatographs	Replace septum	As required	In-House and Outside Vendor
	Check system for gas leaks, loose/fray wires and insulation	With cylinder change/Open system	
	Replace injection port liner	As required	
	ECD wipe test	Every 6 months	
	Thermally Clean ECD	As needed	
	Clean FID	As required	
	Change TCD assembly	As required	
	SCD – Change reaction tube	As required	
	Catalyst check	As required	
Gas Chromatography / Mass Spectrometers	Tune MSD	As needed	In-House and Outside Vendor
	Change Semi-VOA capillary column	As needed	
	Change Semi-VOA injection port septum	As required	
	Change Semi-VOA injection port liner	As required	
	Replace trap (VOA)	As required	
	Clean ion source	As required	
	Change filament	As required	
	Change electron multiplier	As required	
	Vacuum System: • Mechanical pumps: change oil, change trap pellets (HP only) • Diffusion pump: check oil, check cooling fan, change oil • Turbo pump	• Check every 6 months, check level monthly, change at least annually or sooner is necessary • As required • Replace as required	In-House
	Air Preconcentrators / Autosampler: • Change traps • Inspect Rotors • Calibrate Mass Flow Controllers	• As required • As required • Every 6 months	In-House

Instrument	Applicable Activity	Frequency	Performed
HPLC	Replace/clean check valve filter	As required	In-House
	Replace lamp UV/vis detector	As required	
	Replace flow cell	As required	
	Check flow	Quarterly	
Analytical Balances	Clean pan and compartment	Prior to and after use	In-House
	Check with NIST traceable weights	Prior to use	
Refrigerators and Freezers	Monitor Temperature	Daily	In-House
	Adjust Temperature	As required	
	Clean, Defrost	As required	
Ovens	Clean	As needed or if temperature is outside limit	In-House
pH probes	Condition probe	When fluctuations occur	In-House
	Change Filling Solution	Weekly	
Ammonia ISE	Store in storage solution	Between uses	In-House
UV-visible Spectrophotometer	Wavelength check	Annually	In-House
Restek Thermal Gas Purifier	Check getter tube	Monthly, change as required	In-House

6.5 Metrological Traceability

6.5.1 Traceability is defined as the property of a measurement result or value of a standard which can be related to stated references through an unbroken chain, each with stated uncertainties and is documented for all material used to perform calibrations. All measurements made by the laboratory required an unbroken chain to National Metrology Institute (NMI), Reference Standards or Reference Materials. The documentation, a certificate of analysis containing, at a minimum, the manufacturer, address, accreditation number (where applicable), how traceability was achieved, the traceable values, their associated uncertainty, and the unique serial or laboratory identification number of the equipment or standard reference material (SRM) shall serve as initial point in the chain of traceability. The unique serial number or laboratory identification number is used throughout the laboratory to trace equipment and materials back to the original certificate of analysis.

6.5.2 Reference Standards and Reference Materials

a) Reference Standards

Reference standards used by the laboratory are calibrated at determined intervals by outside vendors for the following equipment. These reference standards are maintained under the control of QA personnel and are used for verifying intermediate materials used by the laboratory. Quality Assurance is responsible for maintaining records and schedules of calibration.

- Reference Thermometers
- Reference Weights

Intermediate checks are used in the laboratory to verify performance of support equipment and are verified to traceable reference standards. Records of such verifications are retained by Quality Assurance.

b) Reference Materials

Reference materials used at ALS must be of the grade or quality specified by the pertinent analytical procedure or methodology.

Purchased reference materials must be traceable to a National Metrology Institute (NMI) or equivalent national or international standards where possible.

6.5.3 Reference Standards are calibrated by vendors certified to ISO 17025:2017.

Reference Materials are purchased, whenever possible. ALS uses reference materials from Guide 34 or ISO 17034 accredited vendors.

Second source reference materials are purchased and used in the testing process as an independent verification of primary reference materials.

6.5.4 Reference material information is recorded in the appropriate logbook(s) and materials are stored under conditions that provide maximum protection against deterioration and contamination.

The logbook entry includes such information as an assigned logbook identification code, the source of the material (i.e. vendor identification), solvent (if applicable) and concentration of analyte(s), reference to the certificate of analysis and an assigned expiration date. The date that the standard is received in the laboratory is marked on the container. When the reference material is used for the first time, the date of usage and the initials of the analyst are also recorded on the container.

Stock solutions and calibration standard solutions are prepared fresh as often as necessary according to their stability. All standard solutions are properly labeled as to analyte concentration, solvent, date, preparer, and expiration date; these entries are also recorded in the appropriate notebook(s) following the *SOP for Making Entries onto Analytical Record*s. Prior to sample analysis, all calibration reference materials are verified with a second, independent source of the material.

6.6 Externally Provided Products and Services

6.6.1 Laboratories contracted to perform analytical services for ALS must maintain quality programs consistent with the quality requirements of ALS. Before a laboratory performs subcontracted work for ALS, the Quality Assurance Manager must verify the acceptability of the quality program.

Analytical services are subcontracted when the laboratory needs to balance workload or when the requested analyses are not performed by the laboratory. Subcontracting, to capable qualified laboratories is only done with the knowledge and approval of the client. Subcontracting to another ALS Environmental laboratory is preferred over external-laboratory subcontracting.

ALS uses vendors which supply the level of quality required to perform testing activities. ALS maintains a relationship with multiple vendors and uses vendors with comparable certifications or accreditations.

6.6.2 *ALS SOP for Procurement and Control of Laboratory Services and Supplies* outlines the process, evaluation, criteria and records maintained from the evaluation and reevaluation of supplies and services. Procedures used to qualify external subcontract laboratory are described in the *SOP for Qualification of Subcontract Laboratories.*

6.6.3 Processes are designed to ensure that materials and services purchased meet the quality specifications of ALS. Procurement services are provided at ALS by administrative personnel. Procurement and receiving quality requirements established by ALS are followed. All requisitions for purchase are approved by ALS management and specify 1) the level of service required or 2) the quality/specifications of material required.

The quality level of reagents and materials (grade, traceability, etc.) required is specified in the analytical SOPs. Department supervisors ensure that the proper materials are purchased. Inspection and verification of material ordered is performed at the time of receipt by receiving personnel. The receipt of materials not meeting specification in the purchase requisition requires investigation. The receiving staff labels the material with the date received. Expiration dates are assigned as appropriate for the material. Storage conditions and expiration dates are specified in the analytical SOP. The *SOP for Handling Consumable Materials* provides default expiration requirements. Supplies and services that are critical in maintaining the quality of laboratory testing are procured from pre-approved vendors.

Receipt procedures include technical review of the purchase order/request to verify that what was received is identical to the item ordered. The laboratory checks new lots of reagents for unacceptable levels of contamination prior to use in sample preservation, sample preparation, and sample analysis by following the *SOP for Handling Consumable Materials*.

7.0 Process Requirements

7.1 Review of Requests, Tenders and Contracts

Project Managers are responsible for maintaining, archiving, and retrieving all contracts, project requirements and QAPPs provided to ALS by clients and related to projects completed by ALS. Procedures for client communication and documentation are listed in the *SOP for Project Management.*

All Requests for Proposal (RFP) documents are reviewed by Project Managers, Business Development, and appropriate managerial staff prior to signing any contracts or otherwise agreeing to perform the work. The specific methods to be used are agreed upon between the laboratory and the client. A capability review is performed to determine if the laboratory has or needs to obtain certification to perform the work, to determine if the laboratory has the resources (personnel, equipment, materials, capacity, skills, expertise) to perform the work, and if the laboratory is able to meet the client's required reporting and QC limits. The results of this review are communicated to the client and any potential conflict, deficiency, lack of appropriate accreditation status, or concerns of the ability to complete the client's work are resolved before any work commences. The client should be notified at this time if work is expected to be subcontracted.

ALS Environmental utilizes a number of different methods to ensure that adequate resources are available for service demands. Senior staff meetings, tracking of outstanding proposals and an accurate, current synopsis of incoming work all assist the senior staff in properly allocating sufficient resources. Status/production meetings are also conducted regularly with the laboratory and project managers to inform the staff of the status of incoming work, future projects, or project requirements.

If a contract needs to be amended after work has commenced, the contract review process is repeated and any amendments are communicated to all affected personnel. Changes in accreditation status affecting ongoing projects must be reported to the client. The laboratory shall afford clients cooperation to clarify the client's request and to monitor the laboratory's performance in relation to the work performed, provided that the laboratory ensures confidentiality to other clients.

7.2 Selection, Verification, and Validation of Methods

7.2.1 SOPs are written for all environmental testing methods, any modified reference methods, and any in-house developed methods. All SOPs are reviewed using document control procedure. The *SOP for Method Development* outlines procedures for performing method development and evaluating significant method changes for implementation.

All analytical methods and preparatory method combinations are routinely tracked and ALS maintains statistical control limits and reporting limits. The laboratory can perform using limits provided by clients or from referenced sources in the absence of historical data. The *SOP for Control Limits* describes how control limits are established and updated.

ALS Environmental strives to perform published methods as described in the referenced documents. If there is a material deviation from the published method, the method is cited as a "Modified" method in the analytical report. Modifications to the published methods are listed in the standard operating procedure. Standard operating procedures are available to analysts and are also available to our clients for review, especially those for "Modified" methods. Client approval is obtained for the use of "Modified" methods prior to the performance of the analysis.

When a client requests a modification to an SOP, policy, or standard specification the Project Manager must discuss the proposed deviation with the laboratory supervisor and obtain approval to accept the project. The Laboratory Director and QA Manager may also be involved. All project-specific requirements must be on-file and with the service request upon logging in the samples. The Project Manager is responsible for documenting the approved or allowed deviation from the SOP. A Project-Specific Communication Form, LIMS comments, or similar, may be used to document such deviations.

When a client request necessitates a deviation or departure from company policies or procedure involving any non-technical function, the allowed deviation must be approved by the laboratory or the Laboratory Director. Frequent departure from policy is not encouraged. However, if frequent departure from any policy is noted, the Laboratory Director will address the possible need for a change in policy.

7.2.2 The policy of ALS is to apply analytical methods that have been approved, validated, and published by government agencies, professional societies and organizations, respected private entities, and other recognized authorities. These methods have been validated for their intended use and ALS uses the demonstration of competency procedures, calibration of instruments and LOD/LOQ procedures to verify laboratory capability.

Validation procedures describe three different classifications of validations for method modification. New methods, permanent modifications to a published method which will be used in subsequent laboratory determinations, and temporary modifications applied only to immediate analytical projects. These methods are used with approval from the clients.

The essential quality control elements for modification and validation include:

Calibration - Number of levels and acceptance criteria should meet or exceed requirements used for the reference method.

QC Samples - QC samples prepared in the specific matrix, are assessed. If possible the recoveries are compared to method or historical control limits used for the reference method.

Sensitivity - Method Detection Limit is the lowest analyte concentration that produces a response detectable above the noise level of the system and Reporting Limit is the lowest level at which the analyte can be accurately and precisely measured. Procedures for generating Method Detection and Reporting limits can be found in the *SOP for Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation.*

If validation reports are required to validate methods, these reports must address the following elements and follow established testing industry protocols:

Calibration – a demonstration of a concentration range where the analyte response is proportional to concentration.

Sensitivity – Method Detection Limit is the lowest analyte concentration that produces a response detectable above the noise level of the system and Reporting Limit is the lowest level at which the analyte can be accurately and precisely measured.

Selectivity - the ability of the method to accurately measure the analyte response in the presence of all potential sample components.

Precision and Bias - Precision – the type of variability that can be expected among test results. Bias - systematic error that contributes to the difference between the mean of a large number of test results and an accepted reference value.

Robustness – the ability of the procedure to remain unaffected by small changes in parameters or matrix.

7.2.3 Demonstration of Capability

A demonstration of capability (DOC) is made prior to using any new test method or when a technician is new to the method. This demonstration is made following regulatory, accreditation, or method specified procedures. In general, this demonstration does not test the performance of the method in real world samples, but in the applicable clean matrix free of target analytes and interferences.

A quality control sample material may be obtained from an outside source or may be prepared in the laboratory. The analyte(s) is (are) diluted in a volume of clean matrix (for analytes which do not lend themselves to spiking the demonstration of capability may be performed using quality control samples). Where specified, the method-required concentration levels are used. Four aliquots are prepared and analyzed according to the test procedure. The mean recovery and standard deviations are calculated and compared to the corresponding acceptance criteria for precision and accuracy in the test method or laboratory-generated acceptance criteria (if there are not established mandatory criteria). All parameters must meet the acceptance criteria. Where spike levels are not specified, actual Laboratory Control Sample results may be used to meet this requirement, provided acceptance criteria are met.

7.2.4 Method Detection Limits and Method Reporting Limits & Limits of Detection/ Quantitation

Method Detection Limits (MDL) for methods performed at ALS Environmental-Simi Valley are determined during initial method set up and if any significant changes are made. The MDLs are determined by following the *SOP for Performing Method Detection Limits Studies and Establishing Limits of Detection and Quantitation,* which is based on the procedure in 40 CFR Part 136, Appendix B. The US EPA published a Method Update Rule (MUR) on August 28, 2017 which updated the MDL procedure in 40 CFR Part 136. As required by DoD protocol, the validity of MDLs is verified using LOD verification samples.

The Method Reporting Limit (MRL) is the lowest amount of an analyte in a sample that can be quantitatively determined with stated, acceptable precision and accuracy under stated analytical conditions (i.e. limit of quantitation - LOQ). LOQ are analyzed on an annual basis and cannot be lower than the lowest calibration standard. Current MDLs and MRLs are available from the laboratory.

7.2.5 Specialized Procedures

ALS Environmental not only strives to provide results that are scientifically sound, legally defensible, and of known and documented quality; but also strives to provide the best solution to analytical challenges. Procedures using specialized instrumentation and methodology have been developed to improve sensitivity (provide lower detection limits), selectivity (minimize interferences while maintaining sensitivity), and overall data quality for low concentration applications. Examples are specialized GC/MS analyses and low level organics analyses.

7.3 Sampling

The quality of analytical results is highly dependent upon the quality of the procedures used to collect, preserve and store samples.

ALS Environmental-Simi Valley does not provide sampling services. The laboratory only provides materials needed for sample collection; therefore, ALS Environmental-Simi Valley recommends that clients follow sampling guidelines described in the specific reference methods including 40 CFR 136 and/or USEPA SW-846, NIOSH, OSHA, ASTM, and SCAQMD as appropriate.

When transporting samples to the laboratory, the most expedient but lawful route of transport should be utilized. Also, the hazardous potential of the samples needs to be considered when shipping samples via air freight or passenger airlines.

Subsampling of air samples is not appropriate. If applicable for other sample matrices, method SOPs are followed to obtain representative sub-samples.

7.4 Handling of Test or Calibration Items

Standard operating procedures have been established for all aspects of sample management within the laboratory including sample receiving, handling, acceptance, log-in, protection, storage, retention, transportation, and disposal. The procedures include provisions necessary to protect the integrity of the sample (as received) and to protect the interests of the laboratory as well as the client. These procedures ensure that samples are handled properly and that all associated documentation is complete and consistent. The sample handling factors that must be taken into account to ensure accurate, defensible analytical results include but are not limited to:

- Amount of sample taken (sampling)
- Type of container used
- Existence and type of sample preservation
- Holding Time
- Proper custodial documentation
- Sample storage, tracking and/or transfer
- Retention
- Disposal

A record of all procedures to which a sample is subjected while in the possession of the laboratory including acceptance, rejection, login, identification, preservation checks, storage, tracking, and disposal are documented and maintained. In addition, all indirect procedures which support each record of a sample and protects the integrity of a sample is documented and maintained (i.e., refrigerator and freezer temperature checks, thermometer calibrations, etc.).

7.4.1 Preservation

ALS Environmental-Simi Valley uses sample preservation, container, and holding time recommendations published in a number of referenced documents including, but not limited to USEPA SW 846, USEPA 600/4-79-020, USEPA 600/R-93-100 (inorganic substances), EPA/625/R-96/010b (air samples), and EPA 40CFR part 136 and associated Method Update Rules. The complete citation for each of these and other references can be found in Section 10 of this document. The appropriate container, preservation and holding time information are summarized in Appendix F. Additional information on this is addressed in each corresponding method SOP.

7.4.2 Shipping of Containers and Samples

ALS Environmental-Simi Valley provides sample containers to clients via media requests for all matrices (air, water, etc.) with the appropriate preservatives (as applicable). These containers include Tedlar bags, specially prepared stainless steel canisters, silica-gel tubes, etc. ALS Environmental-Simi Valley keeps client-specific shipping requirements on file and utilizes all major transportation carriers to guarantee that sample shipping requirements (same-day, overnight, etc.) are met. The procedures for all requirements directed toward media requests follow the requirements detailed in the *SOP for Media Request Fulfillment*.

7.4.3 Sample Receiving and Acceptance

It is the policy of ALS Environmental-Simi Valley to check and record the condition of each sample (i.e. pressure, temperature, etc.) delivered to the Sample Management Office (SMO) and received by the Sample Management Custodian or alternates against certain acceptance criteria as documented in the *SOP for Sample Receiving, Acceptance, and Log-In*. This policy is available to all sample management personnel for reference. Any samples, which deviate from these outlined areas, will be clearly flagged with the nature and substance of the deviation. Assessment and condition checks utilized by ALS Environmental-Simi Valley for the acceptance or rejection of samples are based on the criteria found in Appendix F, applicable Quality Assurance Project Plan (QAPP), permit, program or rule where appropriate. This verification of sample integrity is conducted by the Sample Custodian and may be dependent on the matrix (i.e., temperature, preservation, and headspace) being submitted.

Any abnormalities or departures from specified condition requirements (as described herein) as observed during the initial assessment are recorded. When there is any doubt as to the suitability of a sample for testing, including signs of damage, when a sample does not conform to the description provided, or when the test method required is not specified in sufficient detail the appropriate Project Manager (PM) is notified.

The Project Manager shall consult with the client, whenever possible, regarding specific integrity issues documented during sample receipt for further instructions before proceeding and retain a written record of discussion. There may be instances where the client is unavailable, in which case the PM shall document all attempts at contacting the client.

There may be a need to inform the client that a sample(s) is rejected and cannot be accepted for analysis into the laboratory. This situation includes, but is not limited to loss of sample or insufficient amount (subsampling may be performed if it would not cause loss of sample integrity, but the procedure must be indicated with the test results). Subsampling of air samples is not appropriate.

The procedures for sample documentation, handling acceptance requirements and deviations from the sample acceptance policy are discussed in detail in the *SOP for Sample Receiving, Acceptance and Log-In*. This procedure is also in place to ensure samples are received and properly logged into the laboratory, and that all associated sample documentation, including Chain-of-Custody (COC) records are complete and consistent with the samples received. All associated documentation, including chain of custody forms, memos, transmittal forms, and phone logs, are kept with each project file.

7.4.4 Sample Log-in

Each sample is logged into the laboratory in such a way as to ensure traceability and cross-reference with regards to the unique laboratory job number, sample identifications and client sample identifications. The laboratory identification is retained throughout the life of the sample in the laboratory. The identification system is designed and operated to ensure that samples cannot be confused physically or in laboratory documentation. Additional information is provided in the *SOP for Sample Receiving, Acceptance, and Log-In*.

7.4.5 Sample Custody

A sample is in someone's "custody" if:

- It is in one's actual physical possession.
- It is in one's view, after being in one's physical possession.
- It is in one's physical possession and then locked up so that no one can tamper with it
- It is kept in a secured area, restricted to authorized personnel only.

Chain-of-Custody (COC) records are used to establish the legal custody of samples, showing the continuous possession of samples from sample collection and transportation to final destination at the laboratory. Custody of each sample is maintained from receipt through disposal (internally utilizing LIMS). When environmental samples are shipped to other laboratories for analysis, the sample management office follows formalized procedures for maintaining the chain of custody, which is written in SOPs for *Sample Receiving, Acceptance and Login* and *Laboratory Storage, Analysis, and Tracking*. An example to our facilities' Chain-of-Custody is depicted in Figure 7-1.

Laboratory security and access is important in maintaining the integrity of samples received at ALS Environmental-Simi Valley. Refer to section 6.3.4 for details regarding security of facilities.

7.4.6 Sample Storage, Analysis and Tracking

The procedures and requirements for documenting the storage, analysis and tracking as well as maintaining integrity of samples are detailed in the *SOP for Laboratory Storage, Analysis, and Tracking*.

7.4.7 Sample Retention and Waste Disposal

Upon completion of all analyses, the laboratory samples are retained in accordance with the requirements specified in the method SOPs and the *Simi Valley Lab Waste Management Plan*. The samples are disposed according to approved disposal practices or returned to the client (if applicable). All samples are characterized according to hazardous/non-hazardous waste criteria and are segregated accordingly. This evaluation is generally based on results from analyses performed on the sample by ALS Environmental-Simi Valley or an approved subcontract laboratory. It should be noted that all wastes produced at the laboratory, including the laboratory's own various hazardous waste streams, are treated in accordance with all applicable local, State and Federal laws. Complete documentation is maintained for samples from initial receipt through final disposal. This ensures an accurate record of the samples from "cradle to grave."

7.4.8 Intra-laboratory / Inter-laboratory Transfer of Samples

When environmental samples are shipped to another laboratory for analysis, samples are properly packed for shipment and preserved if necessary. Sample bottles are wrapped in protective material and placed in a plastic bag (preferably Ziploc®) to avoid any possible cross-contamination of samples during the transportation process. Blue or wet ice is used for temperature preservation, where necessary.

Figure 7-1
Air Chain of Custody Form

Air - Chain of Custody Record & Analytical Service Request

Page _____ of _____

2655 Park Center Drive, Suite A
Simi Valley, California 93065
Phone (805) 526-7161
Fax (805) 526-7270

Requested Turnaround Time in Business Days (Surcharges) please circle
1 Day (100%) 2 Day (75%) 3 Day (50%) 4 Day (35%) 5 Day (25%) 10 Day-Standard

ALS Project No.

ALS Contact:

Company Name & Address (Reporting Information)

Project Name

Project Number

Project Manager

P.O. # / Billing Information

Phone

Fax

Email Address for Result Reporting

Sampler (Print & Sign)

Analysis Method

Comments
e.g. Actual Preservative or specific instructions

Client Sample ID	Laboratory ID Number	Date Collected	Time Collected	Canister ID (Bar code # - AC, SC, etc.)	Flow Controller ID (Bar code #- FC #)	Canister Start Pressure "Hg	Canister End Pressure "Hg/psig	Sample Volume			

Report Tier Levels - please select
Tier I - Results (Default if not specified) ____ Tier III (Results + QC & Calibration Summaries) ____
Tier II (Results + QC Summaries) ____ Tier IV (Data Validation Package) 10% Surcharge ____

EDD required Yes / No
Type: _____ Units: _____

Chain of Custody Seal: (Circle)
INTACT BROKEN ABSENT

Project Requirements (MRLs, QAPP)

Relinquished by: (Signature)	Date:	Time:	Received by: (Signature)	Date:	Time:
Relinquished by: (Signature)	Date:	Time:	Received by: (Signature)	Date:	Time:

Cooler / Blank Temperature ____ °C

Figure 7-2

ALS Environmental
Sample Acceptance Check Form

Client: _____ Work order: _____
Project: _____
Sample(s) received on: _____ Date opened: _____ by: _____

Note: This form is used for all samples received by ALS. The use of this form for custody seals is strictly meant to indicate presence/absence and not as an indication of compliance or nonconformity. Thermal preservation and pH will only be evaluated either at the request of the client and/or as required by the method/SOP.

		Yes	No	N/A
1	Were **sample containers** properly marked with client sample ID?	☐	☐	☐
2	Did **sample containers** arrive in good condition?	☐	☐	☐
3	Were **chain-of-custody** papers used and filled out?	☐	☐	☐
4	Did **sample container labels** and/or tags agree with custody papers?	☐	☐	☐
5	Was **sample volume** received adequate for analysis?	☐	☐	☐
6	Are samples within specified holding times?	☐	☐	☐
7	Was proper **temperature** (thermal preservation) of cooler at receipt adhered to?	☐	☐	☐
8	Were **custody seals** on outside of cooler/Box/Container?	☐	☐	☐
	Location of seal(s)? _____ Sealing Lid?	☐	☐	☐
	Were signature and date included?	☐	☐	☐
	Were seals intact?	☐	☐	☐
9	Do containers have appropriate **preservation**, according to method/SOP or Client specified information?	☐	☐	☐
	Is there a client indication that the submitted samples are **pH** preserved?	☐	☐	☐
	Were VOA vials checked for presence/absence of air bubbles?	☐	☐	☐
	Does the client/method/SOP require that the analyst check the sample pH and if necessary alter it?	☐	☐	☐
10	**Tubes:** Are the tubes capped and intact?	☐	☐	☐
11	**Badges:** Are the badges properly capped and intact?	☐	☐	☐
	Are dual bed badges separated and individually capped and intact?	☐	☐	☐

Lab Sample ID	Container Description	Required pH *	Received pH	Adjusted pH	VOA Headspace (Presence/Absence)	Receipt / Preservation Comments

Explain any discrepancies: (include lab sample ID numbers): _____

RSK - MEEPP, HCL (pH<2); RSK - CO2, (pH 5-8); Sulfur (pH>4)

7.5 Technical Records

7.5.1 Documentation and Archiving of Sample Analysis Data

ALS Environmental maintains a records system which ensures that all laboratory records of analysis data are retained and available. The archiving system includes, but is not limited to, the following items (where applicable) for each set of analyses performed:

- Benchsheets describing sample preparation (if appropriate) and analysis;
- Instrument parameters (or reference to the data acquisition method);
- Sample analysis sequence;
- Instrument printouts, including chromatograms and peak integration reports for all samples, standards, blanks, spikes, duplicates and reruns;
- Applicable standard identification numbers;
- Chain of custody, service request and sample acceptance check forms;
- Initial calibration and data review checklist(s);
- Copies of report sheets submitted to the work request file; and
- Copies of Nonconformity and Corrective Action Reports, if necessary.

Individual sets of analyses are identified by analysis date and service request number. Since many analyses are performed with computer-based data systems, the final sample concentrations can be automatically calculated. If additional calculations are needed, they are written on the integration report or securely stapled to the chromatogram, if done on a separate sheet.

For organics analysis, data applicable to all analyses within the batch, such as GCMS tunes, CCVs, batch QC, and analysis sequences; are kept using a separate documentation system. This system is used to archive data on a batch-specific basis and is segregated according to the date of analysis. This system also includes results for the most recent calibration curves, as well as method validation results.

Additional technical record documentation details can be found in the *SOP for Making Entries onto Analytical Records* and *SOP for Laboratory Storage, Analysis and Tracking.*

7.6 Evaluation of Measurement Uncertainty

Uncertainty is associated with most of the results obtained in the laboratory testing conducted by ALS. It is meaningful to estimate the extent of the uncertainty associated with each result generated by the laboratory. It is also useful to recognize that this measurement of uncertainty is likely to be much less than that associated with sample collection activities.

In practice, the uncertainty of a result may arise from many possible sources. ALS has considered the relative contribution of major sources of error. The approach to estimating uncertainty adopted by the laboratory resulted in the conclusion that many sources of error are insignificant compared to the processes of sample preparation, calibration, and instrumental measurement. The uncertainty associated with the processes can be estimated from quality control data. Accordingly, ALS estimates uncertainty from data derived from quality control samples carried through the entire analytical process.

When requested by the client or relevant to the validity of reported results, the estimation of measurement uncertainty will be provided to a client or regulatory agency. How the uncertainty will be reported may be dictated by the client's reporting specifications. Procedures for determining and reporting uncertainty are given in the

SOP for Estimation of Uncertainty of Analytical Measurements. The estimation of uncertainty applied by ALS relates only to measurements conducted in the laboratory. Uncertainty associated with processes conducted external to the laboratory (e.g., sampling activities) are not considered.

7.7 Ensuring the Validity of Results

A primary focus of ALS Environmental's QA Program is to ensure the accuracy, precision and comparability of all analytical results. Prior to using a procedure for the analysis on field samples, acceptable method performance is established by performing demonstration of capability analyses. Performance characteristics are established by performing method detection limit studies and assessing accuracy and precision according to the reference method. ALS Environmental has established Quality Control (QC) objectives for precision and accuracy that are used to determine the acceptability of the data that is generated. These QC limits are either specified in the test methodology or are statistically derived based on the laboratory's historical data. Quality Control objectives are defined below.

7.7.1 Analytical Batch

The basic unit for analytical quality control is the analytical batch. The definition that ALS Environmental-Simi Valley has adopted for the analytical batch is listed below. The overriding principle for describing an analytical batch is that all the samples in a batch, both field samples and quality control samples are to be handled exactly the same way, and all of the data from each analysis is to be manipulated in exactly the same manner. The minimum requirements of an analytical batch are:

1) The number of (field) samples in a batch is not to exceed 20.
2) All (field) samples in a batch are of the same matrix.
3) The QC samples to be processed with the (field) samples include:
   a) Method Blank (a.k.a. Laboratory Reagent Blank)

      Function: Determination of laboratory contamination

   b) Laboratory Control Sample

      Function: Assessment of method performance

   c) Matrix Spiked (field) Sample (a.k.a. Laboratory Fortified Sample Matrix)*

      Function: Assessment of matrix bias

   d) Duplicate Matrix Spiked (field) Sample or Duplicate (field) Sample (a.k.a. Laboratory Duplicate)*

      Function: Assessment of batch precision

   * A sample identified as a field blank, an equipment blank, or a trip blank is not to be matrix spiked or duplicated.
4) A single lot of reagents is used to process the batch of samples.
5) Each operation within the analysis is performed by a single analyst, technician, chemist, or by a team of analysts/technicians/chemists.

6) Samples are analyzed in a continuous manner over a timeframe not to exceed 24-hours between the start of processing of the first and last sample of the batch.

7) (Field) samples are assigned to batches commencing at the time that sample processing begins. For example: for analysis of metals, sample processing begins when the samples are digested. For analysis of organic constituents, it begins when the samples are extracted.

8) The QC samples are to be analyzed in conjunction with the associated field samples prepared with them. However, for tests which have a separate sample preparation step that defines a batch (extraction, etc.), the QC samples in the batch do not require analysis each time a field sample within the preparation batch is analyzed (multiple instrument sequences to analyze all field samples in the batch need not include re-analyses of the QC samples).

9) The batch is to be assigned a unique identification number that can be used to correlate the QC samples with the field samples.

10) Batch QC refers to the QC samples that are analyzed in a batch of (field) samples.

11) Project-specific requirements may be exceptions. If project, program, or method requirements are more stringent than these laboratory minimum requirements, then the project, program, or method requirements will take precedence. However, if the project, program, or method requirements are less stringent than these laboratory minimum requirements, these laboratory minimum requirements will take precedence.

Note: Matrix spiked samples are often <u>not feasible</u> for air matrices. Therefore, the MS shall be used as required by the test method and as specified by the corresponding method SOP.

7.7.2 <u>Quality Control Objectives</u>

7.7.2.1 <u>Accuracy</u> - Accuracy is a measure of the closeness of an individual measurement (or an average of multiple measurements) to the true or expected value. Accuracy is determined by calculating the mean value of results from ongoing analyses of laboratory-fortified blanks, standard reference materials, and standard solutions. In addition, laboratory-fortified (i.e. matrix-spiked) samples are also measured; this indicates the accuracy or bias in the actual sample matrix. Accuracy is expressed as percent recovery (% REC.) of the measured value, relative to the true or expected value. If a measurement process produces results whose mean is not the true or expected value, the process is said to be biased. Bias is the systematic error either inherent in a method of analysis (e.g., extraction efficiencies) or caused by an artifact of the measurement system (e.g., contamination).

ALS Environmental utilizes several quality control measures to eliminate analytical bias, including systematic analysis of method blanks, laboratory control samples and independent calibration verification standards. Because bias can be positive or negative, and because several types of bias can occur simultaneously, only the net, or total, bias can be evaluated in a measurement.

7.7.2.2 <u>Precision</u> - Precision is the ability of an analytical method or instrument to reproduce its own measurement. It is a measure of the variability, or

random error, in sampling, sample handling and in laboratory analysis. The American Society of Testing and Materials (ASTM) recognizes two levels of precision: repeatability - the random error associated with measurements made by a single test operator on identical aliquots of test material in a given laboratory, with the same apparatus, under constant operating conditions, and reproducibility - the random error associated with measurements made by different test operators, in different laboratories, using the same method but different equipment to analyze identical samples of test material.

"Within-batch" precision is measured using replicate sample or QC analyses and is expressed as the relative percent difference (RPD) between the measurements. The "batch-to-batch" precision is determined from the variance observed in the analysis of standard solutions or laboratory control samples from multiple analytical batches.

7.7.2.3 Control Limits - The control limits for accuracy and precision originate from two different sources. For analyses having enough QC data, control limits are calculated at the 99% confidence limits. For analyses not having enough QC data, or where the method is prescriptive, control limits are taken from the method on which the procedure is based. If the method does not have stated control limits, then control limits are assigned method-default or reasonable values. Control limits are updated periodically when new statistical limits are generated for the appropriate surrogate, laboratory control sample, and matrix spike compounds or when method prescribed limits change. The updated limits are reviewed by the QA Manager. The new control limits replace the previous limits and data is assessed using the new values. Current acceptance limits for accuracy and precision are available from the laboratory. For inorganics, the precision limit values listed are for laboratory duplicates. For organics, the precision limit values listed are for duplicate laboratory control samples or duplicate matrix spike analyses.

7.7.2.4 Representativeness - Representativeness is the degree to which the field sample, being properly preserved, free of contamination, and analyzed within holding time, represents the overall sample site or material. This can be extended to the sample itself, in that representativeness is the degree to which the subsample that is analyzed represents the entire field sample submitted for analysis. ALS Environmental has sample handling procedures to ensure that the sample used for analysis is representative of the entire sample. Further, analytical SOPs specify appropriate sample handling and sample sizes to further ensure the sample aliquot that is analyzed is representative of entire sample. Air samples received by the laboratory in canisters and bags are considered to be homogenous and therefore, no special sample preparation procedures are necessary.

7.7.2.5 Comparability – Comparability expresses the confidence with which one data set can be compared to another and is directly affected by data quality (accuracy and precision) and sample handling (sampling, preservation, etc). Only data of known quality can be compared. The objective is to generate data of known quality with the highest level of comparability, completeness, and usability. This is achieved by employing the quality controls listed below and standard operating procedures for the handling and analysis of all samples. Data is reported in units specified by the client and using ALS Environmental or project-specified data qualifiers.

7.7.3 Quality Control Procedures

The specific types, frequencies, and processes for quality control sample analysis are described in detail in method-specific standard operating procedures and listed below. These sample types and frequencies have been adopted for each method and a definition of each type of QC sample is provided below.

7.7.3.1 Method Blank (a.k.a. Laboratory Reagent Blank)

The method blank is an analyte-free matrix (air, water, etc.) subjected to the entire analytical process. The method blank is analyzed to demonstrate that the analytical system itself does not introduce contamination. The method blank results should be below the Method Reporting Limit (MRL) or, if required for DoD projects, < ½ MRL for the analyte(s) being tested. Otherwise, corrective action must be taken. A method blank is included with the analysis of every sample preparation batch, every 20 samples, or as stated in the method, whichever is more frequent.

7.7.3.2 Calibration Blanks

For some methods, calibration blanks are prepared along with calibration standards in order to create a calibration curve. Calibration blanks are free of the analyte of interest and, where applicable, provide the zero point of the calibration curve. Additional project-specific requirements may also apply to calibration blanks.

7.7.3.3 Continuing Calibration Blanks

Continuing calibration blanks (CCBs) are solutions of analyte-free water, reagent, or solvent that are analyzed in order to verify the system is contamination-free when CCV standards are analyzed.

The frequency of CCB analysis is once every ten samples or as indicated in the method, whichever is greater. Additional project-specific requirements may also apply to continuing calibration blanks.

7.7.3.4 Calibration Standards

Calibration standards are vapors, liquids or solutions of known concentration prepared from primary standard or stock standard materials. Calibration standards are used to calibrate the instrument response with respect to analyte concentration. Standards are analyzed in accordance with the requirements stated in the particular method being used.

7.7.3.5 Initial (or Independent) Calibration Verification Standards

Initial (or independent) calibration verification standards (ICVs) are standards that are analyzed *after* calibration but *prior to* sample analysis, in order to verify the validity and accuracy of the standards used for calibration. Once it is determined that there is no defect or error in the calibration standard(s), standards are considered valid and may be used for subsequent calibrations and quantitative determinations (as expiration dates and methods allow). The ICV standards are prepared from materials obtained from a source independent of that used for preparing the calibration standards ("second-source"). ICVs are also analyzed in accordance with method-specific requirements.

7.7.3.6 Continuing Calibration Verification Standards

Continuing calibration verification standards (CCVs) are midrange standards that are analyzed in order to verify that the calibration of the analytical system is still acceptable. The frequency of CCV analysis is either once every ten samples, or as indicated in the method.

7.7.3.7 Internal Standards

Internal standards are known amounts of specific compounds that are added to each sample prior to instrument analysis. Internal standards are generally used for GC/MS procedures to correct sample results that have been affected by changes in instrument conditions or changes caused by matrix effects. The requirements for evaluation of internal standards are specified in each method and SOP.

7.7.3.8 Surrogates

Surrogates are organic compounds which are similar in chemical composition and chromatographic behavior to the analytes of interest, but which are not normally found in environmental samples. Depending on the analytical method, one or more of these compounds is added to method blanks, calibration and check standards, and samples (including duplicates, matrix spike samples, duplicate matrix spike samples and laboratory control samples) prior to extraction and analysis in order to monitor the method performance on each sample. The percent recovery is calculated for each surrogate, and the recovery is a measurement of the overall method performance.

Recovery (%) = (M/T) x 100

Where: M = The measured concentration of analyte,
T = The theoretical concentration of analyte added.

7.7.3.9 Laboratory Control Samples

The laboratory control sample (LCS) is an aliquot of analyte-free liquid, solid or air matrix to which known amounts of the method analyte(s) is (are) added. A reference material of known matrix type, containing certified amounts of target analytes, may also be used as an LCS. An LCS is prepared and analyzed at a minimum frequency of one LCS per 20 samples, with every analytical batch or as stated in the method, whichever is more frequent. The LCS sample is prepared and analyzed in exactly the same manner as the field samples.

The percent recovery of the target analytes in the LCS is compared to established control limits and assists in determining whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements at the required reporting limit. Comparison of batch-to-batch LCS analyses enables the laboratory to evaluate batch-to-batch precision and accuracy.

Recovery (%) = (M/T) x 100

Where: M = The measured concentration of analyte,
T = The theoretical concentration of analyte added.

7.7.3.10 Laboratory Fortified Blanks - LFB

A laboratory blank fortified at the MRL used to verify the minimum reporting limit. The LFB is carried through the entire extraction and analytical procedure. LFBs are not currently performed at this location,

7.7.3.11 Matrix Spikes (a.k.a. Laboratory Fortified Sample Matrix)

Matrix spiked samples are aliquots of samples to which a known amount of the target analyte (or analytes) is (are) added. The samples are then prepared and analyzed in the same analytical batch, and in exactly the same manner as are routine samples. For the appropriate methods, matrix spiked samples are prepared and analyzed and at a minimum frequency of one spiked sample (and one duplicate spiked sample, if appropriate) per twenty samples. The spike recovery measures the effects of interferences caused by the sample matrix and reflects the accuracy of the method for the particular matrix in question. Spike recoveries are calculated as follows:

Recovery (%) = (S - A) x 100 ÷ T

Where: S = The observed concentration of analyte in the spiked sample,
A = The analyte concentration in the original sample, and
T = The theoretical concentration of analyte added to the spiked sample.

Note: Matrix spiked samples are often not feasible for air matrices. Therefore, the MS shall be used as required by the test method and as specified by the corresponding method SOP.

7.7.3.12 Laboratory Duplicates and Duplicate Matrix Spikes

Duplicates are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. Depending on the method of analysis, either a duplicate analysis (and/or a matrix spiked sample) or a matrix spiked sample and duplicate matrix spiked sample (MS/DMS) are analyzed. The relative percent difference between duplicate analyses or between an MS and DMS is a measure of the precision for a given method and analytical batch. The relative percent difference (RPD) for these analyses is calculated as follows:

Relative Percent Difference (RPD) = (S1 - S2) x 100 ÷ S_{ave}

Where S1 and S2 = The observed concentrations of analyte in the sample and its duplicate, or in the matrix spike and its duplicate matrix spike, and
S_{ave} = The average of observed analyte concentrations in the sample and its duplicate, or in the matrix spike and its duplicate matrix spike.

Depending on the method of analysis, either duplicates (and/or matrix spikes) or MS/DMS analyses are performed at a minimum frequency of one set per 20 samples. If an insufficient quantity of sample is available to perform a laboratory duplicate or duplicate matrix spikes, duplicate LCSs will be prepared and analyzed.

7.7.3.13 Control Charting

The generation of control charts is routinely performed at ALS Environmental. Where appropriate, Surrogate, Matrix Spike and LCS recoveries are monitored and charted. In addition, the laboratory also monitors the Relative Percent Difference (RPD) measurement of precision. Control charts are available to each department to monitor the data generated and identify trends in the analytical results. If trends in the data are perceived, various means of corrective action may then be employed in order to prevent future problems with the analytical system(s). Finally, data quality reports using control charts are generated for specific clients and projects pursuant to contract requirements. The control charting procedure is described in the SOP for *Control Limits*.

7.7.3.14 Glassware Washing

Glassware washing and maintenance play a crucial role in the daily operation of a laboratory. The glassware used at ALS Environmental undergoes a rigorous cleansing procedure prior to every usage. The *SOP for Glassware Cleaning* outlines the various procedures used at ALS Environmental-Simi Valley; each procedure is specific to the end-use of the equipment as well as to the overall analytical requirements of the project. In addition, other equipment that may be routinely used at the laboratory is also cleaned following instructions in the appropriate SOP.

7.7.3.15 Collection Efficiency

In the case of sampling trains (consisting of one or more multi-section sorbent tubes), which are received intact by the laboratory, the “front” and “back” sections shall be separated if required by the client. Each section shall be processed and analyzed separately and the analytical results reported accordingly.

7.7.3.16 Desorption Efficiency and Method Reporting Limits (Industrial Hygiene)

Desorption efficiency (DE) is the ability of an analytical method to recover the analyte from the collection media. Desorption efficiencies are determined initially and for each analyte to be reported. In addition, a DE study is performed each time there is a change in the test method, or with each new lot of media. Desorption efficiency shall be determined using sorbent media from the same lot number used for the field samples, if possible, and of the identical size and type. The DE values are used to correct the sample results (for all samples except passive samplers) before reporting.

Minimum reporting limits for each reportable analyte are determined initially by the analysis of spiked media, prepared at the desired reporting limit and carried through the entire analytical process. The reporting limit is verified or re-established annually (or if there is a change in methodology or instrumentation) and instrument performance is checked with each analytical batch through the analysis of an analytical standard prepared at the reporting limit.

7.7.3.17 Field and Trip Blanks

Field and trip blanks are analyzed when they are submitted to the laboratory for analysis. The actual field samples are flagged (when analytes are found in the blank) if and only if the laboratory is able to

analyze the samples in the same analytical sequence as the corresponding field or trip blank. If this is not possible due to client submission restrictions then the results for the samples and blanks shall be reported independently with no flag. However, an explanation of this is included in the final report. This laboratory does not feel that Summa canisters are suitable for use as trip blanks. It is for this reason that the results for these types of containers are reported as separate samples and flagging is not considered appropriate.

7.7.3.18 Analysis of Performance Evaluation Samples (PT)

ALS Environmental-Simi Valley participates in the analysis of interlaboratory proficiency testing (PT) samples. Participation in PT studies is performed on a regular basis and is designed to evaluate all analytical areas of the laboratory. General procedures for these analyses are described in the *SOP for Proficiency Sample Testing Analysis*. ALS Environmental-Simi Valley routinely participates in the following studies:

- Air and Emissions PT studies, 2 per year
- Other studies as required for specific certifications, accreditations, or validations.

PT samples are processed by entering them into the LIMS system as samples (assigned Service Request, due date, testing requirements, etc.) and are processed the same as field samples. The laboratory sections handle samples the same as field samples, performing the analyses following method requirements and performing data review. The laboratory sections submit results to the QA Manager for subsequent reporting to the appropriate agencies or study provider. Results of the performance evaluation samples and audits are reviewed by the QA Manager, Laboratory Director, and the laboratory staff. For any results outside acceptance criteria, the analysis data is reviewed to identify a root cause for the deficiency, and corrective action is taken and documented through nonconformance (NCAR) procedures.

7.8 Reporting of Results

ALS Environmental reports the analytical data produced in its laboratories to the client via the certified analytical report. This report includes a transmittal letter, a case narrative, client project information, specific test results, quality control data, chain of custody information, and any other project-specific support documentation. The following procedures describe our data reduction, validation and reporting procedures.

7.8.1 Data Reduction and Review

Results are generated by the analyst who performs the analysis and works up the data. All data is initially reviewed and processed by analysts using appropriate methods (e.g., chromatographic software, instrument printouts, hand calculation, etc.). Equations used for calculation of results are found in the applicable analytical SOPs. The resulting data set is either manually entered into an electronic report form or is electronically transferred into the report from the software used to process the original data set (e.g., chromatographic software). The data is then reviewed by the analyst for accuracy. Once the primary analyst has checked the data for accuracy and acceptability, the supervisor or second qualified analyst reviews the data for errors. Where calculations are not performed using a validated software system, the reviewer rechecks a minimum of 10% of the calculations. When the entire data set has been found to be acceptable it is turned into the reporting department where final reports are generated and then validated by a Data

Validation Coordinator. The hardcopy or electronic final report is physically or electronically signed by the project manager and the final report may be stored electronically or in hardcopy format. Test analysis data shall be kept in the appropriate service request folder. Data review and reporting procedures are described in the *SOP for Data Review and Reporting.*

Policies and procedures for manual editing of data are established. The analyst making the change must initial and date the edited data entry, without obliteration of the original entry. The policies and procedures are described in the *SOP for Making Entries onto Analytical Records*.

Policies and procedures for electronic manual integration of chromatographic data are established. The analyst performing the integration must document the integration change by printing both the "before" and "after" integrations and including them in the raw data records. The policies and procedures are described in the *SOP for Manual Integration.*

7.8.2 Confirmation Data

Confirmation data will be provided as specified in the method. Identification criteria for GC, LC or GC/MS methods are summarized below:

- GC and LC Methods
  1. The analyte must fall within plus or minus three times the standard deviation (established for the analyte/column) of the retention time of the daily midpoint standard in order to be qualitatively identified. The retention-time windows will be established and documented, as specified in the appropriate Standard Operating Procedure (SOP).
  2. When sample results are confirmed by two dissimilar columns or detectors, the agreement between quantitative results must be evaluated. The relative percent difference between the two results is calculated and evaluated against SOP and/or method criteria.
- GC/MS Methods - Two criteria are used to verify identification:
  1. Elution of the analyte in the sample will occur at the same relative retention time (RRT) as that of the analyte in the standard.
  2. The mass spectrum of the analyte in the sample must, in the opinion of a qualified analyst or the department manager, correspond to the spectrum of the analyte in the standard or the current GC/MS reference library.

7.8.3 Data Review and Validation of Results

The integrity of the data generated is assessed through the evaluation of the sample results, calibrations, and QC samples (method blanks, laboratory control samples, sample duplicates, matrix spikes, trip blanks, etc.). A brief description of the evaluation of these analyses is described below, with details listed in applicable SOPs. The criteria for evaluation of QC samples are listed within each method-specific SOP. Other data evaluation measures may include (as necessary) a check of the accuracy check of the QC standards and a check of the system sensitivity. Data transcriptions and calculations are also reviewed.

Note: Within the scope of this document, all possible data assessment requirements for various project protocols cannot be included in the listing below. This listing gives a general description of data evaluation practices used in the laboratory in compliance with NELAP Quality Systems requirements.

Additional requirements exist for certain programs, such as projects under the DoD QSM protocols, and project-specific QAPPs.

- Method Calibration – Following the analysis of calibration blanks and standards according to the applicable SOP the calibration correlation coefficient, average response factor, etc. is calculated and compared to specified criteria. If the calibration meets criteria analysis may continue. If the calibration fails, any problems are isolated and corrected and the calibration standards reanalyzed. Following calibration and analysis of the independent calibration verification standard(s) the percent difference for the ICV is calculated. If the percent difference is within the specified limits the calibration is complete. If not, the problem associated with the calibration and/or ICV are isolated and corrected and verification and/or calibration is repeated.
- Continuing Calibration Verification (CCV) – Following the analysis of the CCV standard the percent difference is calculated and compared to specified criteria. If the CCV meets the criteria analysis may continue. If the CCV fails, routine corrective action is performed and documented and a 2nd CCV is analyzed. If this CCV meets criteria, analysis may continue, including any reanalysis of samples that were associated with a failing CCV. If the routine corrective action failed to produce an immediate CCV within criteria, then either acceptable performance is demonstrated (after additional corrective action) with two consecutive calibration verifications or a new initial calibration is performed.
- Method Blank – Results for the method blank are calculated as performed for samples. If results are less than the MRL (<½ MRL for DoD projects), the blank may be reported. If not, associated sample results are evaluated to determine the impact of the blank result. If possible, the source of the contamination is determined. If the contamination has affected sample results the blank and samples are reanalyzed. If positive blank results are reported, the blank (and sample) results are flagged with an appropriate flag, qualifier, or footnote.
- Sample Results (Inorganic) – Following sample analysis and calculations (including any dilutions made due to the sample matrix) the result is verified to fall within the calibration range. If not, the sample is diluted and analyzed to bring the result into calibration range. When sample and sample duplicates are analyzed for precision, the calculated RPD is compared to the specified limits.

  The sample and duplicate are reanalyzed if the criteria are exceeded. The samples may require re-preparation and reanalysis. Results are reported when within the calibration range, or as estimates when outside the calibration range. When dilutions are performed the MRL is elevated accordingly.
- Sample Results (Organic) – For GC/MS analyses, it is verified that the analysis was within the prescribed tune window. If not, the sample is reanalyzed. Following sample analysis and calculations (including any dilutions made due to the sample matrix) peak integrations, retention times, and spectra are evaluated to confirm qualitative identification. Internal standard responses and surrogate recoveries are evaluated against specified criteria. If internal standard response does not meet criteria, the sample is diluted and reanalyzed. Results outside of the calibration range are diluted to within the calibration range. When dilutions are performed the MRL is elevated accordingly.

- Surrogate Results (Organic) – The percent recovery of each surrogate is compared to specified control limits. If recoveries are acceptable, the results are reported. If recoveries do not fall within control limits, the sample matrix is evaluated. When matrix interferences are present or documented, the results are reported with a qualifier that matrix interferences are present.

  If no matrix interferences are present and there is no cause for the outlier, the sample is reanalyzed. However, if the recovery is above the upper control limit with non-detected target analytes, the sample may be reported. All surrogate recovery outliers are appropriately qualified on the report.

- Duplicate Sample and/or Duplicate Matrix Spike Results – The RPD is calculated and compared to the specified control limits. If the RPD is within the control limits the result is reported. If not, an evaluation of the sample is made to verify that a homogenous sample was used and the results are compared to the MRL. The samples and duplicates are reanalyzed and if re-analysis also produces out-of-control results, the results are reported with an appropriate qualifier.

- Laboratory Control Sample Results – Following analysis of the LCS the percent recovery is calculated and compared to specified control limits. If the recovery is within control limits, the analysis is in control and results may be reported. If not, this indicates that the analysis is not in control. Samples associated with the 'out of control' LCS, shall be considered suspect and the samples reanalyzed or the data reported with the appropriate qualifiers.

- Matrix Spike Results – Following analysis of the MS the percent recovery is calculated and compared to specified control limits. If the recovery is within control limits the results may be reported. If not, and the LCS is within control limits, this indicates that the matrix potentially biases analyte recovery. It is verified that the spike level is at least five times the background level. If not, the results are reported with a qualifier that the background level is too high for accurate recovery determination. If matrix interferences are present or results indicate a potential problem with sample preparation, steps may be taken to improve results; such as dilution and reanalysis, or re-preparation and reanalysis. Results that do not meet acceptance limits are reported with an appropriate qualifier.

7.8.4 Data Reporting

When an analyst determines that a data package has met the data quality objectives (and/or any client-specific data quality objectives) of the method and has qualified any anomalies in a clear, acceptable fashion, the data package will undergo a peer review by a trained chemist. Prior to release of the report to the client, the Project Manager reviews and approves the entire report for completeness and to ensure that any and all client-specified objectives were successfully achieved. The original raw test data, along with a copy of the final report, is retained by service request number for archival purposes. ALS Environmental maintains control of analytical results by adhering to standard operating procedures and by observing sample custody requirements. All data is calculated and reported in units consistent with project specifications, to enable easy comparison of data from report to report.

To the extent possible, samples shall be reported only if all QC measures are acceptable. If a QC measure is found to be out of control, and the data is to be reported, all samples associated with the failed quality control measure shall be reported with the appropriate data qualifier(s) (See Appendix H). The *SOP for*

Data Review and Reporting addresses the flagging and qualification of data. The ALS Environmental-defined data qualifiers, state-specific data qualifiers, or project-defined data qualifiers are used depending on project requirements. A case narrative may be written by the analyst or project manager to explain problems with a specific analysis or sample, etc.

For subcontracted analyses, the Project Manager verifies that the report received from the subcontractor is complete. This includes checking that the correct analyses were performed, the analyses were performed for each sample as requested, a report is provided for each analysis, and the report is signed. The Project Manager accepts the report if all verification items are complete. Acceptance is demonstrated by forwarding the report to the ALS Environmental client.

7.8.5 Deliverables

In order to meet individual project needs, ALS Environmental provides several levels of analytical reports. Standard specifications for each level of deliverable are described in Table 7-1. Variations may be provided based on client or project specifications.

When requested, ALS Environmental provides Electronic Data Deliverables (EDDs) in the format specified by client need or project specification. ALS Environmental is capable of generating EDDs with many different formats and specifications. The EDD is prepared by report production staff using the electronic version of the laboratory report to minimize transcription errors. User guides and EDD specification outlines are used in preparing the EDD. The EDD is reviewed and compared to the final report for accuracy.

7.8.6 Electronic Signatures It is a policy of ALS Environmental to allow the use of electronic signatures. For data reporting an electronic signature may be applied to the report by an approved report signatory and is binding to the same extent as a handwritten wet signature.

To authenticate the electronic signature the identity of the signatory is verified before their electronic signature can be created. Each electronic signature shall be unique to a single individual and shall not be used by any other individual. These signatures are established using only defined procedures within the software and are verified using the two distinct components of *username* and *password*. The report may not be changed once the signature has been applied.

Additionally, as a form of ‘signature’ used for LIMS, email, and certain internal documentation processes (e.g. acknowledgements, attestations, audit trails, etc.), and other electronic tools the user’s system login credentials are used to verify and authenticate the identity of the user. Following login, these credentials are used to identify and document the user.

Table 7-1
Descriptions of ALS Environmental Standard Data Deliverables

Tier I. Routine Certified Analytical Report includes the following:

1. Transmittal letter
2. Chain of custody documents and sample/cooler receipt documentation
3. Sample analytical results
4. Method blank results
5. Surrogate recovery results and acceptance criteria for applicable organic methods
6. Dates of sample preparation and analysis for all tests
7. Case narrative - optional

Tier II. In addition to the Tier I Deliverables, this includes the following:

1. Matrix spike result(s) with calculated recovery and including associated acceptance criteria
2. Duplicate or duplicate matrix spike result(s) (as appropriate to method), with calculated relative percent difference
3. Laboratory Control Sample result(s) with calculated recovery and including associated acceptance criteria
4. Case narrative - optional

Tier III. Data Validation Package. In addition to the Tier II Deliverables, this includes the following:

1. Case narrative - required
2. Summary forms for all associated QC and Calibration parameters, with associated control criteria/acceptance limits

Note: Other summary forms specified in QAPPs or project/program protocols, or those related to specialized analyses will be included.

Tier IV. Full Data Validation Package:

1. All raw data associated with the sample analysis, including but not limited to:
   a. Preparation and analysis bench sheets and instrument printouts,
   b. For organics analyses, all applicable chromatograms, spectral, confirmation, and manual integration raw data. For GC/MS this includes tuning results, mass spectra of all positive hits, and the results and spectra of TIC compounds when requested.
   c. QC data,
   d. Calibration data (initial, verification, continuing, etc),
   e. Calibration blanks or instrument blanks (as appropriate to method).
2. If a project QAPP or program protocol applies, the report will be presented as required by the QAPP.

7.9 Complaints

The laboratory maintains a system for dealing with customer complaints. Feedback is used and analyzed to improve the quality of services. The laboratory maintains and documents timely communication with the client for the purpose of seeking feedback and clarifying customer requests. The person who initially receives the feedback (typically the Project Manager) is responsible for documenting the complaint. If the Project Manager is unable to satisfy the customer, the complaint is brought to the attention of the Client Services Manager, Laboratory Director, or QA Manager for final resolution. The resolution is documented. The procedure is described in the *SOP for Handling Customer Feedback*.

7.10 Nonconforming Work

7.10.1 The ALS SOP for handling nonconformance is the *SOP for Nonconformance and Corrective Action.*

This laboratory procedure shall be implemented when any aspect of its laboratory activities or results of this work do not conform to its own procedures or the agreed requirements of the customer. The procedure ensures that:

- ✓ The responsibilities and authorities for the management of nonconforming work are defined;
- ✓ Actions (including halting or repeating of work and withholding of reports, as necessary) are based upon the risk levels established by the laboratory.
- ✓ Any employee may stop work when a task cannot be performed safely or the quality of data is determined to be or could be negatively affected. Metrics utilized for work stoppage may include but are not limited to exceeding instrument or sample control limits, QC trending, instrument problems, etc. The appropriate manager shall be consulted for any work stoppage;
- ✓ An evaluation is made of the significance of the nonconforming work, including an impact analysis on previous results;
- ✓ A decision is taken on the acceptability of the nonconforming work;
- ✓ Where necessary, the customer is notified and work is recalled;
- ✓ The responsibility for authorizing the resumption of work is defined.

7.10.2 The laboratory retains records on all nonconformance.

7.10.3 Quality Assurance Manager or designee reviews all nonconformance for completeness and adds comments as necessary on the acceptance. If this evaluation determines the problem has or can reoccur or it is against the laboratories own policies or procedures the event requires a corrective action as described in section 8.7.

7.11 Control of Data and Information Management

7.11.1 The generation, compilation, reporting, and archiving of electronic data is a critical component of laboratory operations. In order to generate data of known and acceptable quality, the quality assurance systems and quality control practices for electronic data systems must be complete and comprehensive and in keeping with the overall quality assurance objectives of the organization. ALS Environmental management provides the tools and resources to implement electronic data systems and establishes information technology standards and policies. Laboratory employees have access to all data and information through the internet, intranet, network locations and hard copy

7.11.2 Practices are defined for assuring the quality of the computer software used throughout all laboratory operations to generate, compile, report, and store electronic data. Software used for these functions is documented and validated by ALS computer support staff or by the vendor from whom it is purchased. These practices are described in the *SOP for Software and Data Quality Assurance*.

The purpose of the SOP is to describe the policies and practices for the procurement, configuration management, development, validation and verification, data security, maintenance, and use of computer software. The policies and practices described in the plan apply to purchased computer software as well as to internally developed computer software. Key components of this plan are policies for software validation and control.

A continuing effort is made at ALS to increase the use of automated data handling, improve efficiency, and minimize human error.

Software errors are treated as a nonconformance under section 7.10 or as a corrective action under 8.7.

7.11.3 The local ALS Environmental Information Technology (IT) department is established to provide technical support for all computing systems. Access to ALS networks are controlled through passwords and Windows security. The IT department staff continually monitors the performance and output of operating systems. The IT department oversees routine system maintenance and data backups to ensure the integrity of all electronic data described in the *SOP for Electronic Data Backup, Archiving, and Restoration*. A software inventory is maintained. Additional IT responsibilities are described in the *SOP for Software and Data Quality Assurance*.

ALS Environmental has various systems in place to address specific data management needs. The Laboratory Information Management System (LIMS) is used to manage sample information and invoicing. Access is controlled by password. This system defines sample identification, analysis specifications, and provides a means of sample tracking. This system is used during sample login to generate the internal service request. Included on the service request is a summary of client information, sample identification, required analyses, work instructions, and deliverable requirements.

Where possible, instrument data acquired locally is immediately moved to a server (Microsoft Windows Server 2008 R2). This provides a reliable, easily maintained, high-volume acquisition and storage system for electronic data files. With password entry, users may access the system from many available computer stations, improving efficiency and flexibility. The server is also used for data reporting, EDD generation, and administrative functions. Access to these systems is controlled by password. A standardized EDI (electronic data interchange) format is used as a reporting platform, providing functionality and flexibility for end users. With a common standardized communication platform, the EDI provides data reporting in a variety of hardcopy and electronic deliverable formats.

In addition to the local IT department, ALS Environmental corporate IT provides support for network-wide systems. ALS Environmental also has personnel assigned to information management duties such as development and implementation of reporting systems; data acquisition, and Electronic Data Deliverable (EDD) generation.

7.11.4 ALS uses offsite locations from the laboratory but internal to ALS for data storage which are managed in accordance with these procedures.

7.11.5 Access to network locations is managed with Windows security and roles throughout the system.

7.11.6 Calculations and data transfers are checked using the peer review process and through documentation of computer programs by the IT staff.

8.0 Management System Requirements

8.1 Options

8.1.1 The laboratory has implemented **Option A** from the ISO/IEC 17025:2017 standard as a management system. The following sections 8.2 through 8.9 address the required elements of Option A. This manual addresses management systems and demonstrates compliance with this document.

8.2 Management System Documentation

8.2.1 This manual describes the policies and objectives of the ALS management system. The laboratory procedures describe the details on how objectives are accomplished.

8.2.2 Policies and objectives of the management system address how competence is demonstrated and assessed, how testing is objectively reviewed and how consistent operations are accomplished. These are addressed in various procedures that define the processes used.

8.2.3 Evidence of commitment is the review of the manual annually and the records of reading by all employees. Additionally, employees are assigned pertinent procedures as needed to ensure objectivity and consistency.

8.2.4 The policies are supported in this management system with references to the procedures as appropriate.

8.2.5 All employees have access to the Quality Assurance Manual and the supporting procedures.

8.3 Control of Management System Documents

8.3.1 Procedures for control and maintenance of documents are described in the *SOP for Document Control.* The requirements of the SOP apply to all laboratory logbooks (standards, maintenance, run logbooks, etc), certificates of analysis, SOPs, QAMs, quality assurance project plans (QAPPs), Environmental Health & Safety documents, and other controlled ALS Environmental documents. Management system documents generated by the laboratory shall include page numbering and include the total number of pages or a mark to signify the end of the document.

External documents, such as reference methods, accreditation policies and requirements, and reference manuals are maintained under document control policies through the use of hardcopy and network drives. External documents relative to the management system are managed by the QA Manager. To prevent the use of invalid and/or outdated external documents, the laboratory maintains a master list of current documents and their availability. The list is reviewed before making the documents available. External documents are not issued to personnel.

ALS Environmental maintains SOPs for use in both technical and administrative functions (Refer to Appendix G). SOPs are written following standardized format and content requirements as described in the *SOP for Establishing Standard Operating Procedures*. Each SOP is reviewed and approved by a minimum of two

managers (the Laboratory Director and/or Department Manager and the QA Manager). All SOPs undergo a documented review according to the schedule outlined in the *SOP for Establishing Standard Operating Procedures* to make sure current practices are described. The QA Manager maintains a comprehensive list of current SOPs.

Each controlled copy of a controlled document will be released only after a document control number is assigned in accordance with the *SOP for Document Control* and the recipient is recorded on a document distribution list. Filing and distribution is performed by the QA Manager, or designee, and ensures that only the most current version of the document is distributed and in use. All obsolete copies are removed from access and stored for historical purposes.

The contents of this manual are reviewed, revised (as needed) and approved for use at least annually by authorized personnel (QA Manager, Laboratory Director, and Technical Managers) where the scope of the review ensures that it continuously reflects current policies and practices and incorporates all applicable requirements. Additionally, the date the review was completed is indicated by the date of the last approval signature on the title page.

A document control number is assigned to hardcopy logbooks. Completed logbooks that are no longer in use are archived in a master logbook file. Logbook entries are standardized following the *SOP for Making Entries onto Analytical Records*. The entries made into laboratory logbooks are reviewed and approved at a regular interval (quarterly).

8.4 Control of Records

8.4.1 A records system is used which ensures all laboratory records (including raw data, reports, and supporting records) are retained and available. Hardcopy analysis data is retained for five (5) years from the report date unless contractual terms or regulations specify a longer retention time. Electronic data is maintained for a minimum of five (5) years. Hardcopy laboratory logbooks are retained by ALS for a minimum of ten years. Archiving and data backup systems are described in the *SOP for Data and Record Archiving* and *SOP for Electronic Data Backup, Archiving, and Restoration.*

8.4.2 <u>Backup and Security</u>

Laboratory data is either acquired directly to the centralized acquisition server or acquired locally and then transferred to the server. All data is eventually moved to the centralized data acquisition server for reporting and archiving.

Full backups onto a hard drive are performed on all file server information once per day. In addition, the laboratory's data warehouse located in Canada performs an offsite full backup nightly.

Access to sample information and data is on a need-to-know basis. Access is restricted to the person's areas of responsibility. Passwords are required on all systems. No direct external, non-ALS Environmental access is allowed to any of our network systems.

The external e-mail system and Internet access is established via a single gateway to discourage unauthorized entry. ALS Environmental uses a closed system for company e-mail. Files, such as electronic deliverables, are sent through the external e-mail system only via a trusted agent or comparable service. The external messaging system operates through a single secure gateway. E-mail attachments sent in and out of the gateway are subject to a virus scan. Because the Internet is not regulated, we use a limited access approach to provide a

firewall for added security. Virus screening is performed continuously on all network systems with Internet access.

8.5 Actions to Address Risks and Opportunities

ALS views risk management as a key component of its corporate governance responsibilities and an essential process in achieving and mandating a viable organization. ALS is committed to enterprise wide risk management to ensure its corporate governance responsibilities are met and its strategic goals are realized.

Refer to ALS Limited Risk Management Policy and Framework CAR-GL-GRP-POL-007 and Risk Appetite and Tolerance Statement CAR-GL-POL-011 for details.

Risk is defined at ALS as the effect of uncertainty on objectives. Objectives for the organization have different attributes and aspects, such as financial, service, quality, health & safety, environmental stewardship, and are considered at different levels, such as enterprise-wide, operational, and project levels. ALS interprets risk as anything that could impact meeting its corporate strategic objectives, and believes risks can provide positive opportunities as well as having negative impacts.

Tools for evaluating and managing risk include routine procedures such as employee evaluations, control limits trending, sensitivity data evaluation, corrective action reports, nonconforming events, SOP review, internal and external audits, and PT results. .

Risk reporting mechanisms vary from routine reporting mechanisms and immediate action for lower risk situations to immediate notification of the ALS CEO in extreme cases.

Refer to: ALS Code of Conduct, ALS Whistleblower Policy, ALS Integrity Hotline, and Integrity and Compliance Helpline.

Regardless of the mechanism used, the policies and tools provide a framework for categorizing, assessing, analyzing, and addressing risk, as well as monitoring and reviewing actions taken. Roles and responsibilities are defined in the relevant procedures.

Risk severity is evaluated during the decision making process. For each risk there is an opportunity.

Risks to our business and how we address them include:

Impartiality by Employees

Analytical testing is completed with undue pressure to modify results to meet client objectives.

ALS does not view this as a risk. There are many firewalls in the lab process to prevent occurrence.

- Project Managers are in contact with clients but there is no ability to influence testing results
- All data generated must be peer reviewed by a second party
- Lab operations only see samples, sample names and numbers. They do not have direct contact with clients.
- Annual Ethics and Data Integrity Training for all employees
- ALS Code of Conduct, ALS Whistleblower Policy, ALS Integrity Hotline, and Integrity and Compliance Helpline.

Chemical Exposure

Failure to practice procedures as trained, issues with the facility, and poor engineering controls can result in injury to employees, lost time, med/hospital situation, contamination, and can close the site.

ALS has policies, chemical exposure training, and readily available SDS sheets. Employees are expected to offer suggestions for improvement and formally report any conditions where concern for safety is recognized.

Explosion/Chemical Fire

Improper chemical storage and usage along with lack of equipment and facility upkeep can result in loss of life, loss of property, and laboratory down time.

ALS performs inspections and training, keeps an inventory of chemicals, establishes storage locations, and maintains minimal quantities of chemicals.

Supply Disruption

Natural disasters and vendors unable to provide needed supplies can disrupt the business, increase expenses, and result in lost production and lost clients.

ALS maintains multiple sources for supplies, develops relationships with our vendors, and emphasize communication amongst analysts, managers, purchasing personnel and vendors.

Loss of Key Employees

Resignation, leave for personal reasons or for other employment can negatively impact the business.

Communication, cross-training, designated backups, and having a pool of potential replacements minimizes this risk. ALS promotes a positive atmosphere for employees and provides rewards for dedication.

Computer and Instrument Issues

Computer, instrument, or other IT failures can result in loss of revenue, loss of service, and loss of data.

ALS provides necessary IT resources for instruments and computers including replacing older computers, keeping related systems in good repair, and replacing when necessary. ALS continue to build robust data systems and make provisions for stellar back-up storage for all data.

Reputation

Falsifying test results can result in loss of credibility, loss of clients, loss of revenue, and suspension.

All new employees must sign an ethics agreement and have initial ethics and data integrity training. Annually, all employees must take ethics and data integrity refresher training. All data undergoes a proper peer review. ALS maintain a strong quality system.

Legal Ramifications

Not following workplace and environmental laws and failure to practice procedures as trained can result in license revocation, fines, and disruption of the business.

Targeted and ongoing training, inspections, and having established procedures minimizes this risk. ALS continues to follow all laws and regulations.

Loss Time Injury

Failure to practice procedures as trained and not having proper safeguards in place can result in injury to employees, lost time, med/hospital situation, contamination, and can close the site.

Policies, specific task related training, targeted and ongoing training, inspections, workplace safeguards, cross training, and designated backups, minimize this risk. ALS continues to grow the safety program and culture.

Loss of Revenue

Can be caused by various audit fines and contract penalties for late data resulting in loss of revenue and disruption in business.

Policies, specific quality training, targeted and ongoing training, inspections, workplace safeguards, and internal audits minimize this risk. ALS continues to perform lab operations at the highest level.

8.6 Improvement

8.6.1 ALS management is committed to continually improving the effectiveness of the management and quality systems by implementing the requirements of this quality manual. ALS is also committed to improvements of the management systems through compliance with its own policies and procedures. ALS management is also committed to compliance with requirements related to current TNI Standard, DoD QSM, and other client and project related requirements. Various preventive action and improvement processes are used for eliminating potential problems or averting problems before they occur. Details can be found in the *SOP for Preventive Action*.

8.6.2 ALS surveys clients and gains feedback on services provided. This input to management is managed at a corporate level and is reviewed monthly and during the management review processes.

8.7 Corrective Actions

8.7.1 ALS Laboratory operations are governed by documented procedures, requirements, quality assurance plans, project plans, and contracts. When any operation, for any reason, does not conform to the requirements of the governing documents, the aberrant event, item, or situation must be properly documented and evaluated. In addition, appropriate corrective action must be initiated. Procedures for the documentation and resolution of corrective action are detailed in the *SOP for Nonconformance and Corrective Action*. It is the *policy* of ALS that any corrective action which impacts results of testing must include notification to clients.

When work does not conform to established quality control procedures, responsible management will evaluate the significance of the nonconforming work and when required take corrective action to address the nonconformance. Nonconformance are reported to the client using various means (voice, email, narrative, etc). When a

nonconformance occurs that casts doubt on the validity of the test results or additional client instructions are needed, the Project Manager notifies the client the same business day that the nonconformance is confirmed and reported. The QA Manager reviews each problem, ensuring that appropriate corrective action has been taken by the appropriate personnel. The Nonconformity and Corrective Action Report (NCAR) is filed in the associated service request file and a copy is kept by the QA Manager. The QA Manager periodically reviews all NCARs looking for chronic, systematic problems that need more in-depth investigation and alternative corrective action consideration.

Part of the corrective action process involves determining the root cause. Identifying the root cause of a nonconformance can be difficult, but important for implementing effective corrective action. Root cause principles are used to determine assignable causes, which leads to corrective action taken to prevent recurrence.

8.8 Internal Audits

8.8.1 Quality audits are an essential part of ALS Environmental-Simi Valley's quality assurance program. System audits are conducted to qualitatively evaluate the operational details of the QA program. The system audit examines the presence and appropriateness of laboratory systems. External system audits of ALS Environmental-Simi Valley are conducted regularly by various regulatory agencies and clients. Appendix J lists the certification and accreditation programs in which ALS Environmental-Simi Valley participates. Programs and certifications are added as required. Additionally, internal system audits of ALS Environmental-Simi Valley are conducted regularly under the direction of the QA Manager. The internal audit procedures are described in the *SOP for Internal Audits*. The internal audits are performed as follows:

- Comprehensive lab-wide system audit – performed annually. This audit may be broken into sections over the course of a year and is conducted such that all elements of the ALS Quality System are assessed.
- Technical/method audits
- Hardcopy report audits

All audit findings and corrective actions are documented. The results of each audit are reported to the Laboratory Director and Department Managers for review. Any deficiencies identified are summarized in the audit report. Managers must respond with corrective actions correcting the deficiency within a defined timeframe. Should problems impacting data quality be found during an internal audit, any client whose data is adversely impacted will be given written notification within the corrective action period (if not already provided).

Additional internal audits or data evaluations may be performed as needed to address any potential data integrity issues that may arise.

8.9 Management Review

8.9.1 Review of the Management System is completed on an ongoing basis in accordance with the *SOP for Laboratory Management Review.*

8.9.2 Inputs to management reviews may be kept in agenda notes and include but are not limited to:

a) Changes in internal and external issues that are relevant to the laboratory;

b) Fulfilment of objectives;

c) Suitability of policies and procedures;

d) Status of actions from previous management reviews;

e) Outcome of recent internal audits;

f) Corrective actions;

g) Assessments by external bodies;

h) Changes in the volume and type of the work or in the range of laboratory activities;

i) Customer and personnel feedback;

j) Complaints;

k) Effectiveness of any implemented improvements;

l) Adequacy of resources;

m) Results of risk and opportunity identification;

n) Outcome of the assurance of the validity of results; and

o) Other relevant factors, such as monitoring activities and training.

8.9.3 The outputs from the management review shall record all decisions and actions related to at least:

a) The effectiveness of the management system and its processes;

b) Improvement of the laboratory activities related to the fulfilment of the requirements of this document;

c) Provision of required resources;

d) Any need for change.

A summary of these outputs is generated annually.

9.0 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
35	02/1/20	N. Nash	Document control page – updated approval names
			Section 2.0 – updated reference
			Section 5.5 & Table 5-1 – updated to reflect current status
			Section 5.11 – revised regarding internal auditing
			Section 6.4.7.3 – revised to reflect current procedures
			Table 6-1 - revised to reflect current procedures
			Figure 7-2 removed soil / water chain of custody form and replaced with sample acceptance check form
			Section 7.4.2 - revised to reflect current procedures
			Section 7.7.3.10 – added last sentence
			Section 7.7.3.13 – revised second sentence
			Section 8.4.1 – All data shall be maintained a minimum of (5) five years
			Section 8.8.1 - revised to reflect current procedures

Appendix A – updated
Appendix B – updated organization chart; updated resumes
Appendix E – updated equipment list
Appendix F – removed retired methods
Appendix G – updated SOP lists
Appendix I – updated approved signatories
Appendix J – updated laboratory accreditations and certifications

10.0 References for Quality System Standards, External Documents, Manuals, and Test Procedures

The analytical methods used at ALS Environmental generally depend upon the end-use of the data. Since most of our work involves the analysis of environmental samples for regulatory purposes, specified federal and/or state testing methodologies are used and followed closely. Typical methods used at ALS Environmental are taken from the references listed below. Additional QA program documents are listed in Appendix I.

- ISO/IEC 17025:2017, *General requirements for the competence of testing and calibration laboratories.*
- TNI 2016, VOLUME 1, *Management and Technical Requirements for Laboratories Performing Environmental Analysis.*
- DoD/DOE QSM, *Department of Defense (DoD), Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories,* Current Version.
- Naval Sea Systems Command Laboratory Accreditation Program (LAP): S0005-AC-TED-010, Revision 4, March 1, 2020.
- 3M Organic Vapor Monitor Sampling and Analysis Guide, *Organic Vapor Monitors 3500/3510 and Organic Vapor Monitors 3520/3530*, Technical Bulletin 1028, January 1, 2004.
- American Society for Testing and Materials (ASTM), Gaseous Fuel, Coal and Coke, Volume 05.06, September 2006.
- American Society for Testing and Materials (ASTM), Annual Book of ASTM Standards, Philadelphia, PA.
- Arizona Administrative Code, *Department of Health Services – Laboratories*, Title 9, Ch. 14, Article 6. *Licensing of Environmental Laboratories*, R9-14-601 through R9-14-621, October 1, 2016.
- California Environmental Protection Agency Air Resources Board, *Methods for Determining Emissions of Toxic Air Contaminants from Stationary Sources*, Volume 3, July 28, 1997.
- California Code of Regulations (CCR), Title 22, Chapter 11 *Identification and Listing of Hazardous Waste*, 7/20/05.
- Minnesota Administrative Rules, *Department of Health*, Chapter 4740, Laboratories; Accreditation Requirements.
- *Good Automated Laboratory Practices, Principles and Guidance to Regulations For Ensuring Data Integrity In Automated Laboratory Operations*, EPA 2185 (August 1995).
- Environmental Protection Agency, Methods Update Rule (MUR), Guidelines for Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Analysis and

Sampling Procedures; 40 CFR Parts 122, 136, 143, 430, 455 & 465; Final Rule 3/12/07, Effective April 11, 2007.

- 40 CFR Part 60, Test Methods for Standards of Performance for New Stationary Sources, Appendix A.
- 40 CFR Part 63, Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, Appendix A.
- 40 CFR Part 63, National Emission Standards for Hazardous Air Pollutants for Source Categories, Subchapter C.
- 40 CFR Part 136, Appendix B, Definition and Procedure for the Determination of the Method Detection Limit, Revision 2.
- Environmental Protection Agency, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods,* SW-846, Third Edition, 1986 and Updates I (7/92), II (9/94), III (12/96), IIIA (4/98), IIIB (11/04), IVA & IVB. See Chapters 1, 2, 3, 4, 5, 6, and 8.
- Environmental Protection Agency, *Methods for Chemical Analysis of Water and Wastes*, EPA-600/4-79-020, 1983.
- Environmental Protection Agency, *Methods for the Determination of Inorganic Substances in Environmental Samples,* EPA 600/R-93-100, August 1993.
- Environmental Protection Agency, *EPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, Second Edition, EPA/625/R-96-010b, January 1999.
- Environmental Protection Agency, *EPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, Second Edition Addendum, October 4, 2000.
- National Institute for Occupational Safety and Health (NIOSH) *Manual of Analytical Methods*, Third Edition (August 1987); Fourth Edition (August 1994); 1st Supplement Publication 96-135, 2nd Supplement Publication 98-119, 3rd Supplement 2003-154
- National Council for Air and Stream Improvement, Inc. (NCASI). 2007. *Appendix E - Technical Bulletin Cross Reference Guide for NCASI Methods.* Methods Manual (05).
- *SKC 575 Series Passive Sampler Rate/Selection Guide,* Form #37021, Rev 0012.
- *Standard Methods for the Examination of Water and Wastewater*, 20th Edition (1998).
- South Coast Air Quality Management District, *Laboratory Methods of Analysis for Enforcement Samples.*
- U.S. Department of Labor, Occupational Safety and Health Administration *OSHA Analytical Methods Manual.*

11.0 Appendices

The documents listed in this section are dynamic; accordingly they can change without notice or revision to this QAM. Please contact the laboratory for the most current documents.

APPENDIX A – Glossary

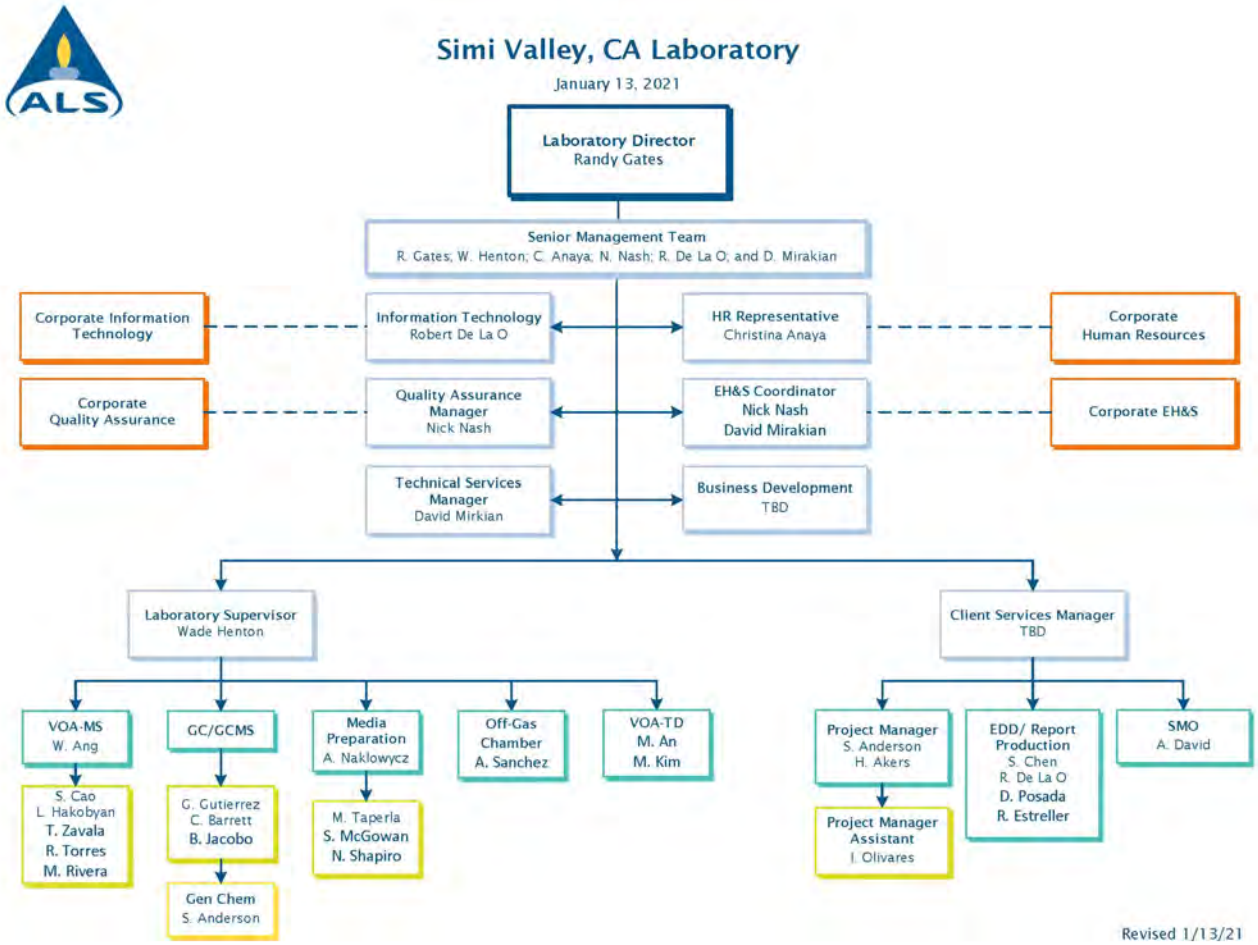
Acronym	Definition
AB	Accrediting Body
ACS	American Chemical Society
ANSI	American National Standards Institute
ASTM	American Society for Testing and Materials
A2LA	American Association for Laboratory Accreditation
BFB	4-Bromofluorobenzene
BTEX	Benzene, Toluene, Ethylbenzene, Xylenes
CAS Number	Chemical Abstract Service Registry Number
CCB	Continuing Calibration Blank sample
CCC	Continuing Calibration Check sample
CCV	Continuing Calibration Verification sample
CDC	Continuing Demonstration of Capability
CDP	Continuing Demonstration of Proficiency
CLP	Contract Laboratory Program (through USEPA)
COC	Chain-of-Custody
DCM	Dichloromethane (aka Methylene Chloride)
DEC	Department of Environmental Conservation
DEQ	Department of Environmental Quality
DHS	Department of Health Services
DOC	Demonstration of Capability
DOE	Department of Ecology (state or federal)
DOH	Department of Health
EPA	U.S. Environmental Protection Agency (aka USEPA)
EPCRA	Emergency Planning & Community Right-to-Know Act
ERA	Environmental Resource Associates
ELAP	Environmental Laboratory Accreditation Program
FID	Flame Ionization Detector
FIFRA	Federal Insecticide, Fungicide & Rodenticide Act
FR	Federal Register
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
HP	Hewlett-Packard (mfg. GC instruments)
HPLC	High Performance Liquid Chromatography

IC	Ion Chromatography
ICAL	Initial Calibration
ICB	Initial Calibration Blank sample
ICV	Initial Calibration Verification sample
IDC	Initial Demonstration of Capability
IDP	Initial Demonstration of Proficiency
IFB	Invitation for Bid
ISO/IEC	International Organization for Standardization/International Electrochemical Commission
LCS	Laboratory Control Sample
LIMS	Laboratory Information Management System
MB	Method Blank
MDL	Method Detection Limit
MRL	Method Reporting Limit
MS	Matrix Spike
MSD	Matrix Spike Duplicate
NA	Not Applicable
NAS	National Academy of Sciences
NELAP	National Environmental Laboratory Accreditation Program
NCASI	National Council for Air and Stream Improvement (for the Paper Industry)
NCI	National Cancer Institute
ND	Not Detected
NIH	National Institute of Health
NIOSH	National Institute for Occupational Safety and Health
NIST	National Institute of Standards and Technology
NPD	Nitrogen Phosphorus Detector
NPDES	National Pollutant Discharge Elimination System
NSF	National Science Foundation
NTIS	National Technical Information System
NTP	National Toxicology Program
OSHA	Occupational Safety and Health Administration
PCBs	Polychlorinated Biphenyls
PE	Performance Evaluation sample
PID	Photoionization Detector
PQL	Practical Quantitation Limit
PT	Proficiency Test

QA	Quality Assurance
QAM	Quality Assurance Manual
QC	Quality Control
RAS	Routine Analytical Services (Contracts through USEPA)
RCRA	Resource Conservation and Recovery Act
RFP	Requests for Proposal
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
SAS	Special Analytical Services (contracts through USEPA)
SIE	Selective Ion Electrode
SIM	Selected Ion Monitoring
SMO	Sample Management Office (aka Sample Receiving)
SOC	Semi-Volatile Organic Compounds
SOP	Standard Operating Procedure
SOQ	Statement of Qualifications
SOW	Statement of Work
SVOAs	Semi-Volatile Organic Analytes
SVOCs	Semi-Volatile Organic Compounds
SW-846	Test Methods for Evaluating Solid Waste, Physical/Chemical Methods
TNI	The NELAC Institute
TPH	Total Petroleum Hydrocarbons
TSCA	Toxic Substances Control Act
UST	Underground Storage Tank
UV	Ultraviolet Spectrophotometer
VOA	Volatile Organic Analyte
VOC	Volatile Organic Compounds
WP	Water Pollution
WS	Water Supply

Units	Definition
mg/kg	Milligrams per Kilogram
mg/L	Milligrams per Liter
mg/m3	Milligrams per Cubic Meter
ng/L	Nanograms per Liter
ppb	Parts Per Billion
ppbV	Parts Per Billion Volume
ppm	Parts Per Million
ppmV	Parts Per Million Volume
ug/L	Micrograms per Liter
ug/m3	Micrograms per Cubic Meter

APPENDIX B – Organization Charts and Key Personnel Qualifications



ALS Group USA, Corp.
2655 Park Center Drive, Suite A
Simi Valley, CA 93065
T +1 805 526 7161

HAYDEN AKERS

Project Manager
2019 - Present
Simi Valley Laboratory

Responsibilities include interfacing with clients to provide technical project management and customer service, including project scheduling, tracking and consulting to determine appropriate sampling and analytical protocols. Coordinates with the laboratory and administration to ensure that analyses are properly executed and meets the clients' needs.

PREVIOUS EXPERIENCE

Technician, 2018 – 2019
ALS Group USA, Corp.
Simi Valley, CA

Responsibilities included canister conditioning and preparation, fulfillment of media requests and shipping samples. Additional responsibilities included training within the department of flow controller and critical orifice calibration and checks.

Research Assistant for Unmanned Global Regulations, 2016
Embry-Riddle Aeronautical University
Prescott, AZ

Researched domestic and international regulations using database analysis to efficiently sort through large amounts of information, and analyzed compiled information for merit and relevance. Utilized Microsoft Word, Excel and PowerPoint to combine useful data into easily understood formats, and delivered findings to group of peers.

EDUCATION

Embry-Riddle Aeronautical University –
Prescott, AZ
BS, Unmanned Aircraft Systems
2017

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Simi Valley, CA 93065
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SUSAN 'SUE' ANDERSON

Project Manager, 2011 – Present
Simi Valley Laboratory

Responsibilities include interfacing with clients to provide technical project management and customer service, including project scheduling, tracking and consulting to determine appropriate sampling and analytical protocols. Coordinates with the laboratory and administration to ensure that analyses are properly executed and meets the clients' needs.

PREVIOUS EXPERIENCE

Project Manager/General Chemistry Technical Manager
2006 – 2011
Columbia Analytical Services, Inc., Simi Valley, CA

Technical Manager responsibilities include training of general chemistry staff, maintenance of MDL studies and standard operating procedures, data evaluation and reporting. Project Manager responsibilities same as listed above.

Project Manager/General Chemistry Technical Manager
2002 – 2006
Project Manager II, 2000 – 2002
Columbia Analytical Services, Inc., Canoga Park, CA

In addition to the Project Manager duties listed above, also responsible for the management of General Chemistry laboratory operations, including the financial aspects. This includes supervision and coordination of work load and training personnel as necessary as well as supervision of method development and certification, maintenance of MDL studies and SOPs, data evaluation and report responsibility. Other duties include participation in the formulation of project strategy and meetings involving major technical issues, working with regional senior management in short and long-range planning, and other duties as assigned.

Scientist I-III, 1992 – 2000
Columbia Analytical Services, Inc., Canoga Park, CA

Responsible for performing inorganic analyses such as: alkalinity, ammonia, BOD, COD, cyanide, sulfide, reactivity, fluoride, pH, hardness, hexavalent chromium, phenols, surfactants, total-dissolved-suspended solid, conductivity, turbidity, nitrate, chloride by titration, turbidimetric sulfate, color, odor, organic lead, residual chlorine, settleable solids, specific gravity, carbon dioxide, TCLP/STLC metals and semi-volatile extraction. Also perform analyses for TRPH and oil and grease and occasionally perform metals digestion. Also ran the Graphite furnace for all furnace metals and was responsible for standard prep and maintenance.

Wet Chemistry, 1990 – 1991
National Environmental Testing, Bartlett, IL

Responsible for the analyses for wastewater parameters and some inorganic analytes.

EDUCATION

University of Illinois – Urbana-Champaign, IL
BS, Biochemistry
1989

ALS Group USA, Corp.
2655 Park Center Drive, Suite A
Simi Valley, CA 93065
T +1 805 526 7161

NICK NASH

Quality Assurance Manager, 2020 - Present
Simi Valley Laboratory

Responsibilities include facilitate ethics and QA training, maintain all training documentation, perform QA orientation for new employees, review data, schedule and perform internal QA audits and prepare written reports, review, approve, and control Standard Operating Procedures, maintain QA Manual, maintain QA records (including archived logbooks, archived certificates of analysis, nonconformity and corrective action reports, MDL studies results, SOP revision and distribution, statistical control limits, PE sample results), serve as document control officer and PC for all PE sample analyses, prepare corrective action report for any unacceptable PE sample results, maintain laboratory's certifications and approvals, facilitator for external QA audits and prepare written response to deficiencies, prepare activity reports to management.

PREVIOUS EXPERIENCE

Data Validation Coordinator, 2019 - 2020
ALS Environmental
Simi Valley, CA

Data validation responsibilities include data review and validation as well as data package compilation, job tracking, archiving and the production of laboratory reports. Interacts with project managers and Quality Assurance Manager to ensure that all reports fulfill client requirements as well as QA/QC needs. Also includes training and mentoring new data validation team members.

Quality Assurance Assistant, 2011-2012
ALS Environmental
Simi Valley, CA

Responsibilities same as listed below.

Quality Assurance Assistant, 2007-2011
Columbia Analytical Services, Inc.
Simi Valley, CA

Responsibilities included assisting with organizing QA training and compiling training documentation, perform certain internal QA systems audits and prepare written reports, organizing and filing QA records (including archived logbooks, archived certificates of analysis, nonconformity and corrective action reports, MDL studies results, SOP revision and distribution, statistical control limits, PE sample results), served as document control officer.

EDUCATION

California State University – Northridge, CA
BS, Systems & Operations Management
2019

College of the Canyons – Santa Clarita, CA
AS, Accounting
2018

College of the Canyons – Santa Clarita, CA
AS, Human Resources Management
2010

AFFILIATIONS

ASQ – American Society for Quality

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Simi Valley, CA 93065
T +1 805 526 7161

WADE HENTON

Laboratory Supervisor/Volatiles (GC) and Semi-Volatiles Technical Manager, 2016 - Present
Simi Valley Laboratory

Laboratory Supervisor responsibilities include planning, directing, and coordinating the operations of the laboratory departments. Duties and responsibilities include formulating policies, managing daily operations, and planning the use of materials and human resources. Reviews performance data to measure productivity and goal achievement and to determine areas needing cost reduction and program improvement to increase efficiency.

Volatiles (GC) and Semi-Volatiles Technical Manager responsibilities include oversight of training of analysts, peer review of analytical data, mentoring of junior analysts, standard operating procedure review, and streamlining methods. Duties also require performance

PREVIOUS EXPERIENCE

Media Preparation Team Leader, 2015 – 2016
Volatiles (GC) Team Leader, 2011 - 2016
ALS Group USA, Corp., Simi Valley, CA

Media Preparation Team Leader responsibilities include waste disposal, canister conditioning and preparation, fulfillment of media requests, shipping, flow controller and critical orifice calibration and calibration checks. Additional responsibilities include coordination of canister maintenance and release and cleaning of canisters for field sampling, training within the department, and sample media inventory. Responsibilities for Volatiles (GC) Team Leader same as Volatiles (GC) Technical Manager responsibilities listed above.

Volatiles (GC) Team Leader, 2000 – 2011
Columbia Analytical Services, Inc., Simi Valley, CA

Responsibilities same as Volatiles (GC) Technical Manager responsibilities listed above.

Scientist V, 1995 – 2000; Scientist IV, 1994 – 1995
Columbia Analytical Services, Inc. (dba Performance Analytical, Inc.)
Los Angeles, CA

Responsibilities include analyzing indoor and ambient air, source emission, and industrial hygiene samples by GC and GC/MS methods.

Analytical Chemist, 1992 – 1994
Coast-to-Coast Analytical Services, Camarillo, CA

Responsibilities included analyzing samples using EPA methods 625, 525 and 1625 as well as developing new methods for GC/MS testing.

Analytical Chemist, 1991 – 1992
Coast-to-Coast Analytical Services, Goleta, CA

Responsibilities included analyzing samples using EPA methods 624 and 524.2 by GC/MS. Used GC/MS methods to perform fuel fingerprinting.

Analytical Chemist, 1986 – 1991
Combustion Engineering Environmental, Camarillo, CA

Responsibilities included method development for GC and HPLC. Analysis of samples using EPA methods 608, 615, 631, 632 and SW846. Other methods used include 8080, 8010, 8020, 8150 and 8030. Oversaw data integrity for the GC Laboratory instrument data network. Data review.

Chemist, 1986
Fortin Industries, Sylmar, CA

R&D and QA/QC on polymer products and metal coatings using differential scanning calorimeters, scanning electron microscope, AA, GC, and HPLC.

EDUCATION

University of California Santa Barbara – Santa Barbara, CA
BS, Chemistry
1985

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ALS Group USA, Corp.
2655 Park Center Drive, Suite A
Simi Valley, CA 93065
T +1 805 526 7161

David M. Mirakian

Technical Services Manager December 2020 - Present
Simi Valley, CA

Technical Services Manager for the Volatiles Gas Chromatography Mass Spectrometry department. Overseas of training of chemists, peer review of analytical data, mentoring of junior analysts, standard operating procedure review and streamlining of methods. Duties also require performance reviews and development of direct reports.

PREVIOUS EXPERIENCE

Stationary Laboratory Manager 12/2017 - 12/2020
Jones Environmental Inc.
Santa Fe Springs, CA

- Led a team of analytical chemists to develop and implement a variety of extractions and analyses for EPA 8000 series and SW-84 schedule analyses targeting VOCs, SVOCs, PCBs, pesticides, and metals
- Trained chemists on detailed maintenance and care for GC-MS, FID, ECD, ICP-AES, and AA
- Produced SOPs compliant with EPA, DTSC, and OSHA guidelines

Screening Scientist 05/2014 - 02/2018
Psychemedics Corporation
Culver City, CA

- Manufactured and tested ELISA plates (luminescence and UV/Vis for drug metabolite testing
- Aided development of 6-drug 344 well ELISA plates, doubling daily lab throughput to 24,000 analyses
- Oversaw total chemiluminescent marijuana screening analyses

Graduate Researcher 09/2014 - 06/2016
CSULA Foster Research Group
Los Angeles, CA

- Developed high-throughput GC-MS and HPLC methods for PAH and SVOC analysis
- Developed accelerated solvent extraction methods for PAH extraction from various static media
- Created a proof-of-concept air quality testing method for application at the undergraduate laboratory level

EDUCATION

CSU - Los Angeles
Los Angeles, CA
MBA - Management
In Progress

CSU - Los Angeles
Los Angeles, CA
MS, Chemistry
2016

CSU - Los Angeles
Los Angeles, CA
BS, Biochemistry
2013

AWARDS & ACHIEVEMENTS

Special Recognition in graduate Studies, CSULA 2020
Special Recognition in graduate Studies, CSULA 2016

PUBLISHED WORK

Mirakian, D. M. Affordable and accessible methods for the detection of polycyclic aromatic hydrocarbons from static sources. M.S. Thesis, CSU Los Angeles, 2016. CSULA Digital Repository. http://hdl.handle.net/1021

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ALS Group USA, Corp.
2655 Park Center Drive, Suite A
Simi Valley, CA 93065
T +1 805 526 7161

RANDY GATES

Regional Manager, July 2019 – Present
ALS Group USA, Corp.

Responsible for six laboratories day to day management of the business units to achieve growth and profit in line with the budget and strategic plan. Responsible for all Occupational Safety and Health Administration, strategic planning, capital planning, and resources.

Laboratory Director, March 2020 – Present
Simi Valley Laboratory

Primary responsibilities include management of all laboratory departments, scheduling, productivity, reporting and evaluation of analytical methodologies, project planning, budgeting, and Quality Assurance/Quality Control protocol oversight. Other responsibilities include conducting facility compliance reviews; providing departmental support for equipment purchases; resolving personnel issues; determining resource allocation; and providing supervision, training, and leadership to key laboratory staff.

PREVIOUS EXPERIENCE

Laboratory Director, July 2018 – July 2019
Truesdail Laboratories, Inc.
Irvine, CA

Responsible for the day to day management of the business unit to achieve growth and profit in line with the budget and strategic plan. Responsible for all Occupational Safety and Health Administration, strategic planning, new employee inductions, and resources.

Chief Operations Officer, 2013 – 2018
Truesdail Laboratories, Inc.
Irvine, CA

Chair of the executive management group, which is accountable to CEO for the delivery of CEO's overall goals and objectives. Oversees the Department Management Team. Responsible for the maximization of the competitiveness, sustainability, and profitability of the business operations. Compiles and delivers the weekly operations status report to the Truesdail Board of Directors.

Controller, 2007 – 2013
Truesdail Laboratories, Inc.
Irvine, CA

Served as Manager of the Accounting and Human Resources Department. Responsibilities included Accounts Payable, Accounts Receivable, Payroll, Building Maintenance and Web Development. Prepared and presented the year-end financial reports to the Board of Directors. Responsible for the approval and processing of all new and terminated employees. Responsible for conducting Safety Orientations for all new hires. Designed and maintained an Emergency Action Plan.

EDUCATION

Western Governors University
BS, Accounting

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APPENDIX C – Ethics and Data Integrity Policy

ETHICS AND DATA INTEGRITY AGREEMENT

I state that I understand the high standards of integrity required of me with regard to the duties I perform and the data I report in connection with my employment at ALS.

I agree that in the performance of my duties at ALS:

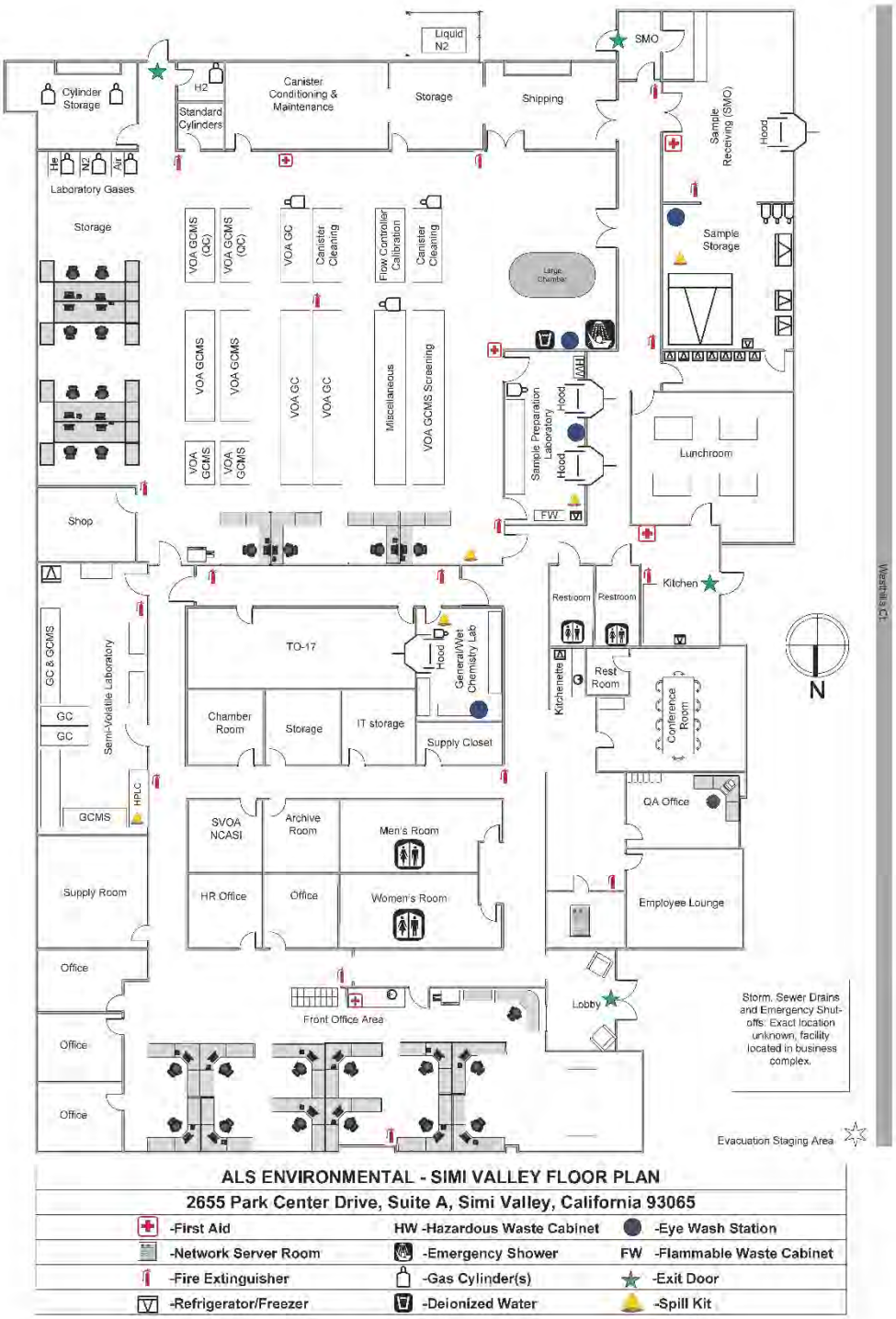
1. I shall not intentionally report data values that are not the actual values obtained;
2. I shall not intentionally report the dates, times and method citations of data analyses that are not the actual dates, times and method citations of analyses;
3. I shall not intentionally represent another individual's work as my own;
4. I shall not intentionally report data values that do not meet established quality control criteria as set forth in the Method and/or Standard Operating Procedures, or as defined by company policy.
5. I agree to inform ALS of any accidental or intentional reporting of non-authentic data by other employees.
6. I have read this ethics and data integrity agreement and understand that failure to comply with the conditions stated above will result in disciplinary action, up to and including termination.
7. I agree to adhere to the following protocols and principals of ethical conduct in my work at ALS. All work assigned to me will be performed using ALS approved methods and procedures and in compliance with the quality assurance protocols defined in the ALS Quality System.
8. I will not intentionally falsify nor improperly manipulate any sample or QC data in any manner. Furthermore, I will not modify data values unless the modification can be technically justified through a measurable analytical process or method acceptable to ALS. All such modifications and their justification will be clearly and thoroughly documented in the raw data and appropriate laboratory record, and will include my initials or signature and the date.
9. I will not make false statements to, or seek to otherwise deceive ALS staff, managers or clients. I will not knowingly, through acts of commission, omission, erasure or destruction, improperly report any test results or conclusions, be they for client samples, QC samples, or standards.
10. I will not condone any accidental or intentional reporting of unauthentic data by other ALS staff and will immediately report such occurrences to my Supervisor, Lab Director, Quality Assurance Manager, or Human Resources. I understand that failure to report such occurrences may subject me to immediate discipline, including termination.
11. If a supervisor, manager, director or other member of the ALS leadership group requests me to engage in or perform an activity that I feel is compromising data validity or defensibility, I have the right to not comply with the request. I also have the right to appeal this action through an ALS local Quality Staff, Corporate Quality Assurance or Human Resources.
12. I understand that if my job includes supervisory responsibilities, I will not instruct, request or direct any subordinate to perform any unethical or non-defensible laboratory practice. Nor will I discourage, intimidate or inhibit a staff member who may choose to appropriately appeal my supervisory instruction, request or directive that may be perceived to be improper, nor retaliate against those who do so.
13. I understand that employees who report violations of this policy will be kept free from intimidation and recrimination arising from such reporting.

I have read, and understand the above policy and realize that failure to adhere to it may result in disciplinary action, up to and including termination. Compliance with this policy will be strictly enforced with all personnel employed by the company.

Employee Name _____ Signature _____

ALS Location_____ Date _____

APPENDIX D – Laboratory Floor Plan



APPENDIX E – Analytical Equipment

Equipment Description - Gas Chromatography	Purchased / Acquired	Location
Screen 02: Hewlett-Packard 5890 with FID/ECD Detectors	-	VOA GC/MS Screen
Screen 03: Hewlett-Packard 5890 with FID Detector	-	VOA GC/MS Screen
GC01: Hewlett-Packard 5890 with FID/TCD Detectors *Fixed Gas Analyzer/Total Combustion Analyzer (TCA)*	1995	VOA GC
GC06: Hewlett-Packard 6890 with ECD/ECD Detectors *Hewlett-Packard 6890 Injector*	1995	SVOA
GC07: Hewlett-Packard 6890 with FID Detector	1995	VOA GC/MS Screen
GC08: Hewlett-Packard 5890 Series II with TCD/FID Detectors	1998	VOA GC
GC09: Hewlett-Packard 5890 Series II with FID Detector	1999	VOA GC/MS Screen
GC10: Hewlett-Packard 5890A with FID/TCD Detectors	1999	VOA GC
GC13: Agilent 6890A combined with Sievers 355 (SCD 1)	2001	VOA GC
GC14: Agilent 6890N with NPD/FID Detectors *Agilent 7683 Injector*	2005	SVOA
GC15: Agilent 6890N with NPD/FID Detectors *Agilent 7683 Injector*	2005	SVOA
GC16: Agilent 6890N with PFPD Detector and *OI Detector Controller* *Agilent 7683 Injector*	2005	SVOA
GC20: Agilent 7890A with FID/TCD Detectors	2008	VOA GC
GC21: Hewlett-Packard 5890 Series II with FID/ECD Detectors	2009	VOA GC
GC22: Agilent 7890A combined with Agilent 355 (SCD 3)	2009	VOA GC
GC23: Hewlett-Packard 6890+ with ECD Detector (combined with MS14)	2007	SVOA
GC30: Agilent 7890B combined with Agilent 355 (SCD 2)	2016	VOA GC
GC31: Hewlett-Packard 6890A with ECD Detector	1999	SVOA

Equipment Description - GC/MS Systems	Purchased / Acquired	Location
MS05: Agilent 6890/5973N MSD *Hewlett-Packard 7673 Injector*	1999	SVOA
MS07: HP 6890A/ Agilent 5973N MSD *Agilent 6890 Injector*	2001	SVOA
MS09: Agilent 6890N/5973inert MSD Tekmar AUTOCAN Autosampler	2005	VOA GC/MS
MS10: HP 6890A/5973 MSD	2006	SVOA
MS13: Agilent 6890N/5975B inert MSD Entech 7200 CTS Preconcentrator	2006	VOA GC/MS
MS14: HP 6890+ with ECD Detector (GC23) & HP 5973 MSD HP 7673 Injector	2007	SVOA
MS16: Agilent 6890N/5975C inert MSD Tekmar AUTOCAN Autosampler	2007	VOA GC/MS
MS18: Agilent 7890A /5975C inert XL MSD Markes TD 100-xr Autosampler	2010	VOA GC/MS
MS19: Agilent 7890A (GC26)/5975C inert XL MSD Tekmar AUTOCAN Autosampler	2011	VOA GC/MS
MS20: Agilent 7890A (GC27)/5975C inert XL MSD Markes TD 100-xr Autosampler	2011	VOA GC/MS
MS21: Agilent 7890A (GC28)/5975C inert XL MSD Entech 7200 / 7016D Autosampler	2012	VOA GC/MS
MS22: Agilent 7890B (GC29)/5977A MSD Markes Unity-xr Thermal Desorber Markes Kori-xr Water Condenser Markes Unity-CIA Advantage-xr	2015	VOA GC/MS
MS23: Agilent 7890B (GC32)/5977B MSD Markes TD 100-xr Autosampler	2017	VOA GC/MS
MS24: Agilent 7890A (GC33)/5975C Inert XL EI/CI MSD Markes TD 100-xr Autosampler	2018	VOA GC/MS
MS25: Agilent 7890B (GC34)/5977B MSD Entech 7200CTS 7016D Autosampler	2019	VOA GC/MS
MS26: Agilent 7890B (GC35)/5977B MSD Markes CIA Advantage Autosampler	2019	VOA GC/MS
Tube Conditioner 02: PerkinElmer TurboMatrix TC 220	2015	VOA GC/MS
Tube Conditioner 03: PerkinElmer TurboMatrix TC 220	2018	VOA GC/MS

Liquid Chromatography	**Purchased / Acquired**	**Location**
LC03: Agilent Infinity LC 1220	2011	SVOA
Spectrophotometer	**Purchased / Acquired**	**Location**
SPM01: Spectronic Instrument 20+ from SC	2001	GENCHEM
pH and Specific Ion Meters	**Purchased / Acquired**	**Location**
pH01: Thermo Orion 920 Selective Ion Meter	2001	GENCHEM
Miscellaneous Equipment	**Purchased / Acquired**	**Location**
US Filter Water Purification System	2006	Main Lab

Note: Purchase/Acquired year may represent when instrument was first maintained by ALS Environmental-Simi Valley or other in-network ALS Laboratory and does not reflect age of instrument.

Air sampling containers / Flow Controllers / Critical Orifices

Six-liter Summa passivated stainless steel canisters

- 1282 Ambient
- 1279 Source
- 202 Standard

Six-liter Silonite passivated stainless steel canisters

- 1260 Ambient
- 465 Source

Three-liter Silco passivated stainless steel canisters (67)

One-liter Summa passivated stainless steel canisters (1124)

One-liter Silonite passivated stainless steel canisters (1017)

Low volume flow controllers for time integrated sampling

- 1062 Ambient
- 108 Source

Low-flow flow controllers for multi-day sampling (48)

Critical orifices (550)

Critical orifices – Sulfur (50)

Automated Summa Canister Conditioning Units

- Twenty-four position, microprocessor controlled conditioners with heater controller, vacuum gauge, humidified nitrogen fill capability and large-capacity vacuum pump (2)
- Fourteen position, microprocessor controlled conditioners with heater controller, vacuum gauge, humidified nitrogen fill capability and large-capacity vacuum pump (1)
- Sixteen position, microprocessor controlled conditioner with heater controller, vacuum gauge, humidified nitrogen fill capability and large-capacity vacuum pump (1)
- Six position, microprocessor controlled conditioner with heater controller, vacuum gauge, humidified nitrogen fill capability and large-capacity vacuum pump (1)
- Twelve position, microprocessor controlled conditioner with heater controller, vacuum gauge, humidified nitrogen fill capability and large-capacity vacuum pump (2)
- Twenty-four position (Bottle Vac Cleaning Manifold), microprocessor controlled conditioners with heater controller, vacuum gauge, humidified nitrogen fill capability and large-capacity vacuum pump (2)

APPENDIX F – Containers, Preservation and Holding Times

Sample Preservation and Holding Times for Performed Methods

Determination (Method)	Matrix	Container	Preservation	Maximum Holding Time	Sample Vol.[c]
Amines (In-House Method)	Air	Treated Alumina Tubes	Sample Receipt-NA; Storage 4˚C±2˚C	30 days	100L
Ammonia (OSHA ID-188/ID-164)	Air	H_2SO_4 Treated Carbon Bead Tubes	Sample Receipt-NA; Storage 4˚C±2˚C	28 days	TWA: 24L STEL: 7.5L
BTU by ASTM D 3588 (SULFUR, ASTM D 5504; C1-C6+, EPA TO-3M; FIXED GASES, 3C)	Gaseous Fuels	Tedlar Bag Mylar Bag Summa Canister Bottle Vac	N/A	<u>Sulfur</u> Bag – 24 hours Canister – 7 days[b] Bottle Vac[a] – 7 days[b] <u>C1-C6+</u> Bag – 72 hours Canister[a] – 30 days[b] Bottle Vac[a] – 30 days[b] <u>3C</u> Bag – 72 hours Canister[a] – 30 days[b] Bottle Vac[a] – 30 days[b]	Bags 500mL Canisters and Bottle Vacs ≥1.0L
Carboxylic Acids (In-House Method)	Air	Treated Silica Gel Tubes	Sample Receipt-NA Storage 4˚C±2˚C	30 days until extraction; 14 days for analysis	100L
Total Gaseous Non-methane Organics (TGNMO) (EPA 25C)	Air	Tedlar Bag Mylar Bag Summa Canister Bottle Vac	N/A	Bag – 72 hours Canister[a] – 30 days[b] Bottle Vac[a] – 30 days[b]	Bags 500mL Canisters and Bottle Vacs ≥1.0L
Fixed Gases (EPA 3C & ASTM D 1946)	Air	Tedlar Bag Mylar Bag Summa Canister Bottle Vac	N/A	Bag – 72 hours Canister[a] – 30 days[b] Bottle Vac[a] – 30 days[b]	Bags 500mL Canisters and Bottle Vacs ≥1.0L
Helium & Hydrogen (EPA 3C Modified)	Air	Summa Canister Bottle Vac	N/A	Canister[a] – 30 days[b] Bottle Vac[a] – 30 days[b]	Bags 500mL Canisters and Bottle Vacs ≥1.0L
Methane, Ethane, Ethene, Propane, Propene (RSK 175)	Aqueous	Glass w/Teflon-Lined Lid	No Headspace HCl to pH<2 4˚C±2˚C	14 days when preserved	(3) 40mL Vials

Sample Preservation and Holding Times for Performed Methods

Determination (Method)	Matrix	Container	Preservation	Maximum Holding Time	Sample Vol.[c]
Carbon Dioxide (RSK 175)	Aqueous	Glass w/Teflon Lined Lid	No Headspace neutral pH (5-8) 4˚C±2˚C	N/A[d]	(3) 40mL Vials
Sulfur Compounds (In-House Method)	Aqueous	Glass w/Teflon Lined Lid	No Headspace; pH>4; 4˚C±2˚C	Following pH adjustment – 24 hours	(2) 40mL Vials
Sulfur Compounds (ASTM D 5504; SCAQMD 307-91; Modified SCAQMD 307-91)	Air	Tedlar Bag Fused Silica Lined Stainless Steel Canister Bottle Vac	No direct sunlight	Bag – 24 hours Canister – 7 days[b] Bottle Vac[a] – 7 days[b]	Bags 500mL Canisters and Bottle Vacs ≥1.0L
C_1-C_6+ (EPA TO-3 Modified)	Air	Tedlar Bag Mylar Bag Summa Canister Bottle Vac	N/A	Bag – 72 hours Canister[a] – 30 days[b] Bottle Vac[a] – 30 days[b]	Bags 500mL Canisters and Bottle Vacs ≥1.0L
Methanol, Ethanol, Isopropyl alcohol, Freon, and Methylene Chloride (EPA TO-3 Modified)	Air	Tedlar Bag Mylar Bag Summa Canister Bottle Vac	N/A	Bag – 72 hours Canister[a] – 30 days[b] Bottle Vac[a] – 30 days[b]	Bags 500mL Canisters and Bottle Vacs ≥1.0L
Total Petroleum Hydrocarbons (TPHG) (EPA TO-3 Modified)	Air	Tedlar Bag Mylar Bag Summa Canister Bottle Vac	N/A	Bag – 72 hours Canister[a] – 30 days[b] Bottle Vac[a] – 30 days[b]	Bags 500mL Canisters and Bottle Vacs ≥1.0L
Formaldehyde & Other Carbonyl Compounds (EPA TO-11A)	Air	DNPH-Coated Silica Gel Cartridge w/ Polypropylene Cap; SKC UME[x] and Bacharach GMD 570 Passive Monitors (formaldehyde only)	Sample Receipt, 4˚C±2˚C; Laboratory Preservation, 4˚C±2	14 days until extraction; 30 days for analysis	100 – 150L
Volatile Organic Compounds (EPA TO-14A & TO-15)	Air	Tedlar Bag, Summa Canister (1L, 6L) Bottle Vac	N/A	Bag – 72 hours Canister – 30 days Bottle Vac[a] – 30 days[b]	Bags 500mL Canisters 1.0L/6.0 Bottle Vacs 1.0L

Sample Preservation and Holding Times for Performed Methods

Determination (Method)	Matrix	Container	Preservation	Maximum Holding Time	Sample Vol.[c]
Volatile Organic Compounds (EPA TO-17)	Air	Sorbent Tubes w/Swagelock Caps & PTFE Ferrules	<4˚C; organic solvent free environment; Laboratory Storage, 4˚C±2˚C	30 days	1-4L
Volatile Organic Compounds (EPA 325B)	Air	Sorbent Tubes w/Swagelock Caps & PTFE Ferrules	Laboratory Storage <23˚C	30 days	1-4L
Air-Phase Petroleum Hydrocarbons (MADEP APH)	Air	Summa Canister Bottle Vac	N/A	28 days Bottle Vac[a] – 30days[b]	Canisters 1.0L/6.0 Bottle Vacs 1.0L
Butyl Cellosolve (2-butoxyethanol) (NIOSH 1403)	Air	Charcoal Tube	Sample Receipt-NA; Store sample and extract ≤4˚C	14 days until desorption; 30 days for analysis	Project Specific
Orthorhombic Cyclooctasulfur (ASTM C471M-14)	Solid Wallboard	Ziploc Bag	Sample Receipt-NA; Storage 4˚C±2˚C; Extract -10˚C to -20˚C	Extracts – 40 days for analysis	2"x2"
Siloxanes (In-House Method)	Air	SPE Cartidges Tedlar Bags	N/A	14 days until extraction; Tedlar Bags – transfer onto sorbent tube within 72 hours. 30 days for analysis	30L Cartridges Bags 500ml

Footnotes:

a.	Some methods do not specify the utilization of canisters; therefore, there is no required hold time and this will be noted in the case narrative.
b.	Laboratory recommended hold time; therefore, samples analyzed outside this hold time will be noted in the case narrative accordingly.
c.	Sample volumes are the minimum, which should be received by the laboratory; however, canister volumes should match the canister size utilized.
d.	There is no holding time requirement available and laboratory studies are not available indicating the validity of data prior to or following a specified length of time. Therefore, no holding time notation or qualifier will be adhered to results.

APPENDIX G – Standard Operating Procedures

Corporate SOP Titles	SOP ID
Laboratory Ethics and Data Integrity	CE-GEN001

Local Administrative SOP Titles	SOP Code
Data and Record Archiving	ADM-ARC
Internal Audits	ADM-AUDIT
Batches and Sequences	ADM-BATCH_SEQ
Control Limits	ADM-CNTRL_LMT
Handling Consumable Materials	ADM-CONSUM
Handling Customer Feedback	ADM-CUST_FDBK
Electronic Data Backup, Archiving, and Restoration	ADM-DATA_BU
Making Entries Onto Analytical Records	ADM-DATA_ENTRY
Data Recall	ADM-DATA_RECALL
Data Review and Reporting	ADM-DATA_REV
Document Control	ADM-DOC_CNTRL
Glassware Cleaning	ADM-GLASS
Analytical Instrument Acquisition, Reassignment, Maintenance and Documentation	ADM-INSTRUM
Laboratory Storage, Analysis, and Tracking	ADM-LABSAT
Policy for the use of Accreditation Organization Names, Symbols, and Logos	ADM-LOGOS
Manual Integration	ADM-MAN_INT
Management of Change	ADM-MGMT_CHG
Laboratory Management Review	ADM-MGMT_REV
Media Request Fulfillment	ADM-MEDIA_REQ
Method Development	ADM-METH_DEV
Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation	ADM-MDL_LOD_LOQ
Nonconformance and Corrective Action	ADM-NCAR
Preventive Action	ADM-PREV_ACT
Proficiency Testing	ADM-PT
Project Management	ADM-PMGMT

Procurement and Control of Laboratory Services and Supplies	ADM-PROC
ALS Environmental Induction Training for Quality Assurance	ADM-QA_ORIEN
Software and Data Quality Assurance	ADM-SFTWREQA
Significant Figures	ADM-SIG_FIG
Qualification of Subcontract Laboratories and Inter-Company Subcontracting Protocol	ADM-SUB_LABS
Establishing Standard Operating Procedures	ADM-SOP
Calibration and Use of Laboratory Support Equipment	ADM-SUPEQ
Training Policy	ADM-TRNG
Estimation of Uncertainty of Analytical Measurements	ADM-UNCERT
Cleaning and Certification of Summa Canisters and Other Specially Prepared Canisters	SMO-CAN_CERT
Evaluation and Pressurization of Specially Prepared Stainless Steel Canisters	SMO-CAN_PRESS
Flow Controllers and Critical Orifices	SMO-FLOW_CNTRL
Sample Receiving, Acceptance and Log-In	SMO-SMPL_REC

Volatile SOP Titles	SOP Code
Calculating Heat Value, Compressibility Factor, and Relative Density of Gaseous Fuels in Accordance with ASTM D 3588	VOA-BTU
Samples Preparation in Glass Chambers	VOA-CHAMBER
Dissolved Gas Analysis in Aqueous Samples Using a GC Headspace Equilibration Technique	VOA-DISGAS
Sample Preparation of Drywall for Sulfur Analysis and the Determination of Copper Corrosion	VOA-DRYWALL
Determination of Total Gaseous Nonmethane Organic (TGNMO) Emissions as Carbon in Landfill Gases in Accordance with EPA Method 25C	VOA-EPA25C
Determination of Methane, Carbon Monoxide, Carbon Dioxide, and Total Gaseous Nonmethane Organic (TGNMO) Emissions as Carbon in Landfill Gases According to Modified EPA Method 25C	VOA-EPA25CM
Determination of Hydrogen, Carbon Monoxide, Carbon Dioxide, Nitrogen, Methane, and Oxygen using Gas Chromatography with Thermal Conductivity Detection (TCD) in Accordance with EPA 3C or ASTM D 1946	VOA-EPA3C
Determination of Volatile Organic Compounds from Fugitive and Area Sources	VOA-EPA325B
Analysis of Hydrogen and Helium using Gas Chromatography with Thermal Conductivity Detection (TCD)	VOA-HHe

Analysis of Sulfur Compounds in a Gaseous Matrix by Gas Chromatography with Sulfur Chemiluminescence Detection per ASTM D 5504 and Modified SCAQMD Method 307	VOA-S307M_SCD
Analysis of Sulfur Compounds in Liquid Samples by Gas Chromatography with Sulfur Chemiluminescence Detection	VOA-SH_2O_SCD
Analysis of C1-C6+ using Gas Chromatography with Flame Ionization Detection (FID) in Accordance with a Modification of EPA Compendium Method TO-3	VOA-TO3C1C6
Analysis of Various Compounds using Gas Chromatography with Flame Ionization Detection (FID) in Accordance with a Modification of EPA Compendium Method TO-3	VOA-TO3MeOH
Analysis of Total Petroleum Hydrocarbons as Gasoline in Air by Gas Chromatography with Flame Ionization Detection	VOA-TPHG_TO3
Determination of Air-Phase Petroleum Hydrocarbons by Gas Chromatography/Mass Spectrometry (GC/MS)	VOA-MAPH
Determination of Volatile Organic Compounds in Air Samples Collected in Specially Prepared Canisters and Gas Collection Bags and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)	VOA-TO15
Determination of Volatile Organic Compounds in Ambient Air Using Active or Passive Sampling Onto Sorbent Tubes	VOA-TO17

Semi-Volatile SOP Titles	SOP Code
Determination of Formaldehyde and Other Carbonyl Compounds in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) EPA Compendium Method T0-11A	SVO-11A
Determination of Volatile Amines in Ambient Air Using Gas Chromatography Equipped with a Nitrogen Phosphorus Detector (NPD)	SVO-AMINES
Determination of Carboxylic Acids in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS)	SVO-CACIDS
Preparation and Analysis of 2-Butoxyethanol on Coconut Shell Charcoal Tubes and Analyzed using GC/FID	SVO-NIOSH1403
Determination of P-9290 Target Compounds from a Chamber and Specific P-9290 Quality Control Parameters	SVO-P9290
Preparation and Analysis of Orthorhombic Cyclooctasulfur by Gas Chromatography/Electron Capture Detector (GC/ECD)	SVO-S8_ECD
Determination of Siloxanes in Biogas using Gas Chromatography/Mass Spectrometry (GC/MS)	SVO-SILOXANES

General Chemistry (WET) SOP Titles	SOP Code
Ammonia in Air by Ion Selective Electrode	WET-NH_3Air

APPENDIX H – Data Qualifiers

CODE	CATEGORY	DESCRIPTION
BC	RESULT	Reported results are not blank corrected.
BH	RESULT	Results indicate breakthrough; back section of tube greater than front section.
BT	RESULT	Results indicated possible breakthrough; back section ≥10% front section.
DE	RESULT	Reported results are corrected for desorption efficiency.
RA	RESULT	Result not available.
G	GENERAL	Improper container.
G1	GENERAL	Unpreserved or improperly preserved sample.
X	GENERAL	See case narrative.
H1	HOLD TIME	Sample analysis performed past holding time. See case narrative.
H2	HOLD TIME	Initial analysis within holding time. Reanalysis for the required dilution was past holding time.
H3	HOLD TIME	Sample was received and analyzed past holding time.
H4	HOLD TIME	Sample was extracted past required extraction holding time, but analyzed within analysis holding time. See case narrative.
i	MATRIX	The MDL/MRL has been elevated due to matrix interference.
M	MATRIX	Matrix interference; results may be biased (high/low).
M1	MATRIX	Matrix interference due to coelution with a non-target compound. (TO-15 only)
Q	PETROLEUM	The chromatographic fingerprint of the sample resembles a petroleum product, but the elution pattern indicates the presence of a greater amount of lighter/heavier molecular weight constituents than the calibration standard.
Y	PETROLEUM	The chromatogram resembles a petroleum product but does not match the calibration standard.
Z	PETROLEUM	The chromatogram does not resemble a petroleum product.
#	QC	The control limit criterion is not applicable. See case narrative.
*	QC	The result is an outlier. See case narrative.
B	QC	Analyte detected in both the sample and associated method blank.
I	QC	Internal standard not within the specified limits. See case narrative.
L	QC	Laboratory control sample recovery outside the specified limits; results may be biased (high/low).
N	QC	The matrix spike sample recovery is not within control limits. See case narrative.
R	QC	Duplicate precision not met.

CODE	CATEGORY	DESCRIPTION
R1	QC	Duplicate precision not within the specified limits; however, the results are below the MRL and considered estimated.
S	QC	Surrogate recovery not within specified limits.
V	QC	The continuing calibration verification standard was outside (biased high/low) the specified limits for this compound.
C	RESULT	Result identification confirmed.
CE	RESULT	Co-elution.
D	RESULT	The reported result is from a dilution.
E	RESULT	Estimated; concentration exceeded calibration range.
J	RESULT	The result is an estimated concentration that is less than the MRL but greater than or equal to the MDL.
J1	RESULT	The analyte was positively identified below the method reporting limit prior to utilizing the dilution factor; the associated numerical value is considered estimated.
K	RESULT	Analyte was detected above the method reporting limit prior to normalization.
ND	RESULT	Compound was analyzed for, but not detected above the laboratory reporting/detection limit.
P	RESULT	The confirmation criterion was exceeded. The relative percent difference was greater than 40/25% between the two analytical results.
U	RESULT	Compound was analyzed for, but not detected (ND) at or above the MRL/MDL.
W	RESULT	Result quantified, but the corresponding peak was detected outside the generated retention time window.
UJ	RESULT	The analyte was not detected; however, the result is estimated due to discrepancies in meeting certain analyte-specific quality control criteria.
Ui	RESULT	The compound was analyzed for, but was not detected ("Non-detect") at or above the MRL/MDL; however, the MRL/MDL has been elevated due to matrix interference.
T	TIC	Analyte is a tentatively identified compound, result is estimated.

APPENDIX I – Master List of Controlled Documents

Controlled Documents*	Document Code
Health and Safety Manual	ALS-SIMI VALLEY
Lab Waste Management Plan	SV-HSE-001
Emergency Response Plan	SV-HSE-002
Disaster Management Plan	SV-HSE-003
Quality Assurance Manual	ALSMV-QAM

*Refer to Appendix G for a list of the laboratory's controlled standard operating procedures.

QA Program Files	
Item	**Location / Name**
Approved Signatories List	QA Manual Appendix I
Approved Subcontract Laboratories	Q:\Approved Sub-Contract Labs\Subcontract Lab List
Control Limit\Chart Status	Q:\Control Charts\CntrlChrt(status1).xls
Job Descriptions	HR Department
Master List of Controlled Documents (Logbooks, SOPs, etc.)	Q:\Master List of Controlled Documents\Master List of Controlled Documents.xls
MDL,LOD,LOQ Status	Q:\MDL Status\MDL Status Table (EACH DEPT).xls
Personnel Resumes, Transcripts	HR and QA Departments
Simi Valley Certification Status	Q:\Certifications\Cert Status.xls
Simi Valley Data Quality Objectives	Q:\MDL_MRL\DQO Spreadsheet.xls
Technical Training Status	Q:\Training\TRAINING STATUS.xls

Approved Signatories	
Name	**Title**
Randy Gates, B.S.	Laboratory Director
David Mirakian, B.S., M.S.	Technical Manager (Volatiles GC/MS) / Environmental Health and Safety Coordinator
Nick Nash, A.S, B.S.	Quality Assurance Manager
Wade Henton, B.S.	Volatiles (GC)/Semi-Volatiles Technical Manager
Wida Ang, B.S., M.S.	Team Leader (Volatiles GC/MS)
Sue Anderson, B.S.	Project Manager
Hayden Akers, B.S.	Project Manager

APPENDIX J – Laboratory Accreditations

State of Alaska Department of Environmental Conservation's Contaminated Sites Laboratory Approval Program (CS-LAP)

Approval No. 17-019
Approved Method(s):

- EPA TO-15
- EPA TO-17

State of Arizona, Department of Health Services

License No. AZ0694
Approved Method(s):

- EPA TO-15
- EPA 3C

Department of Defense, Environmental Laboratory Accreditation Program (DoD-ELAP)

Perry Johnson Laboratory Accreditation, Inc. Accreditation No. 65818
Approved Method(s):

- EPA TO-15
- EPA TO-17
- RSK 175
- EPA 3C
- ASTM D 1946-90
- SOP VOA-EPA3C (EPA 3C Modified)
- SOP VOA-TPHG_TO3 (TPHG by Modified EPA TO-3)
- SOP VOA-TO3C1C6 (Hydrocarbons and ranges by Modified EPA TO-3)
- SOP VOA-TO15 (EPA TO-15 Modified)
- SOP VOA-TO17 (EPA TO-17 Modified)

State of Florida, Department of Health (NELAP-Secondary)

Laboratory ID No.: E871020
Approved Method(s):

- EPA TO-15
- EPA TO-17

State of Louisiana, Department of Environmental Quality (NELAP-Secondary)

Certificate No.: 05071
Approved Method(s):

- EPA TO-15
- EPA 325B

State of Maine, Department of Health and Human Services

Certificate No.: 2016036

Approved Methods

- EPA TO-15
- MADEP APH

State of Minnesota, Department of Health, Environmental Laboratory Certification Program (NELAP-Secondary)

Laboratory ID: 006-999-456

Approved Method(s):

- EPA TO-15

Off-gas testing and gas sampling and analysis in support of U.S. Navy Deep Submergence Systems

SOPs:

- SMO-Can_Cert
- SMO-Can_Press
- SMO-Flow_Cntrl
- SMO-Smpl_Rec
- SVO-11A
- SVO-NIOSH1403
- SVO-P9290
- VOA-EPA25CM
- VOA-TO15

Gas analysis in support of U.S. Navy Lithium Battery Testing

SOPs:

- SMO-SMPL_REC
- VOA-S307M_SCD
- WET-NH3Air
- SVO-11A
- SVO-Acids
- SVO-Siloxanes
- SVO-Amines
- VOA-EPA3C
- VOA-TO3C1C6
- SVO-P9290
- VOA-EPA25CM
- VOA-TO15

State of New Jersey, Department of Environmental Protection (NELAP-Secondary)

Laboratory ID: CA009

Approved Method(s):

- EPA TO-15

State of New York, Department of Health (NELAP –Secondary)
Laboratory ID No. 11221
Approved Method(s):
- EPA TO-15
- EPA TO-17

State of Oregon, Environmental Laboratory Accreditation Program (NELAP-Primary)
Laboratory ID: 4068
Approved Method(s):

- ASTM C471M-14
- ASTM D5504-12
- EPA 325B 2013
- EPA RSK-175
- EPA TO-15
- EPA TO-17
- MADEP APH

Commonwealth of Pennsylvania, Department of Environmental Protection Bureau of Laboratories
Registration Number: 68-03307

State of Texas, Texas Commission on Environmental Quality (NELAP-Secondary)
Certificate # T104704413-19-10
Approved Method(s):
- EPA TO-15

State of Utah, Department of Health, Environmental Laboratory Certification Program (NELAP-Secondary)
Certificate # CA016272019-10
Approved Method(s):
- EPA TO-15

State of Washington, Department of Ecology
Laboratory ID: C946
Approved Method(s):
- EPA TO-15
- EPA RSK-175
- EPA 25CM

Note 1: This Quality Assurance Manual is revised annually with DoD-ELAP and NELAP-Primary Certificates, and the Scope of Accreditations/Parameters are revised annually (where necessary). During this interim period Certificates may expire and the Scope of Accreditations/Parameters may change; therefore, these may not be updated until the next revision.

Note 2: Current Certificates and Scope of Accreditations/Parameters are on file and displayed in the front hallway. Updated or Specific Certificates and Scope of Accreditations/Parameters are available upon request.

PERRY JOHNSON LABORATORY ACCREDITATION, INC.

Certificate of Accreditation

Perry Johnson Laboratory Accreditation, Inc. has assessed the Laboratory of:

ALS Environmental
2655 Park Center Drive, Suite A, Simi Valley, CA 93065

(Hereinafter called the Organization) and hereby declares that Organization has met the requirements of ISO/IEC 17025:2017 "General Requirements for the competence of Testing and Calibration Laboratories" and the DoD Quality Systems Manual for Environmental Laboratories Version 5.3 January 2017 and is accredited is accordance with the:

United States Department of Defense
Environmental Laboratory Accreditation Program
(DoD-ELAP)

This accreditation demonstrates technical competence for a defined scope and the operation of a laboratory quality management system (as outlined by the joint ISO-ILAC-IAF Communiqué dated April 2017):

This accreditation demonstrates technical competence for the defined scope:
Environmental Testing
(As detailed in the supplement)

Accreditation claims for such testing and/or calibration services shall only be made from addresses referenced within this certificate. This Accreditation is granted subject to the system rules governing the Accreditation referred to above, and the Organization hereby covenants with the Accreditation body's duty to observe and comply with the said rules.

For PJLA:

Initial Accreditation Date:	*Issue Date:*	*Expiration Date:*
January 11, 2010	March 26, 2020	May 31, 2022

Accreditation No:	*Certificate No:*
65818	L20-149

Tracy Szerszen
President/Operations Manager

Perry Johnson Laboratory
Accreditation, Inc. (PJLA)
755 W. Big Beaver, Suite 1325
Troy, Michigan 48084

The validity of this certificate is maintained through ongoing assessments based on a continuous accreditation cycle. The validity of this certificate should be confirmed through the PJLA website: www.pjlabs.com

Page 1 of 6

Certificate of Accreditation: Supplement

ISO/IEC 17025:2017 and DoD-ELAP

ALS Environmental

2655 Park Center Drive, Suite A, Simi Valley, CA 93065
Contact Name: Chaney Arend Phone: 805-526-7161

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Air	ASTM D 1946-90, VOA-EPA3C	GC/TCD	Carbon Monoxide
Air	ASTM D 1946-90, VOA-EPA3C	GC/TCD	Hydrogen
Air	EPA 3C, ASTM D 1946-90, VOA-EPA3C	GC/TCD	Carbon Dioxide
Air	EPA 3C, ASTM D 1946-90, VOA-EPA3C	GC/TCD	Methane
Air	EPA 3C, ASTM D 1946-90, VOA-EPA3C	GC/TCD	Nitrogen
Air	EPA 3C, ASTM D 1946-90, VOA-EPA3C	GC/TCD	Oxygen
Air	EPA TO-15, VOA-TO15	GC/MS	1,2,3-Trimethylbenzene
Air	EPA TO-15, VOA-TO15	GC/MS	1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon 114)
Air	EPA TO-15, VOA-TO15	GC/MS	1-Butanol
Air	EPA TO-15, VOA-TO15	GC/MS	2-Butanone (MEK)
Air	EPA TO-15, VOA-TO15	GC/MS	2-Hexanone
Air	EPA TO-15, VOA-TO15	GC/MS	3-Ethyltoluene
Air	EPA TO-15, VOA-TO15	GC/MS	4-Ethyltoluene
Air	EPA TO-15, VOA-TO15	GC/MS	4-Methyl-2-Pentanone
Air	EPA TO-15, VOA-TO15	GC/MS	Acetonitrile
Air	EPA TO-15, VOA-TO15	GC/MS	Acrylonitrile
Air	EPA TO-15, VOA-TO15	GC/MS	Allyl Chloride
Air	EPA TO-15, VOA-TO15	GC/MS	alpha-Methylstyrene
Air	EPA TO-15, VOA-TO15	GC/MS	alpha-Pinene
Air	EPA TO-15, VOA-TO15	GC/MS	Benzyl Chloride
Air	EPA TO-15, VOA-TO15	GC/MS	Bromoform
Air	EPA TO-15, VOA-TO15	GC/MS	Carbon Disulfide
Air	EPA TO-15, VOA-TO15	GC/MS	Cumene
Air	EPA TO-15, VOA-TO15	GC/MS	Cyclohexane
Air	EPA TO-15, VOA-TO15	GC/MS	Cyclohexanone
Air	EPA TO-15, VOA-TO15	GC/MS	Diisopropyl Ether
Air	EPA TO-15, VOA-TO15	GC/MS	d-Limonene
Air	EPA TO-15, VOA-TO15	GC/MS	Ethanol
Air	EPA TO-15, VOA-TO15	GC/MS	Ethyl Acetate
Air	EPA TO-15, VOA-TO15	GC/MS	Ethyl tert-Butyl Ether
Air	EPA TO-15, VOA-TO15	GC/MS	Isooctane
Air	EPA TO-15, VOA-TO15	GC/MS	Isopropyl acetate
Air	EPA TO-15, VOA-TO15	GC/MS	Isopropyl Alcohol
Air	EPA TO-15, VOA-TO15	GC/MS	Methyl Methacrylate
Air	EPA TO-15, VOA-TO15	GC/MS	n-Butyl Acetate
Air	EPA TO-15, VOA-TO15	GC/MS	n-Butylbenzene

Issue: 03/2020 *This supplement is in conjunction with certificate #L20-149* *Page 2 of 6*

Certificate of Accreditation: Supplement

ISO/IEC 17025:2017 and DoD-ELAP

PJLA

ALS Environmental

2655 Park Center Drive, Suite A, Simi Valley, CA 93065
Contact Name: Chaney Arend Phone: 805-526-7161

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Air	EPA TO-15, VOA-TO15	GC/MS	n-Decane
Air	EPA TO-15, VOA-TO15	GC/MS	n-Dodecane
Air	EPA TO-15, VOA-TO15	GC/MS	n-Heptane
Air	EPA TO-15, VOA-TO15	GC/MS	n-Hexane
Air	EPA TO-15, VOA-TO15	GC/MS	n-Nonane
Air	EPA TO-15, VOA-TO15	GC/MS	sec-Butylbenzene
Air	EPA TO-15, VOA-TO15	GC/MS	tert-Amyl Methyl Ether
Air	EPA TO-15, VOA-TO15	GC/MS	tert-Butanol
Air	EPA TO-15, VOA-TO15	GC/MS	2-Ethyltoluene
Air	EPA TO-15, VOA-TO15	GC/MS	n-Octane
Air	EPA TO-15, VOA-TO15	GC/MS	n-Propylbenzene
Air	EPA TO-15, VOA-TO15	GC/MS	n-Undecane
Air	EPA TO-15, VOA-TO15	GC/MS	p-Isopropyltoluene
Air	EPA TO-15, VOA-TO15	GC/MS	Propene
Air	EPA TO-15, VOA-TO15	GC/MS	tert-Butylbenzene
Air	EPA TO-15, VOA-TO15	GC/MS	Tetrahydrofuran
Air	EPA TO-15, VOA-TO15	GC/MS	Vinyl Acetate
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	1,1,1-Trichloroethane
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	1,1,2,2-Tetrachloroethane
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	1,1,2-Trichloroethane
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	1,1-Dichloroethane
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	1,1-Dichloroethene
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	1,2,4-Trichlorobenzene
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	1,2,4-Trimethylbenzene
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	1,2,Dibromo-3-Chloropropane
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	1,2-Dibromoethane
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	1,2-Dichlorobenzene
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	1,2-Dichloroethane
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	1,2-Dichloropropane
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	1,3,5-Trimethylbenzene
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	1,3-Butadiene
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	1,3-Dichlorobenzene
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	1,4-Dichlorobenzene
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	1,4-Dioxane
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	Acetone
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	Acrolein

Issue: 03/2020 *This supplement is in conjunction with certificate #L20-149* *Page 3 of 6*

Certificate of Accreditation: Supplement

ISO/IEC 17025:2017 and DoD-ELAP

ALS Environmental

2655 Park Center Drive, Suite A, Simi Valley, CA 93065
Contact Name: Chaney Arend Phone: 805-526-7161

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	Benzene
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	Bromodichloromethane
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	Bromomethane
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	Carbon Tetrachloride
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	Chlorobenzene
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	Chloroethane
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	Chloroform
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	Chloromethane
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	cis-1,2-Dichloroethene
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	cis-1,3-Dichloropropene
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	Dibromochloromethane
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	Dichlorodifluoromethane (CFC 12)
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	Ethylbenzene
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	Hexachlorobutadiene
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	m-&, p-Xylenes
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	Methyl tert-Butyl Ether
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	Methylene Chloride
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	Naphthalene
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	o-Xylene
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	Tetrachloroethene
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	trans-1,3-Dichloropropene
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	Trichlorotrifluoroethane
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	Vinyl Chloride
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	Styrene
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	Toluene
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	trans-1,2-Dichloroethene
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	Trichloroethene
Air	EPA TO-15, EPA TO-15SIM, VOA-TO15	GC/MS	Trichlorofluoromethane
Air	VOA-TO17/EPA TO-17	GC/MS	1,1,1-Trichloroethane
Air	VOA-TO17/EPA TO-17	GC/MS	1,1,2,2-Tetrachloroethane
Air	VOA-TO17/EPA TO-17	GC/MS	1,1,2-Trichloroethane
Air	VOA-TO17/EPA TO-17	GC/MS	1,1-Dichloroethane
Air	VOA-TO17/EPA TO-17	GC/MS	1,1-Dichloroethene
Air	VOA-TO17/EPA TO-17	GC/MS	1,2,4-Trichlorobenzene
Air	VOA-TO17/EPA TO-17	GC/MS	1,2,4-Trimethylbenzene
Air	VOA-TO17/EPA TO-17	GC/MS	1,2-Dibromo-3-chloropropane

Issue: 03/2020 *This supplement is in conjunction with certificate #L20-149* *Page 4 of 6*

Certificate of Accreditation: Supplement

ISO/IEC 17025:2017 and DoD-ELAP

ALS Environmental

2655 Park Center Drive, Suite A, Simi Valley, CA 93065
Contact Name: Chaney Arend Phone: 805-526-7161

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Air	VOA-TO17/EPA TO-17	GC/MS	1,2-Dibromoethane
Air	VOA-TO17/EPA TO-17	GC/MS	1,2-Dichloro-1,1,2,2-tetrafluoroethane (CFC 114)
Air	VOA-TO17/EPA TO-17	GC/MS	1,2-Dichlorobenzene
Air	VOA-TO17/EPA TO-17	GC/MS	1,2-Dichloroethane
Air	VOA-TO17/EPA TO-17	GC/MS	1,2-Dichloropropane
Air	VOA-TO17/EPA TO-17	GC/MS	1,3,5-Trimethylbenzene
Air	VOA-TO17/EPA TO-17	GC/MS	1,3-Butadiene
Air	VOA-TO17/EPA TO-17	GC/MS	1,3-Dichlorobenzene
Air	VOA-TO17/EPA TO-17	GC/MS	1,4-Dichlorobenzene
Air	VOA-TO17/EPA TO-17	GC/MS	1,4-Dioxane
Air	VOA-TO17/EPA TO-17	GC/MS	2,2,4-Trimethylpentane (Isooctane)
Air	VOA-TO17/EPA TO-17	GC/MS	2-Butanone (MEK)
Air	VOA-TO17/EPA TO-17	GC/MS	2-Hexanone
Air	VOA-TO17/EPA TO-17	GC/MS	2-Propanol (Isopropyl Alcohol)
Air	VOA-TO17/EPA TO-17	GC/MS	4-Methyl-2-pentanone
Air	VOA-TO17/EPA TO-17	GC/MS	Acetone
Air	VOA-TO17/EPA TO-17	GC/MS	Acetonitrile
Air	VOA-TO17/EPA TO-17	GC/MS	Benzene
Air	VOA-TO17/EPA TO-17	GC/MS	Bromodichloromethane
Air	VOA-TO17/EPA TO-17	GC/MS	Bromoform
Air	VOA-TO17/EPA TO-17	GC/MS	Carbon Disulfide
Air	VOA-TO17/EPA TO-17	GC/MS	Carbon Tetrachloride
Air	VOA-TO17/EPA TO-17	GC/MS	Chlorobenzene
Air	VOA-TO17/EPA TO-17	GC/MS	Chloroethane
Air	VOA-TO17/EPA TO-17	GC/MS	Chloroform
Air	VOA-TO17/EPA TO-17	GC/MS	Chloromethane
Air	VOA-TO17/EPA TO-17	GC/MS	cis-1,2-Dichloroethene
Air	VOA-TO17/EPA TO-17	GC/MS	cis-1,3-Dichloropropene
Air	VOA-TO17/EPA TO-17	GC/MS	Cumene
Air	VOA-TO17/EPA TO-17	GC/MS	Cyclohexane
Air	VOA-TO17/EPA TO-17	GC/MS	Dibromochloromethane
Air	VOA-TO17/EPA TO-17	GC/MS	Dichlorodifluoromethane (CFC 12)
Air	VOA-TO17/EPA TO-17	GC/MS	Ethanol
Air	VOA-TO17/EPA TO-17	GC/MS	Ethylbenzene
Air	VOA-TO17/EPA TO-17	GC/MS	Hexachlorobutadiene
Air	VOA-TO17/EPA TO-17	GC/MS	m,p-Xylenes

Issue: 03/2020 *This supplement is in conjunction with certificate #L20-149* *Page 5 of 6*

Certificate of Accreditation: Supplement

ISO/IEC 17025:2017 and DoD-ELAP

ALS Environmental

2655 Park Center Drive, Suite A, Simi Valley, CA 93065
Contact Name: Chaney Arend Phone: 805-526-7161

Accreditation is granted to the facility to perform the following testing:

Matrix	Standard/Method	Technology	Analyte
Air	VOA-TO17/EPA TO-17	GC/MS	Methyl tert-Butyl Ether
Air	VOA-TO17/EPA TO-17	GC/MS	Methylene Chloride
Air	VOA-TO17/EPA TO-17	GC/MS	Naphthalene
Air	VOA-TO17/EPA TO-17	GC/MS	n-Heptane
Air	VOA-TO17/EPA TO-17	GC/MS	n-Hexane
Air	VOA-TO17/EPA TO-17	GC/MS	n-Octane
Air	VOA-TO17/EPA TO-17	GC/MS	o-Xylene
Air	VOA-TO17/EPA TO-17	GC/MS	Styrene
Air	VOA-TO17/EPA TO-17	GC/MS	Tetrachloroethene
Air	VOA-TO17/EPA TO-17	GC/MS	Tetrahydrofuran (THF)
Air	VOA-TO17/EPA TO-17	GC/MS	Toluene
Air	VOA-TO17/EPA TO-17	GC/MS	trans-1,2-Dichloroethene
Air	VOA-TO17/EPA TO-17	GC/MS	trans-1,3-Dichloropropene
Air	VOA-TO17/EPA TO-17	GC/MS	Trichloroethene
Air	VOA-TO17/EPA TO-17	GC/MS	Trichlorofluoromethane
Air	VOA-TO17/EPA TO-17	GC/MS	Trichlorotrifluoroethane
Air	VOA-TO17/EPA TO-17	GC/MS	Vinyl Chloride
Air	VOA-TO3C1C6	GC/FID	C1 - C6+
Air	VOA-TO3C1C6	GC/FID	Ethane
Air	VOA-TO3C1C6	GC/FID	Methane
Air	VOA-TO3C1C6	GC/FID	n-Butane
Air	VOA-TO3C1C6	GC/FID	n-Hexane
Air	VOA-TO3C1C6	GC/FID	n-Pentane
Air	VOA-TO3C1C6	GC/FID	Propane
Air	VOA-TO3C1C6	GC/FID	Total Volatile Petroleum Hydrocarbons (TVPH) as Hexane
Air	VOA-TPHG_TO3	GC/FID	Total Petroleum Hydrocarbons Gasoline (TPHG)
Aqueous	RSK 175	GC/TCD	Carbon Dioxide
Aqueous	RSK 175	GC/FID	Ethane
Aqueous	RSK 175	GC/FID	Ethene
Aqueous	RSK 175	GC/FID	Methane

Issue: 03/2020 *This supplement is in conjunction with certificate #L20-149* *Page 6 of 6*

OREGON

Environmental Laboratory Accreditation Program

ORELAP Fields of Accreditation

ORELAP ID: 4068

ALS Environmental - Simi Valley

EPA CODE: CA01627

2655 Park Center Drive, Suite A

Certificate: 4068 - 007

Simi Valley, CA 93065

Issue Date: 2/16/2020 Expiration Date: 2/15/2021

As of 2/16/2020 this list supersedes all previous lists for this certificate number.

MATRIX	Reference	Code	Analyte	Code	Description
Air					
	ASTM C471M-14 (GC/MS or GC/ECD) ASTM C471M-14 (GC/MS or GC/ECD)			30002256	Gypsum and Gypsum Products
		3964	Orthorhombic Cyclooctasulfur		
	ASTM D5504-12 2012			30032270	Sulfur Compounds in Natural Gas and Gaseous Fuels by GC and Chemiluminescence
		4842	1-Propanethiol		
		6113	2,5-Dimethylthiophene		
		4544	2-Ethylthiophene		
		4843	2-Propanethiol		
		5783	3-Methylthiophene		
		4450	Carbon disulfide		
		7215	Carbonyl sulfide		
		6078	Diethyl Disulfide		
		6081	Diethyl Sulfide		
		4729	Dimethyl disulfide		
		6116	Dimethyl Sulfide		
		7506	Ethanethiol		
		3840	Hydrogen sulfide		
		3725	i-Butanethiol		
		7507	Methanethiol		
		7509	Methyl ethyl sulfide		
		9508	n-Butanethiol		
		9556	t-Butanethiol		
		9574	Tetrahydrothiophene		
		9578	Thiophene		
	EPA 325B 2013			10277437	Sorbent Tubes Coupled with Thermal Desorption and GC/MS
		4375	Benzene		
		4765	Ethylbenzene		
		5240	m+p-xylene		
		5250	o-Xylene		
		5140	Toluene		
	EPA TO-15			10248803	VOCs collected in Canisters by GC/MS
		5160	1,1,1-Trichloroethane		
		5110	1,1,2,2-Tetrachloroethane		
		5185	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)		
		5165	1,1,2-Trichloroethane		

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OREGON

Environmental Laboratory Accreditation Program

ORELAP Fields of Accreditation

ORELAP ID: 4068

ALS Environmental - Simi Valley

EPA CODE: CA01627

2655 Park Center Drive, Suite A

Certificate: 4068 - 007

Simi Valley, CA 93065

Issue Date: 2/16/2020 Expiration Date: 2/15/2021

As of 2/16/2020 this list supersedes all previous lists for this certificate number.

Air	EPA TO-15	4630	1,1-Dichloroethane
		4640	1,1-Dichloroethylene
		5182	1,2,3-Trimethylbenzene
		5155	1,2,4-Trichlorobenzene
		5210	1,2,4-Trimethylbenzene
		4570	1,2-Dibromo-3-chloropropane (DBCP)
		4585	1,2-Dibromoethane (EDB, Ethylene dibromide)
		4695	1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon-114)
		4610	1,2-Dichlorobenzene
		4635	1,2-Dichloroethane (Ethylene dichloride)
		4655	1,2-Dichloropropane
		5215	1,3,5-Trimethylbenzene
		9318	1,3-Butadiene
		4615	1,3-Dichlorobenzene
		4620	1,4-Dichlorobenzene
		4735	1,4-Dioxane (1,4- Diethyleneoxide)
		4836	1-Propene (Propylene)
		5220	2,2,4-Trimethylpentane
		4410	2-Butanone (Methyl ethyl ketone, MEK)
		4538	2-Ethyltoluene
		4860	2-Hexanone (MBK)
		4531	3-Ethyltoluene (1-Methyl-3-ethylbenzene)
		4542	4-Ethyltoluene
		4910	4-Isopropyltoluene (p-Cymene)
		4995	4-Methyl-2-pentanone (MIBK)
		4315	Acetone
		4320	Acetonitrile
		4325	Acrolein (Propenal)
		4340	Acrylonitrile
		4355	Allyl chloride (3-Chloropropene)
		4357	alpha-Methylstyrene
		6698	alpha-Pinene
		4375	Benzene
		5635	Benzyl chloride
		4385	Bromobenzene
		4395	Bromodichloromethane
		4400	Bromoform
		4403	Butyl acetate
		4450	Carbon disulfide
		4455	Carbon tetrachloride
		4475	Chlorobenzene

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Air	EPA TO-15	4575	Chlorodibromomethane
		4485	Chloroethane (Ethyl chloride)
		4505	Chloroform
		4645	cis-1,2-Dichloroethylene
		4680	cis-1,3-Dichloropropene
		4555	Cyclohexane
		4560	Cyclohexanone
		4625	Dichlorodifluoromethane (Freon-12)
		9375	Di-isopropylether (DIPE)
		6208	d-Limonene
		4750	Ethanol
		4755	Ethyl acetate
		4765	Ethylbenzene
		4770	Ethyl-t-butylether (ETBE) (2-Ethoxy-2-methylpropane)
		4835	Hexachlorobutadiene
		4890	Isopropyl acetate
		4895	Isopropyl alcohol (2-Propanol, Isopropanol)
		4900	Isopropylbenzene (Cumene)
		5240	m+p-xylene
		4950	Methyl bromide (Bromomethane)
		4960	Methyl chloride (Chloromethane)
		4990	Methyl methacrylate
		5000	Methyl tert-butyl ether (MTBE)
		4975	Methylene chloride (Dichloromethane)
		5005	Naphthalene
		4425	n-Butyl alcohol (1-Butanol, n-Butanol)
		4435	n-Butylbenzene
		5875	n-Decane
		6235	n-Dodecane
		4825	n-Heptane
		4855	n-Hexane
		5026	n-Nonane
		5027	n-Octane
		5090	n-Propylbenzene
		6747	n-Undecane
		5250	o-Xylene
		4440	sec-Butylbenzene
		5100	Styrene
		4370	T-amylmethylether (TAME)
		4420	tert-Butyl alcohol
		4445	tert-Butylbenzene
		5115	Tetrachloroethylene (Perchloroethylene)

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Air	EPA TO-15	5120	Tetrahydrofuran (THF)		
		5140	Toluene		
		4700	trans-1,2-Dichloroethylene		
		4685	trans-1,3-Dichloropropylene		
		5170	Trichloroethene (Trichloroethylene)		
		5175	Trichlorofluoromethane (Fluorotrichloromethane, Freon 11)		
		5225	Vinyl acetate		
		5235	Vinyl chloride		
		5260	Xylene (total)		
	EPA TO-17			10312206	Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes
		5160	1,1,1-Trichloroethane		
		5110	1,1,2,2-Tetrachloroethane		
		5185	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)		
		5165	1,1,2-Trichloroethane		
		4630	1,1-Dichloroethane		
		4640	1,1-Dichloroethylene		
		5155	1,2,4-Trichlorobenzene		
		5210	1,2,4-Trimethylbenzene		
		4570	1,2-Dibromo-3-chloropropane (DBCP)		
		4585	1,2-Dibromoethane (EDB, Ethylene dibromide)		
		4695	1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon-114)		
		4610	1,2-Dichlorobenzene		
		4635	1,2-Dichloroethane (Ethylene dichloride)		
		4655	1,2-Dichloropropane		
		5215	1,3,5-Trimethylbenzene		
		9318	1,3-Butadiene		
		4615	1,3-Dichlorobenzene		
		4620	1,4-Dichlorobenzene		
		4735	1,4-Dioxane (1,4- Diethyleneoxide)		
		5220	2,2,4-Trimethylpentane		
		4410	2-Butanone (Methyl ethyl ketone, MEK)		
		4860	2-Hexanone (MBK)		
		4995	4-Methyl-2-pentanone (MIBK)		
		4315	Acetone		
		4320	Acetonitrile		
		4375	Benzene		
		4395	Bromodichloromethane		
		4400	Bromoform		
		4450	Carbon disulfide		

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Air	EPA TO-17	4455	Carbon tetrachloride		
		4475	Chlorobenzene		
		4575	Chlorodibromomethane		
		4485	Chloroethane (Ethyl chloride)		
		4505	Chloroform		
		4645	cis-1,2-Dichloroethylene		
		4680	cis-1,3-Dichloropropene		
		4555	Cyclohexane		
		4625	Dichlorodifluoromethane (Freon-12)		
		4750	Ethanol		
		4765	Ethylbenzene		
		4835	Hexachlorobutadiene		
		4895	Isopropyl alcohol (2-Propanol, Isopropanol)		
		4900	Isopropylbenzene (Cumene)		
		5240	m+p-xylene		
		4960	Methyl chloride (Chloromethane)		
		5000	Methyl tert-butyl ether (MTBE)		
		4975	Methylene chloride (Dichloromethane)		
		5005	Naphthalene		
		4825	n-Heptane		
		4855	n-Hexane		
		5027	n-Octane		
		5250	o-Xylene		
		5100	Styrene		
		5115	Tetrachloroethylene (Perchloroethylene)		
		5120	Tetrahydrofuran (THF)		
		5140	Toluene		
		4700	trans-1,2-Dichloroethylene		
		4685	trans-1,3-Dichloropropylene		
		5170	Trichloroethene (Trichloroethylene)		
		5175	Trichlorofluoromethane (Fluorotrichloromethane, Freon 11)		
		5235	Vinyl chloride		
		5260	Xylene (total)		
	MADEP APH			90017188	Air-Phase Petroleum Hydrocarbons
		9318	1,3-Butadiene		
		3792	APH Aliphatics C5-C8		
		3793	APH Aliphatics C9-C12		
		3794	APH Aromatics C9-C10		
		4375	Benzene		
		4765	Ethylbenzene		
		5240	m+p-xylene		
		5000	Methyl tert-butyl ether (MTBE)		

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Air	MADEP APH	5005	Naphthalene		
		5250	o-Xylene		
		5140	Toluene		
Non-Potable Water	EPA RSK-175 (GC-FID)			10212905	Methane, Ethane, and Ethene in water by Headspace GC/FID
		4747	Ethane		
		4752	Ethene		
		4926	Methane		
	EPA RSK-175 (GC-TCD)			10212858	Fixed Gases in water by Headspace GC/TCD
		3755	Carbon dioxide		

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Air - Chain of Custody Record & Analytical Service Request

Page _____ of _____

2655 Park Center Drive, Suite A
Simi Valley, California 93065
Phone (805) 526-7161
Fax (805) 526-7270

Requested Turnaround Time in Business Days (Surcharges) please circle
1 Day (100%) 2 Day (75%) 3 Day (50%) 4 Day (35%) 5 Day (25%) 10 Day-Standard

ALS Project No.

ALS Contact:

Analysis Method

Company Name & Address (Reporting Information)

Project Name

Project Number

Project Manager

P.O. # / Billing Information

Phone

Fax

Email Address for Result Reporting

Sampler (Print & Sign)

Comments
e.g. Actual Preservative or specific instructions

Client Sample ID	Laboratory ID Number	Date Collected	Time Collected	Canister ID (Bar code # - AC, SC, etc.)	Flow Controller ID (Bar code #- FC #)	Canister Start Pressure "Hg	Canister End Pressure "Hg/psig	Sample Volume			

Report Tier Levels - please select

Tier I - Results (Default if not specified) _____
Tier II (Results + QC Summaries) _____
Tier III (Results + QC & Calibration Summaries) _____
Tier IV (Data Validation Package) 10% Surcharge _____

EDD required Yes / No
Type: _____ Units:_____

Chain of Custody Seal: (Circle)
INTACT BROKEN ABSENT

Project Requirements (MRLs, QAPP)

Relinquished by: (Signature)	Date:	Time:	Received by: (Signature)	Date:	Time:
Relinquished by: (Signature)	Date:	Time:	Received by: (Signature)	Date:	Time:

Cooler / Blank Temperature ____°C

Sample Receiving, Acceptance, and Login

DOCUMENT ID: SMO-SMPL_REC, REV 19

Approved By: _____ Date: 5/5/20
Technical Services Manager - Chris Parnell

Approved By: _____ Date: 5/5/2020
Quality Assurance Manager - Chaney Arend

Approved By: _____ Date: 5-5-20
Sample Management Custodian - Al David

Doc Control ID:	UNCONTROLLED	Archived Date:	_____

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1) Scope and Applicability

1.1 The purpose of this standard operating procedure (SOP) is to describe the requirements and guidelines necessary for effective sample receiving as well as the documentation associated with this process. Additionally, this document describes the procedures relating to the Sample Management Office for initiating any subcontract documentation.

1.2 This standard operating procedure (SOP) is applicable to all samples delivered to this laboratory and subcontracted out for analysis.

2) Summary of Procedure

2.1 For the purposes of this document sample receiving is considered to be an all-inclusive system, which comprises sample custody transfer, sample acceptance, and sample login.

2.2 This procedure is essential in identifying compromised samples and ensuring the validity of the laboratory's sample data. Improper sample handling affects the credibility and acceptability of analytical results, regardless of their accuracy and precision. Therefore, it is essential that all samples be properly received and handled and that the documentation maintained accurately reflects the integrity and processing of samples.

3) Definitions

3.1 Custody The guardianship or safe keeping of a sample. A sample is considered to be in a person's custody if it is physically in their possession, or it is in their view after being in their possession, or it was in their possession and then locked up or sealed to prevent tampering, or it is in a secure area.

3.2 Chain of Custody (COC) Record that documents the possession of the samples from the time of collection to receipt in the laboratory. This record generally includes the number and types of containers; the mode of collection; collector; time of collection; preservation; and requested analyses.

3.3 Internal Chain-of-Custody Procedures employed to record the possession of samples from the time of sample receipt until disposal/storage and are performed at the special request of the client. These protocols are handled electronically through LIMS.

3.4 Compromised Samples Those samples which are improperly sampled, insufficiently documented, improperly preserved, collected in improper containers, exceeding holding times and/or not received intact when delivered to a laboratory.

3.5 Holding Times (Maximum Allowable Holding Times) The maximum times that samples may be held prior to preparation and/or analysis and still be considered valid or not compromised. (40 CFR Part 136)

3.6 Preservation Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

3.7 Service Request (SR) / Job File A unique, computer generated laboratory number which is assigned to a sample or group of samples submitted (at the same time) by the client representing one job or project. The job or project includes specific sample management information, analysis data, client correspondence, analysis report and other pertinent information comprising a single sample submission containing one or more samples in a client's project.

3.8 COC Chain-of-Custody

3.9 SACF Sample Acceptance Check Form

3.10 LIMS Laboratory Information Management System

3.11 SMO Sample Management Office

3.12 PM Project Manager (may be referred to in other lab documents as PC/Project Chemist)

3.13 SMC Sample Management Custodian

3.14 SDG Sample Delivery Group

3.15 EDD Electronic Data Deliverable

4) Safety

4.1 Handle all samples as potentially hazardous. Gloves should be worn when handling all samples, safety glasses, and a lab coat shall be worn when handling liquid or soil (solid) samples. Always work under a hood when chemically preserving samples. Also place broken or leaking samples under the hood. Get assistance when confronted with any situation that appears to be dangerous.

4.2 In the event of broken liquid or soil samples, SMO needs to cleanup using one of the following procedures:

- Liquids: Broken glass is handled carefully using disposable gloves and disposed of in the Glass Disposal Box. Remaining sample and cleanup materials are disposed of in accordance with the *Simi Valley Lab Waste Management Plan*.
- Soils: Broken glass is disposed of in the Glass Disposal Box, and the soil is disposed of into the 55-gallon soil drum. This information is noted on the Service Request Form and the PM is notified. Soil that is still intact in a glass jar may be salvaged with client's approval.

5) Responsibilities

5.1 All employees involved with sample receiving, acceptance and login must ensure the procedures described in this document are followed. More specifically, SMO personnel, Project Managers and the Sample Management Custodian are responsible for complying with and implementing the procedures listed in this document.

6) Procedure

6.1 Upon sample receipt, the condition, including any abnormalities or departures from normal or specified conditions as described in the test method or method standard operating procedure must be recorded. All of the information including any other observances must be recorded on the Sample Acceptance Check Form (Attachment 2) and other associated documentation as detailed in the following procedures. Refer to Section 6.4 for the necessary procedures and documentation requirements dictated by abnormalities or departures.

Note: The P-9290 Sample Login Checklist included as Attachment 11 in the *SOP for Determination of P-9290 Target Compounds from a Chamber and Specific Quality Control Parameters* (SVO-P9290) must be initiated for samples received in support of the U.S. Navy Deep Submergence Systems program. This is an additional requirement and does not replace any of the requirements outlined in this SOP.

6.2 Sample Custody

Upon delivery to the laboratory, the sample(s) must be transferred (as soon as possible) to a Sample Management Custodian (SMC) or a representative of the laboratory who accepts and assumes custody of the sample(s). Samples are transported to the laboratory by a number of means including courier, common carrier, sampler or client representative. The acceptance of a sample is achieved by presenting a signature, date and time of receipt in accordance with the requirements of the transmitter and client such as an electronic board (i.e. FedEx) and Chain of Custody Form. Sample shipping containers are examined for the presence and condition of custody seals, locks, shipping waybills, etc. After opening shipping containers, remove any other documents in order to evaluate login priority (see note below) and continue processing the samples.

In the event of infectious pathogen concerns, commonly touched areas of a sample container may be disinfected or sanitized. The preferred method is with the use of a shortwave (254nm) UV light. This wavelength demonstrates highly effective disinfection from viruses and bacteria. The use of alcohol or bleach wipes may cause interference with the sample or sample container and are not recommended. Appropriate PPE is mandatory and includes nitrile gloves, UV-blocking face shield, and lab coat when working with UV light.

Note: Rush requests and samples with short holding times are given top priority for processing. Sample Custodian alerts Project Manager and analysts by calling them and distributing copies of the COC and any other pertinent documentation. Refer to Appendix F in the Quality Assurance Manual for Sample Preservation and Holding Times which list maximum allowable hold times.

6.2.1 Shipping Receipts and Chain of Custody (COC) Forms

6.2.1.1 Packing Slips

A copy of the packing slip must be kept, whenever possible, as part of the permanent chain of custody process and placed in the job file.

6.2.1.2 Chain of Custody Forms

These forms may be identical to the one issued by the laboratory (see Figures 11-1 and 11-2 in the Quality Assurance Manual) or clients may submit samples using a similar form. The SMC or designee shall sign the COC and add the date and time of receipt. In addition, the service request number must be added to the COC form at the time of sample login.

6.2.2 Legal/Internal Chain of Custody (COC)

When samples are logged in using LIMS, the system automatically generates an internal chain of custody each time a sample is scanned into possession for use within the laboratory. This internal COC may be accessed anytime during the laboratory procedures and is provided to the client upon request.

6.3 Sample Receipt and Login

In order to evaluate the state of a sample upon receipt, the laboratory must evaluate certain parameters including container type, volume and preservation (thermal and chemical). Compare the findings against the specified criteria in Sample Preservation and Holding Times Tables in the most recent Quality Assurance Manual (Appendix F). Refer to Section 6.4 for the discrepancy/exception and the rejection of samples procedures.

Important: For odorous samples, refer to Section 6.9 for the handling procedure.

6.3.1 Service Request Form

A Service Request form (Attachment 3) shall be completed in LIMS for all samples received by the laboratory using the information provided on the sample receipt documentation (e.g., COC) and data collected by the SMC. A copy of this completed form shall accompany the sample(s). The following includes a description of the key components.

1. Service Request Number: Client's job file number (automatically assigned)
2. Report Name: Name of Client that shall be on report.
3. Reporting Address: Address of the Client that will be on the report.
4. Project Name: Client's referenced study or project name.
5. Project Number: Client's reference study or project number.
6. ISR Number (if applicable): Internal Service Request (between laboratories in the network using the same LIMS system)
7. Date Received: Date the laboratory actually received samples.
8. Purchase Order: Client's purchase order number or verbal notation (default).
9. Project Manager: The PM responsible for all client activity for job file.
10. TAT: Sample turnaround time (normal TAT, if not specified).
11. Initials: Initials of SMC or alternate logging in the sample(s).
12. Sample Type: Type/container of sample submitted by client.
13. Comments: Any comments concerning the sample or samples being submitted including short hold times.
14. Tier: QC level if one is given on the ISR or COC.
15. EDD: If EDD is required or not.
16. Method: Specified method for the samples to be analyzed.
17. Sample ID: Client's specified sample identification.
18. Test(s) Required: Number of methods for analysis on the samples.
19. Date Collected: Sampling date for each sample.
20. Time Collected: Sampling time for each sample.
21. Sample Type: Sample matrix for each sample.

Note: Some of the information (client's project name or number) may not be provided and will not be included on the form.

6.3.2 LIMS Login

Prior to sample arrival, the Project Manager may create a sample delivery group (SDG) in LIMS based on project information and in accordance with the *SOP for Project Management*. Analysis information associated with each sample is stored in this SDG. When samples arrive, the custodian uses this SDG as a template to create a job folder specific to the samples received. The custodian could either manually

search SDG information from LIMS or find it by scanning the barcode of the bottle order form (also known as Bottle Order \ Sample Supplies Summary form).

Once the correct SDG has been selected, a sample template is chosen from the SDG template that best matches the analyses stated on the COC for each sample included on the COC. Once all the samples are chosen the custodian creates a unique job folder. Job folder is then edited as necessary (e.g., project name and number, date and time of sample collection, and client sample IDs).

Each sample container for a sample is given a unique lab code by the LIMS system. This lab code is express in the format of PYYJJJJJ-sss.ccc.

Where:

"P" is the current lab ID code for Simi Valley,
"YY" is the two-digit year code (e.g., 20 for Y2020),
"JJJJJ" is the five-digit job number (e.g., 00001 for the first project),
"sss" is a three-digit sample ID number;
"ccc" is the three-digit container ID number.

An example for the second container of the first sample for the first job of year for 2020 would be P2000001-001.002. The alphanumeric code before the dash is the job number, the number after the dash is sample ID and the number after the period is container ID.

6.3.3 Sample Acceptance Check Form The SMC shall complete and generate a Sample Acceptance Check form (Attachment 2) based on the information specified in this section. This form is given to the PM and electronically accessible so that Chemists may input additional preservation check information. Refer to the Note in Section 6.1 for additional requirement applicable to samples received in support of the U.S Navy Deep Submergence Systems program.

Once the samples have been checked and the SACF produced, the form is to be saved at G:\\STARLIMS\Sample Acceptance Check form (as SR#_Client_Project) so that additional information such as pH may be added.

6.3.3.1 Sample Acceptance Policy Sample containers are removed and organized according to the COC identification and analyses. The sample conditions are checked to ensure sample integrity has not been compromised. These steps are listed to complete the criteria for the acceptance or rejection of samples but they do not necessarily occur in this order. Each point is an evaluation requirement which must be used to complete the Sample Acceptance Check form.

- Sample submission documents are properly used, fully completed (in ink) and shall include the client, sample identification, project name or location, date and time of collection, collector's name, sample type, preservation type (if applicable) and any special remarks concerning the sample.
- Proper sample labeling is considered: unique sample identification (ID), durable labels (labels that are not easily removed) and the use of ink.
- Sample containers checked for integrity (broken, leaking, Tedlar® bags are received flat, under inflated or with the valve open, passivated stainless steel canisters are received under an

unacceptable vacuum or with the valve open, etc.). Reject samples with broken or leaking containers.

- Sample container labels and/or tags agree with the sample documentation (ID, required analyses, etc.).
- Adherence to specified holding times (see Appendix F in the Quality Assurance Manual)
- Appropriate containers (size, type) are received for the requested analyses (see Appendix F in the Quality Assurance Manual).
- Proper temperatures of sample containers, if applicable (see Appendix F in the Quality Assurance Manual).
- Adequate sample volume (see Appendix F in the Quality Assurance Manual)
- Assessment of proper sample preservation, where applicable (see Appendix F in the Quality Assurance Manual). Reject samples preserved with the inappropriate preservatives for which the requested analysis has been compromised (e.g., cyanide samples preserved with acid).
- Any notation made by other persons accepting the sample and any evaluations made and noted on the associated documentation.

Once the samples have been checked against the Sample Acceptance Policy, the sample custodian must generate a Sample Acceptance Check form, sample identification labels, and Service Request form (optional). The Project Manager is responsible for generating and emailing the Sample Receipt Acknowledgment form (Section 6.5) if requested. The sample login forms and labels must be completed to properly track laboratory samples.

6.3.3.2 Measurement of Temperature The temperature of all coolers containing samples requiring thermal preservation shall be taken using a verified thermometer calibrated against NIST standards and the data recorded (with correction factor applied) on the Sample Acceptance Check form (Attachment 2).

An infrared thermometer shall be used to take the temperature reading of samples. Alternatively, a reading shall be taken by placing the thermometer in the cooler so as to give an accurate reflection of the cooler temperature (i.e. not directly on ice or blue ice and at approximate sample level or in the temperature blank, if supplied). The lid must be closed to allow enough time for the thermometer to reach equilibrium (i.e., a minimum of five minutes) before the temperature reading is taken and recorded. The arrival temperature check is considered acceptable if the following is adhered to:

- Samples have a temperature of +/-2˚C of the required temperature or the method specified range; or
- Samples with a required temperature of 4˚C have a temperature ranging from just above freezing of water to 6˚C; or
- IMPORTANT: The US EPA has published revisions to the Code of Federal Regulations at 40 CFR 136 and 40 CFR 141. These revisions, known as the Method Update Rule (MUR), became effective 4/11/07 and contains a revised approved methods tables and temperature requirements. A number of the methods have been updated and for those methods the temperature requirement has been updated to

≤6˚C. Refer to Appendix F in the most recent Quality Assurance Manual for the specific methods that are affected.

Note: Samples that are hand delivered to the laboratory immediately following collection may not meet these criteria. This is considered acceptable if there is evidence that the chilling process has begun such as arrival on ice. Include a notation on the Sample Acceptance Check Form.

6.3.3.3 Chemical Preservation A pH measurement may be required on certain tests, the pH value shall be documented on the Sample Acceptance Check Form. Perform this check in accordance with the applicable method SOP and the *SOP for Laboratory Storage, Analysis, and Tracking.*

The pH of the sample shall be checked with a narrow ranged pH indicator strip (preferable). Take a small aliquot of the sample with a transfer pipette and place a few drops onto the pH indicator strip. Ensure that a new pipette is used for every sample container to prevent cross-contamination. Refer to Section 6.7 on specific information for subcontracted jobs.

6.3.3.4 Headspace Check for headspace in VOA vials. Pay close attention to samples that are opaque; bubbles may not be easily observed. Samples with heavy sediments may stick to the vial, making it appears to have no bubble when the vial is inverted. Any bubble in the sample should not exceed 5-6 mm.

6.3.3.5 Reusable media The pressure of each canister and glass bottle shall be checked and recorded to ensure the sample has the appropriate volume. Initial and final pressures are noted on the Service Request Form and on the back of the sample tag. Refer to the *SOP for Evaluation and Pressurization of Specially Prepared Stainless Steel Canisters* for additional details.

At the time of sample submission, ambient air sampling canisters will likely have a vacuum (negative pressure). If the canister has a negative pressure, the gauge will read in inches of Mercury (inHg) or pounds per square inch (psig) depending on the gauge used. If the reading is inHg, the value must be converted to psig (A conversion chart may be used and is located in the *SOP for Evaluation and Pressurization of Specially Prepared Stainless Steel Canisters* Attachment B). Vacuum readings entered in inHg to the system will be automatically converted to psig.

Returned canisters and glass bottles that are not samples are logged in and handled following the same procedures. Canisters received at an initial pressure *lower than* -9.8 psig (-20.0 inHg) are shelved on a canister rack outside SMO (P-102) for the canister department to clean. Canisters received that have an initial pressure *higher than* -9.8 psig (-20.0 inHg) are placed on a canister rack in SMO for screening before they are returned to the canister department for cleaning. This procedure must be performed in accordance with the *SOP for Evaluation and Pressurization of Specially Prepared Stainless Steel Canisters.*

Thermal desorption tubes that are not samples are logged in according to their bar code ID and the analysis is marked cancelled.

6.3.3.6 Sample Login Contingency Plan This section is designed to detail the sample custody and receipt procedure for samples that are delivered to the laboratory late in the day or when the SMC or designee is not present. If sample(s) are delivered under thermal preservation, laboratory personnel shall evaluate the cooler temperature per Section 6.3.3.2. The temperature must be noted on the COC form along with the date and initial of the person making the notation. Refer to the Quality Assurance Manual for information on preservation requirements, which are listed by method and sample type. The person, following acceptance, evaluation and analysis (if performed), should place the samples in the appropriate storage location in accordance with the *SOP for Laboratory Storage, Analysis, and Tracking* and submit the paper work to SMO in order for the login process to be completed.

6.3.3.7 Short Hold Times When samples are delivered to the laboratory with little remaining on the hold time it may be possible for the analysis to proceed prior to the login process. The following are circumstances where this is allowed.

- Tedlar bag samples only
- If there is no time for sample(s) evaluation and login prior to hold time expiration and an analyst is able to analyze the sample(s) immediately.

However, there are requirements that must be followed by the analyst(s) if the samples are to be analyzed prior to sample login.

- At a minimum, the analyst shall review/compare the chain of custody with the samples received to ensure that the sample identifications, etc. are correct.
- It is imperative that the client sample ID be referenced on all laboratory analytical documentation.
- Also, the analyst should check the integrity (i.e. leaking or flat Tedlar bag) of the samples and make any notations on the associated documentation.
- Additionally, once the samples have been analyzed they are to be immediately delivered back to SMO for the sample acceptance and login procedures detailed in this SOP.

6.3.3.8 Sample Identification Labels After samples have been logged into the computer and the lab ID assigned, the SMC shall print labels for each sample container received. Each computer-generated label is affixed to the appropriate sample container, where possible. Certain sample containers, such as solid absorbent cartridges, are placed in a sealed bag identified with the job number and all the laboratory ID codes associated with each sample in the bag.

6.3.3.9 Sample Login/Labeling Verification After labels have been applied to the corresponding sample containers they should be verified by a second person to ensure proper labeling. Place all associated documentation into the job file and submit to the Project Manager.

- Once the documentation has been generated and the labeling verification has been performed, the custodian must complete the first section of the LIMS Sample Login Verification Form (Attachment 4).
- The Project Manager responsible for the project verifies login information. This process is documented on the LIMS Sample Login Verification form. It is only after this secondary review that the job folder is released out of the login console to the job in progress area, making the analysis information available to the analysts.

Note: In instances where the Project Manager performs Sample Receipt and Login a second Project Manager must perform review of the login. The same employee may not both log in a sample and approve the login.

6.4 Discrepancy / Sample Rejection Procedures

Any discrepancies or concerns are noted on the Sample Acceptance Check Form (per Sample Acceptance Policy, see Section 6.3.3.1) and immediately communicated to the appropriate Project Manager. If and when there is any doubt as to the suitability of a sample to be tested such as a leaking valve, broken container, etc. the SMC shall inform the PM. Regardless of the discrepancy, the PM shall be responsible for coordinating all correspondences and consulting with the client for further instructions before the laboratory may proceed. However, when there are short holding time constraints, the laboratory may complete the sample analysis, where possible for all samples in the client's job file including the sample in question.

6.4.1 Chemical Preservation for Water and Soil Samples Contact the PM and if the PM approves adding preservative to bring sample within the proper range, be sure to record the specific sample container identifications, preservative added, including type, lot number(s), and final pH on the Sample Acceptance Check form (Attachment 2) (even if subcontracting). Refer to Section 6.7 for information on sub-contracting and splitting samples, where appropriate. When chemical preservation is performed in the laboratory the Preservative Tracking Log (Attachment 2, *SOP for Media Request Fulfillment*) must be utilized for documentation purposes.

6.4.2 Login Revisions Changes to SR forms may be made by anyone authorized for sample login and Project Management capabilities; however, it is recommended that whenever possible documentation of the reasons for the changes and the person making those corrections is documented and any copies of the original must be retained and marked as obsolete.

6.5 Sample Receipt Acknowledgment

An acknowledgment form (Attachment 5) may be accessed and emailed to the client, along with a PDF of any other requested documentation.

6.6 Job File and LIMS Documentation

The sample documentation shall be maintained in each client's job file in accordance with current procedures and shall at a minimum include:

- Original chain of custody form (if utilized) with the laboratory job number
- Service Request Form
- Sample Acceptance Check Form
- Sample Login Verification Checklist

- Any documentation including memos or transmittal forms, which are transmitted to the laboratory by the common carrier, courier, sampler, or client.
- Any internal documentation which is pertinent to the handling and/or analysis of the samples.

Note: The original and all copies and revised versions of documentation must be kept in the associated job file.

Once the samples have been received, accepted (or rejected) and logged into the laboratory system, a job file (referencing the corresponding service request number) must be created and all receipt, acceptance and login documentation included. The COC is to be scanned into a PDF and attached to the LIMS job file. The job file must be submitted to the appropriate Project Manager for approval. The job file will be kept in a designated area for the inclusion of all the remaining documentation for the project including analytical data, invoices, etc.

6.7 Sample Transfer between Laboratories

The following must be adhered to for all samples, extracts, digestates and split samples that are transferred, carried or shipped from one laboratory to another (between In-Network laboratories and to laboratories outside of the Network). Samples are generally prepared for shipping by packing bubble wrapped glass containers in a cooler filled with blue ice (or ice). Custody seals are signed and dated and placed on the front of the cooler. The cooler is then sealed with packaging tape.

Samples not analyzed at the laboratory are subcontracted to pre-approved laboratories (internal and or external). Samples are logged in for the required tests and assigned a subcontract lab (as assigned by the PM in the SDG, by flagging the team column of the folder with the appropriate sublab). A subcontract COC is printed from LIMS once the login has been completed. The subcontract COC is then placed in the job folder after a copy of document is made.

Note: If LIMS does not have the appropriate test or sub-contract laboratory code, a Request for Test Code or "Sublab" form is filled out and submitted to Kelso IT. In addition, if the sublab is not specified in the SDG, it will automatically be flagged and a subcontract lab must be selected. Contact the PM, if this occurs.

6.7.1 In-Network Sample Transfer This laboratory, when transferring samples to an In-Network laboratory, could either initiate a new chain of custody record or use a photocopy of the original chain of custody record. The SR number from the originating laboratory may remain the same when subcontracting to a laboratory within LIMS; and any documentation generated by the laboratory would be included in that job file.

6.7.1.1 A new chain of custody record may be initiated if the number of samples or analyses is small enough so that it is not too time consuming to write out the new chain of custody record. The sample custodian at this laboratory must accurately transfer the entire client and sample information to the new chain of custody record and sign and date relinquishing it and the samples.

6.7.1.2 A photocopy of the original chain of custody record may be used when the number of samples or analyses is large or the chain of custody record is complicated and it would take a lot of time to rewrite the client and sample information on a new chain of custody record. On the chain-of-

custody-record-photocopy, the sample custodian preferably using blue ink must:

- Indicate which samples have been sent by crossing out the samples retained;
- Correct the number of sample containers actually being transferred by crossing out the number and writing the number of bottles sent;
- Indicate which analyses the subcontract network laboratory will be performing by highlighting the analyses to be performed and/or crossing out the analyses not subcontracted;
- Write the service request number of the originating laboratory on both the original chain of custody record and on the chain-of-custody-record-photocopy; and
- Sign the chain-of-custody-record-photocopy relinquishing it and the samples.

A photocopy of this completed document shall be placed in this laboratory's project file. The receiving network laboratory should treat this photocopied chain of custody record as its official chain of custody record for their project file. This chain-of-custody-record-photocopy must be signed, preferably using blue ink, when the samples are received and logged in at the receiving network laboratory. It will be retained by the receiving network laboratory and a photocopy returned to the originating network laboratory with the final analytical report.

6.7.2 Sample Transfer to an Out of Network Laboratory (Interlaboratory Transfer)

The originating laboratory, when transferring samples to a laboratory outside the network, must initiate a new chain of custody record. This will help to protect the identity of our customer from the outside laboratory and maintain client confidentiality. The sample custodian will indicate that this laboratory is the client on this new chain of custody record and must accurately transfer all the sample and analysis information. Also, the purchase order number is to be included on the new chain of custody record. The new chain of custody record must be signed and dated relinquishing it and the samples.

6.7.3 pH Adjustment Certain methods require a pH check and adjustment to be recorded on the Sample Acceptance Check form. After performing pH adjustment place a yellow tape with the words "pH Check" and "date and time" of adjustment across the top of the bottle. Measure pH after 16 hours; adjust pH if necessary, and repeat the process until proper pH is obtained. The analyst will perform the pH check at the time of analysis.

If received within two weeks of collection, acid preserve upon receipt in the laboratory to lower pH to <2. Following acidification, the sample should be mixed, held for 16 hours, and then verified to be pH <2 just prior to sending out to sub-contract network or out of network laboratory. If for some reason such as high alkalinity, the sample pH is verified to be >2, more acid must be added, and the sample held for 16 hours until verified to be pH <2.

6.7.4 Splitting Samples Avoid splitting whole volume analysis samples; e.g., BNA, pesticides, PCBs. Make appropriate sample splits by pouring sample into containers with appropriate preservative already added.

6.8 Storage and Documentation Distribution

When all samples have been labeled and verified, they are to be placed in the designated storage areas per the *SOP for Laboratory Storage, Analysis, and Tracking*. Where necessary, there are refrigerators and freezers dedicated for specific storage requirements (e.g., Wet Chem, SVOA, etc.) and specific locations entered in the Sample Location module of LIMS.

All documentation (e.g. COCs, Sample Acceptance Check Form, Sample Login Verification, etc.) are to be placed inside the Job Folder and given to the PM. The PM will then distribute the folder to the appropriate department.

6.9 Odorous Sample Storage Odorous samples (ex., Tedlar bags or VOAs for sulfur) are to be placed in the SMO hood for login and labeled with a "HIGH SULFUR CONCENTRATION" caution sticker. The PM is to be contacted so that the best course of action may be taken to prevent any laboratory contamination. Following login, every possible precaution is to be taken when storing the samples; therefore, wherever they are stored must minimize any cross-contamination between stored samples and into the lab air for possible contamination into laboratory systems. Segregation of samples must be performed as necessary to ensure that no contamination occurs between samples, extracts, and standards. After analysis, the odorous samples are returned to the SMO hood for disposal the next day upon PM approval.

7) Quality Assurance

7.1 Internal system audits shall be performed by the Quality Assurance Manager to assess adherence to the guidelines described in this SOP.

8) Documentation and Records

8.1 Forms, Checklists and other required documentation to be maintained are listed in Section 6.6.

9) Summary of Changes

Table 9.1 Summary of Revision Changes

Revision Number	Effective Date	Document Editor	Description of Changes
19.0	05/09/2020	C. Arend	Applied updated SOP formatting style to cover page and updated approval names.
		C. Arend	4.2 – first bullet – updated reference
			6.1 – added Note
		N. Nash	6.2 – 2nd paragraph new
		C. Arend	6.3.2 – updated year in example
		C. Arend	6.3.3 – added last sentence to first paragraph
		C. Arend	6.3.3.9 – added Note
		C. Arend	10.3 – updated reference
		C. Arend	10.4 – updated reference
		C. Arend	Attachment 3 – updated
		C. Arend	Attachment 5 - updated

10) References and Related Documents

10.1 2009 TNI Standard and 2016 TNI Standard.

10.2 US EPA Methods Update Rule (MUR), effective 4/11/07.

10.3 DoD/DoE QSM, *Department of Defense (DoD), Department of Energy (DoE) Quality Systems Manual (QSM) for Environmental Laboratories*, Current Version.

10.4 *General Requirements for the Competence of Testing and Calibration Laboratories*, ISO/IEC 17025:2017.

10.5 Minnesota Administrative Rules, Department of Health, Chapter 4740, Laboratories; Accreditation Requirements.

11) Attachments

11.1 Attachments

Attachment 1	Training plan for Sample Receiving
Attachment 2	Sample Acceptance Check Form
Attachment 3	Service Request Form
Attachment 4	Sample Login Verification Form (also included in the *SOP for Project Management*)
Attachment 5	Sample Acknowledgement Form

Note: Forms are examples and may be modified as long as the minimum requirements of this document are met.

Attachment 1

Training Plan for Sample Receiving

Training Plan for Sample Receiving, Acceptance, and Login

Trainee _____ Trainer _____ Date _____

1. Read SOP — Trainer ____ Trainee ____ Date _____
2. Read Holding Time, Matrix Table (Appendix F of QA Manual) — Trainer ____ Trainee ____ Date _____
3. Demonstrated understanding of — Trainer ____ Trainee ____ Date _____

   Sample Acceptance Check Form & Chain of Custody Form
4. Demonstrated familiarity with related SOPs — Trainer ____ Trainee ____ Date _____

   SOP for Making Entries onto Analytical Records
   SOP for Laboratory Sample Storage, Analysis, and Tracking
   SOP for Nonconformance and Corrective Action
   SOP for Media Request Fulfillment
5. Sample Receipt — Trainer ____ Trainee ____ Date _____

   ☐Understands & knows Sample Hold Times for different methods, media and matrices (or where to find info.)
   ☐Understands Sample Receipt Procedures during business hours as well as after hours
   ☐Knows acceptable temperature for cooler/samples received and how to evaluate and document information
   ☐Knows how to check liquid samples for air bubbles and how to document information
   ☐Knows how to check samples for integrity & if they are compromised (& what this means), how to document
   ☐Knows appropriate containers for samples received according to requested analyses
   ☐Knows adequate sample volume for the analyses requested
   ☐Knows the proper preservation of samples received according to the requested analyses
   ☐Knows when & why the project manager needs to be notified
   ☐Knows how to check canister pressures
6. Sample Login — Trainer ____ Trainee ____ Date _____

   ☐Understands procedure of login and can successfully accomplish the task
   ☐Understands every field of the SR form
   ☐Able to generate a completed project/job – SR form
   ☐Understands the Sample Acceptance Check Form and how to utilize it for different media
   ☐Understands the Sample Receipt Acknowledgment Form and how to utilize it
   ☐Understands the SR form "Draft" copy and know when to utilize it
   ☐Understands the notes that are required at the top of the SR form (i.e., pressurize with helium) and why
   ☐Understands the documentation that must accompany canisters to pressurization
   ☐Understands when an NCAR must be generated in SMO
   ☐Able to submit hardcopy project requirements and how to document special requirements (& what is important to include) on SR form
   ☐Knows steps in documenting samples received outside of hold time
   ☐Know how to properly label samples during login
7. Freezer and Refrigerator Temperature Readings — Trainer ____ Trainee ____ Date _____

   ☐Read *SOP for Calibration and Use of Laboratory Support Equipment*
   ☐Logbooks (Calibration logbook & Freezer / Fridge Temperature logbook)
   ☐Knows required temperatures
   ☐Understands what to do if a temperature exceeds the required temperature (i.e., documentation, notification of QA)
   ☐Ability to calibrate thermometers using appropriate NIST traceable thermometer
   ☐Understands how to apply correction factors to applicable laboratory thermometers
   ☐Reset digital thermometers when appropriate

Attachment 2

Sample Acceptance Check Form

ALS Environmental
Sample Acceptance Check Form

Client: _____ Work order: _____
Project: _____
Sample(s) received on: _____ Date opened: _____ by: _____

Note: This form is used for all samples received by ALS. The use of this form for custody seals is strictly meant to indicate presence/absence and not as an indication of compliance or nonconformity. Thermal preservation and pH will only be evaluated either at the request of the client and/or as required by the method/SOP.

		Yes	No	N/A
1	Were **sample containers** properly marked with client sample ID?	☐	☐	☐
2	Did **sample containers** arrive in good condition?	☐	☐	☐
3	Were **chain-of-custody** papers used and filled out?	☐	☐	☐
4	Did **sample container labels** and/or tags agree with custody papers?	☐	☐	☐
5	Was **sample volume** received adequate for analysis?	☐	☐	☐
6	Are samples within specified holding times?	☐	☐	☐
7	Was proper **temperature** (thermal preservation) of cooler at receipt adhered to?	☐	☐	☐
8	Were **custody seals** on outside of cooler/Box/Container?	☐	☐	☐
	Location of seal(s)? _____ Sealing Lid?	☐	☐	☐
	Were signature and date included?	☐	☐	☐
	Were seals intact?	☐	☐	☐
9	Do containers have appropriate **preservation**, according to method/SOP or Client specified information?	☐	☐	☐
	Is there a client indication that the submitted samples are **pH** preserved?	☐	☐	☐
	Were **VOA vials** checked for presence/absence of air bubbles?	☐	☐	☐
	Does the client/method/SOP require that the analyst check the sample pH and if necessary alter it?	☐	☐	☐
10	**Tubes:** Are the tubes capped and intact?	☐	☐	☐
11	**Badges:** Are the badges properly capped and intact?	☐	☐	☐
	Are dual bed badges separated and individually capped and intact?	☐	☐	☐

Lab Sample ID	Container Description	Required pH *	Received pH	Adjusted pH	VOA Headspace (Presence/Absence)	Receipt / Preservation Comments

Explain any discrepancies: (include lab sample ID numbers): _____

RSK - MEEPP, HCL (pH<2); RSK - CO2, (pH 5-8); Sulfur (pH>4)

SACF.xls - Page 1 of 1 05/25/18 3:54 PM

Attachment 3

Service Request Form

Service Request Summary

1 - 1 mL-Glass Vial Unpreserved

Location: P-04

Folder #: **P2000375**
Client Name: ALS Environmental - Simi Valley
Project Name: Phenova PT Study
Project Number: AE0120
P.O. Number:

Report To: Chaney Arend
ALS Environmental - Simi Valley
2655 Park Center Drive, Suite A
Simi Valley, CA 93065
Phone Number: 805-526-7161
Cell Number:
Fax Number:
E-mail: chaney.arend@alsglobal.com

Project Chemist: Chaney Arend
Logged By: DENISE.POSADA
Date/Time Received: 1/23/20 0915
Date/Time Logged: 1/24/20 09:42
Archive? N
Folder Due Date: 3/5/20
Internal Due Date: 2/26/20
QAP: LAB QAP
Qualifier Set: Lab Standard
Formset: Lab Standard
Report to MDL?: N
Merged?: Y Batch QC?: N
PC Approved?: Y
State of Sampling Location:
EDD: No EDD Specified

Lab Samp No.	Client Samp No.	Matrix	Collected	VOA GCMS AIR TO-17/VOC Sorbent
P2000375-001	PT-VOATD-AIR	Air	1/20/20 0000	I

Folder Comments:

See attached for analyte list. All QC Must Pass.

Test Comments:

Group	Test/Method	Samples	Comments
VOA GCMS AIR	VOC Sorbent/TO-17	1	Concentrations range from 5-100ng/tube.

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Attachment 4

Sample Login Verification Form

Sample Login and Verification Checklist

Service Request Number, Client & Project Name	(place folder label here)	SDG Used	PM

Sample(s) delivered by: (circle) Client / ALS Emp. / DHL / GSO / FedEx / UPS / Other_____

Yes	No	N/A	SMO Verification	
			Project number has been correctly entered.	
			Sample IDs from the COC have been correctly entered.	
			Sample date and time collected for each sample has been entered correctly.	
			Date received is correct.	
			Container tags are reconciled and applied to correct containers.	By:
			Container tags have been verified by a second person.	By:
			The analyst and PM have been alerted of Short HT or Rush samples.	Notified:
			Sample receipt discrepancies have been noted on Sample Acc. Check Form.	
			Login Completed	By: Date:

Yes	No	N/A	Client Services Login Verification	
			Folder due date is correct.	
			Project Number, Dates, Times, and Sample IDs are correct.	
			Pricing and Rush charges are correct.	
			The subcontract containers have been tagged and sub COC has been generated.	Sub Lab:
			Samples requiring an MS/MSD are properly indicated in the folder.	
			All non-analytical tasks (encores, EDDs, etc.) are logged in and priced correctly.	
			Client has been notified regarding holding time exceedences and sample receipt discrepancies. Notified by email □ verbally □ voicemail □	By: Date:
			Login Approved (red button)	By: Date:

Yes	No	N/A	Client Services Folder Approval	
			Pricing is correct and approved. (Prepaid work is properly indicated with check or credit card.)	
			Hazardous waste designation has been set properly for each sample.	
			Report and/or EDD are complete.	
			Folder Release	By: Date:

Comments:

Attachment 5

Sample Acknowledgement Form

ALS Environmental
2655 Park Center Drive, Suite A
Simi Valley, CA 93065

Confirmation of Sample Receipt

To:	Chaney Arend	**From:**	Chaney Arend
Email:	chaney.arend@alsglobal.com	**Email:**	Chaney.Arend@alsglobal.com
Fax:		**Fax:**	
Phone:	805-526-7161	**Phone:**	805-526-7161 x2084

Samples for analysis have been received by ALS Environmental on 1/23/20 and assigned our Service Request number **P2000375**. **Please verify the following information and notify me of any corrections as soon as possible.**

The estimated completion date for this work is: **3/5/20**

Client: ALS Environmental - Simi Valley
Project: Phenova PT Study/AE0120

EDD Required: No

Tier: I

Report To: Chaney Arend
ALS Environmental - Simi Valley
2655 Park Center Drive, Suite A
Simi Valley, CA 93065

Billing Address: Chaney Arend
ALS Environmental - Simi Valley
2655 Park Center Drive, Suite A
Simi Valley, CA 93065

Comments: See attached for analyte list. All QC Must Pass.

Thank you for your business!

A - Test is Authorized H - Test is On Hold HP - Test is On Hold Pending Input P - Test is Authorized for Prep Only C - Test has been Cancelled * - Test has assigned QC

P2000375-001	PT-VOATD-AIR	Air	12/20/2000	A

TO-17 VOC Sorbent

Test Comments:

Group	Test/Method	Samples	Comments
VOA GCMS AIR	TO-17/VOC Sorbent	1	Concentrations range from 5-100ug/tube.

Dissolved Gas Analysis in Aqueous Samples using a Headspace Equilibration Technique

DOCUMENT ID: VOA-DISGAS, REV 18

Approved By: _____ Date: 3/10/2020
Laboratory Director – Trey Teall

Approved By: _____ Date: 3/10/2020
Quality Assurance Manager – Chaney Arend

Approved By: _____ Date: 3/10/20
Technical Manager (Volatiles GC) – Wade Henton

Doc Control ID:	UNCONTROLLED	Archived Date:	_____

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1) Scope and Applicability

1.1 This gas chromatographic method is used for the analysis of dissolved carbon dioxide, methane, ethane, ethene (ethylene), propylene (propene), and propane in groundwater and other aqueous samples. This method is appropriate for quantifying target-dissolved gases from approximately 1.0µg/L to high mg/L values. It is easily adaptable for the analysis of other dissolved gases in water matrix samples. The approximate number of analyses (including sample preparation) which can be performed in one eight hour day is twenty.

1.2 The reported MDL and MRL are listed in Attachment D of this document and may be adjusted if required for specific project requirements; however, the capability of achieving other MRLs must be demonstrated.

2) Summary of Procedure

2.1 An aqueous sample is collected with zero headspace and delivered to the laboratory usually in a 40mL VOA vial. A headspace is generated by displacing twenty percent (20%) of the sample volume with either nitrogen or helium gas. The sample is shook and then equilibrated at ~20°C for two to four hours, depending on the analytes of interest. An aliquot of equilibrated headspace usually 100µL is drawn using a gastight syringe and directly injected onto a capillary chromatographic column where the analytes are separated and detected using a flame ionization detector (FID) and/or thermal conductivity detector (TCD). The concentration of the dissolved gas in the original sample is calculated by using Henry's Law Constant for each analyte, the determined concentration of the gas in the headspace, the submitted sample container volume, and the sample temperature.

3) Definitions

3.1 May This action, activity, or procedural step is neither required nor prohibited.

3.2 Must Not This action, activity, or procedural step is prohibited.

3.3 Must This action, activity, or procedural step is required.

3.4 Shall This action, activity, or procedural step is required.

3.5 Should This action, activity, or procedural step is suggested, but not required.

3.6 Analytical Sequence The analytical sequence describes exactly how the field and QC samples in an analytical batch are to be analyzed.

3.7 Field Sample A sample collected and delivered to the laboratory for analysis.

3.8 Batch QC Batch QC refers to the QC samples that are analyzed in an analytical batch of field samples and includes the Method Control Sample (MCS), Laboratory Control Sample (LCS), Matrix Spike (MS), Duplicate Matrix Spike (DMS) or Laboratory Duplicate (LD), etc.

3.9 Calibration Standard (Initial Calibration – ICAL) A calibration standard is an analyte at a known concentration prepared from a primary standard, which is, in turn, prepared from a stock standard material. A calibration standard is analyzed at specific concentrations and used to calibrate the response of the measurement system with respect to analyte concentration.

3.10 Initial (or Independent) Calibration Verification (ICV) Standard An ICV is a standard that is prepared from materials obtained from a source other than the source for the

calibration standards and is analyzed after the measurement system is calibrated, but prior to sample analysis in order to verify the calibration of the measurement system.

3.11 Method Control Sample (MCS) An analyte-free (except carbon dioxide) matrix to which either nitrogen or helium gas is added in the same quantities or proportions as used in field sample processing and carried through the entire analytical process. It is used to evaluate the process for contamination from the laboratory with the exception of carbon dioxide.

3.12 Laboratory Control Sample (LCS) A laboratory control sample is an analyte-free matrix to which a known quantity of analyte(s) is (are) added. The LCS is subjected to the same processing as field samples and is carried through the entire analytical process. The percent recovery of the analyte(s) in the LCS is used to assess method performance with respect to the particular matrix in question.

3.13 External Standard Calibration External standard calibration involves comparison of instrument responses from the sample to the responses from the target compounds in the calibration standards.

3.14 Analytical Batch A group of samples which behave similarly with respect to the sampling or the test procedures being employed and are processed as a unit using the sample lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods. In an analytical batch of samples, the time period is 24 hours or up to twenty sample injections, whichever comes first of continuous operation without interruption.

3.15 Reagent Blank (RB) A reagent blank for this method is analyte-free helium that is analyzed to verify the zero point of the analytical system and to verify freedom from carryover.

3.16 Continuing Calibration Verification (CCV) Standard A continuing calibration verification standard is a calibration standard that is analyzed periodically to verify the continuing calibration of the measurement system.

3.17 Precision Precision of a method is how close results are to one another.

3.18 Bias The bias of a method is an expression of how close the result(s) (produced by the method) is(are) to the true value.

3.19 Manual Integration This term applies to a data file in which setpoints have been changed and reintegration has occurred under the changed setpoints; baselines have been adjusted; peak integration start and stop "ticks" have been changed; and peak area or peak height has been adjusted. In addition, these are changed after the time of data collection and data file generation.

3.20 Laboratory Duplicate Separate aliquots (two) of a sample taken from the same container under laboratory conditions and processed and analyzed independently. Since a submitted sample must not be opened, laboratory duplicates, for the purpose of this analysis, shall be duplicate manual injections.

3.21 Duplicate Field Sample Replicate containers of a sample submitted to the laboratory for analysis.

3.22 Limit of Detection (LOD) The smallest amount or concentration of a substance that must be present in a sample in order to be detected at a high level of confidence (99%). At the LOD, the false negative rate (Type II error) is 1%. (DoD Clarification). For consistency purposes, the LOD may be referred to as the MDL once it is reported; however, full verification will be on file in the laboratory per the procedures detailed in this document.

3.23 Limit of Quantitation (LOQ) The lowest concentration that produces a quantitative result within specified limits of precision and bias. For DoD projects, the LOQ shall be set at or above the concentration of the lowest initial calibration standard. (DoD Clarification). For consistency purposes and since the LOQ and MRL are equivalent with regards to laboratory procedure, the LOQ will be referred to as the MRL in this document and once it is reported. Full verification will be on file in the laboratory per the procedures detailed in the document.

3.24 Detection Limit (DL) / Method Detection Limit (MDL) The smallest analyte concentration that can be demonstrated to be different from zero or a blank concentration at the 99% level of confidence. At the DL, the false positive rate (Type 1 error) is 1%. (DoD Clarification). For consistency purposes, the DL may be referred to as MDL.

4) Responsibilities

4.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review and reporting per the corresponding standard operating procedures. Laboratory personnel that have successfully demonstrated the ability to generate acceptable results according to this SOP are approved to perform sample analysis and interpretation of the results.

4.2 The department supervisor/manager or designee shall perform final review and sign-off on the data.

5) Interferences

5.1 Sample Contamination Care must be taken to prevent ambient air intrusion into the sample container during headspace generation and laboratory analysis. The sampling syringe should be flushed a minimum of 2-3 times with the gas being used to create the headspace (i.e. helium or nitrogen) in order to remove residual ambient air. An aliquot of the headspace gas, greater than needed is drawn, and the syringe plunger is adjusted to the appropriate volume *immediately* before injection.

5.2 Sample Preservation If the sample is to be analyzed for carbon dioxide it must not be preserved with hydrochloric acid at the time of collection. The addition of acid changes Henry's Law Constant for carbon dioxide and may artificially elevate the CO_2 result. The lower pH [increased (H+)] converts HCO_3^- in solution to CO_2.

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+$$

$$K_A = \frac{[HCO_3^-][H^+]}{[CO_2][H_2O]}$$

5.3 Sample Temperature Since the sample temperature is used in the final calculation, excessive handling of the sample should be avoided. The samples are considered ambient at the time of analysis. Henry's law constants are only available for certain analytes at certain temperatures, therefore, 20°C is used as it most closely approximates the actual ambient temperature of the laboratory. See Section 13.10.3 for the available Henry's Law Constant values.

5.4 Carbon Dioxide Concentrations in Water Carbon dioxide is found naturally dissolved in water, therefore, the method control sample may contain this analyte.

5.5 Methane Interference There is an interference that elutes at the same time as methane. This interference may be due to septa bleed. The evaluation of method blank data along with spiked blank samples when performing method detection limits studies ensures this interference is taken into consideration when establishing the method detection limit.

6) Safety

6.1 Each compound, mixture of compounds, standards, as well as samples, should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest level possible through the use of hoods (to minimize inhalation). For proper handing, use and disposal refer to the laboratory's Environmental, Health and Safety Manual, SDS (located in the safety cubicle in the front office), as well as the *Simi Valley Lab Waste Management Plan*.

6.2 Safety Data Sheets Safety data sheets (SDS) are available and should be reviewed as part of employee training. Care should be taken when handling standard material in neat or highly concentrated form.

6.3 Protective Clothing At a minimum, personal protective clothing such as safety glasses and gloves should be worn when utilizing procedures detailed in this document.

6.4 Pressurized Gases The use of pressurized gases is required for this procedure. Care must be taken when moving cylinders. All gas cylinders must be secured to a wall or an immovable counter with a chain or a cylinder clamp at all times. The regulator should never remain on small cylinders following use. Sources of flammable gases (i.e. pressurized hydrogen) shall be clearly labeled.

6.5 Syringes Care should be taken to avoid personal injury as a result or improper handling techniques.

7) Sample Collection, Containers, Preservation, and Storage

7.1 Sample pH should be adjusted by the client at the time of collection to <2 with 1:1 HCl unless carbon dioxide concentration is to be evaluated. In addition, the laboratory shall receive samples in airtight borosilicate glass bottles or vials with Teflon-lined septa, at a temperature of ≤ 4˚C with zero headspace (both evaluated by Sample Management upon receipt). The sample must be stored in the laboratory at 4˚C ± 2˚C and analyzed within 14 days (except carbon dioxide; no criteria) after sample collection, unless otherwise specified by the client. If the analysis is for carbon dioxide, it is recommended whenever possible, that the sample preparation take place within approximately 5 days from date of collection.

7.2 The analyst shall take the pH of the exact vial that was analyzed (especially if reporting CO2) using pH paper or strips. This reading must follow completion of the analysis and after review of all the QC results associated with the samples in order to prevent a loss of sample integrity. The analyst must record the information per vial including any comments on the Sample Acceptance Check Form accompanying the sample. The information that is to be included is the sample pH, method of analysis, and date and initials of the analyst that performed the pH evaluation.

7.3 Since there is no specific requirement for pH preservation (with the exception of carbon dioxide), the Project Manager (PM) in charge need not be contacted if the submitted samples were not preserved. However, if the client has specified instructions for pH preservation and there is a deviation, the PM must be notified and the PM shall decide whether the client should be contacted. All documentation must be retained regarding the outcome of the PM's decision as well as the client's reply. The pH should be noted (or must be included on the Sample Acceptance Check Form) on the final report.

7.4 When cross-contamination is a possibility, samples suspected of containing high concentrations of target analytes shall be isolated from other samples in a separate refrigerator designated for high concentration RSK175 samples. In the event that the client informs the project manager of potentially high concentration samples prior to

sample receipt, the project manager must notify SMO so that the samples can be stored appropriately.

8) Apparatus and Equipment

8.1 Gas Chromatograph The analysis is performed using a Hewlett-Packard Model 5890 Series II Gas Chromatograph or equivalent equipped with a flame ionization detector (FID) and thermal conductivity detector (TCD), using a split injection.

8.2 Column The analytical columns used to separate the gases are as follows:

Thermal Conductivity Detector ..... Carboxen 1010, 0.53mm x 30m
Flame Ionization Detector .....J&W MXT-QPlot, 0.53mm x 30m

Gas Chromatograph Column Conditioning Initial conditioning of the chromatographic column is required prior to use of the system. The column should be conditioned with a continuous flow of laboratory helium (UHP/ZERO 99.999% purity or better) and temperature programmed from 35 degrees Celsius to 225 degrees Celsius at a rate of five degrees per minute. The column should then be held at 225 degrees Celsius overnight.

8.3 Sample Preparation and Analysis

8.3.1 Headspace Generation Kit

- A 10mL gas-tight syringe equipped with a 2 inch sidehole needle (gauge 22)
- 1/8 inch outer diameter Teflon tubing
- 100mL graduated cylinder
- Rubber stopper with two 1/8 inch holes

8.3.2 Syringes

- 250µL
- 500µL
- 1.0mL
- 10mL

8.3.3 pH Paper

Range: 0-14

9) Standards, Reagents, and Consumable Materials

9.1 All standards and reagents, must be prepared, handled and labeled in accordance with the *SOP for Handling Consumable Materials*. For purchased standards, a unique standard identification number, all concentrations, received date, expiration date, and balance gas, as well as analyst's initials must be identified on the label. Each prepared standard, must include a unique standard identification number, the exact concentration of each analyte, expiration date, and balance gas, as well as analyst's initials (the date prepared shall be included in the laboratory standard identification number).

9.2 Certificates of analysis (CofA) must be maintained for all purchased standards, nitrogen, helium, hydrogen and zero air cylinders. All of the information listed above must be included on the CofA and turned in to the Quality Assurance Department for traceability purposes.

9.3 Purchased Stock Standards

The exact concentration specified in this section may change with each cylinder received; refer to the most recent Certificate of Analysis.

9.3.1 Matheson or Equivalent

Methane .....~4%
Oxygen.....~5%
Carbon dioxide .....~5%
Hydrogen.....~4%
Carbon monoxide ...~5%
Helium.....Balance

Methane.....~1%
Oxygen .....~1%
Carbon dioxide .....~1%
Hydrogen .....~1%
Carbon monoxide ....~1%
Helium .....Balance

Note: 1% = 10,000ppm

9.3.2 Scotty Mix 48 or Equivalent

Compound	Approximate Concentration (ppm by vol.)
Methane	15
Ethylene	15
Ethane	15
Propane	15
Acetylene	15
Propylene	15
Propyne	15
n-Butane	15
Balance: Nitrogen	

These stock standards contain compounds that are not reported. The actual concentrations of these standards may change with each purchase.

9.3.3 Neat Standards

Compound	Approximate Concentration (ppm)
Carbon dioxide	990,000
Ethylene (Ethene)	990,000
Methane	990,000
Propylene	990,000
Propane	990,000
Ethane	990,000

The specific concentrations of these standards may change with each purchase. If utilizing an ultra-high purity (UHP) gas cylinder, the certificate must be on file and it shall meet all of the minimum UHP requirements with respect to impurity content.

9.4 Calibration Standards

9.4.1 Initial Calibration (ICAL) and Continuing Calibration Verification (CCV) Standards
Working standards shall be prepared from higher concentration stock standards purchased from commercial vendors.

9.4.1.1 Procedure Aliquots of the stock standards are spiked into a cleaned and evacuated 6 liter canister (*SOP for Cleaning and Certification of Summa Canisters and Other Specially Prepared Containers)* by using gastight syringes. The canister is then balanced with helium or nitrogen per the

SOP for Evaluation and Pressurization of Specially Prepared Stainless Steel Canisters.

Step 1: Determine the actual pressurized volume of the 6L canister by the use of the following equation.

PV = PDF(V) (Equation 1)

Where:

PV Pressurized canister volume (L)

PDF Pressure Dilution Factor, where PDF = $\frac{p_{atm} + p_f}{p_{atm} - p_i}$

P_f Final Canister Pressure

P_i Initial Canister Pressure

V Volume of canister at 1atm

p_{atm} Pressure at 1atm = 14.7

Example:

$$\frac{14.7+65}{14.7-0}(6L) = 32.53L$$

Step 2: Determine the amount required to achieve the desired concentration(s) by utilizing the following equation.

$$S = \frac{(C_1)(PV)}{(C_2)} x \frac{1000mL}{1L} \quad \text{(Equation 2)}$$

Where:

S Spike amount required in order to obtain the desired concentration (mL)

C_1 Desired concentration (ppm)

C_2 Concentration of source (ppm)

PV Pressurized volume of canister determined in Step 1 (L)

The concentrations listed in this table are based on the purchased neat standards and may change with each purchased standard. However, the nominal concentration values should remain close to that listed below.

Compound	Source Conc. (ppm)	Introduce (mL)	Nominal Conc. (ppm)
Carbon dioxide	998,000	326	10,000
Methane	990,000	82.15	2500
Ethene	10,000	1626.5	500
Ethane	990,000	16.43	500
Propane	990,000	16.43	500
Propene	10,000	1626.5	500

Note: The exact volumes injected, to make a working standard, must be used to determine the final concentration of the standard.

In order to achieve all of the desired concentrations for each analyte in the ICAL or CCV, additional standard dilutions may be required. These dilutions may be prepared in glass dilution bombs (i.e., 125mL) or Tedlar bags and are achieved by following step 3 below.

Step 3: Determine the correct injection amount based on the desired final concentration for a target analyte by utilizing the following equation.

Using $C_1V_1 = C_2V_2$

Where:

C_1=Initial concentration (i.e., 2500ppm methane stock solution)
C_2=Final desired concentration (i.e., 2.5ppm)
V_2=Final volume (125mL or 125000uL – glass dilution bomb)
V_1=Solve for V_1 (uL)

Step 4: To perform the ICAL or to analyze a CCV, determine the correct instrument injection volume for an analyte by utilizing the following equation.

$$I = \frac{C_2}{C_1}$$

where:

I required injection (mL)
C_1 Source (initial) concentration (ppm)
C_2 Desired concentration (ppm)

9.4.2 Initial Calibration Verification (ICV) Standard This standard must be from a second source and used as a verification of the initial calibration. Prepare the same as an ICAL standard.

DoD compliance: Second source standards must be obtained from a second manufacturer or must be from a second lot obtained from the same manufacturer (independently prepared from different source materials).

9.4.3 Laboratory Control Sample Spike The same standard as the ICV may be used to spike the LCS and LCSD.

9.4.4 Matrix Spike The standard as detailed in Section 9.4.1 is used to spike the MS and MSD.

9.5 Gases

9.5.1 Helium 99.999%, carrier gas, sample preparation displacement gas
9.5.2 Hydrogen 99.999%, fuel source for FID
9.5.3 Nitrogen 99.999%, makeup gas
9.5.4 Zero Air Ultra

9.6 Reagent Water

Boiled Deionized Water or Equivalent

9.7 Storage and Expiration Dates

9.7.1 Neat Standards

Neat standards are purchased in gas cylinders and are stored at ambient temperature for a period of five years or as recommended by the manufacturer.

9.7.2 Stock Standards

Stock standards are purchased in gas cylinders and are stored at an ambient temperature for a period of two years or as recommended by the manufacturer.

9.7.3 Calibration Standards (ICAL, ICV and CCV)

Store each standard at an ambient temperature for a period detailed below, depending on the container.

Specially Prepared Canister - two years
Tedlar Bag - 3 days
Glass dilution bomb - 3 days

10) Preventive Maintenance

10.1 A maintenance log must be kept documenting maintenance performed on each analytical system. The serial number(s) of each instrument must be noted in the front of the logbook, which must be kept current. An entry shall be made in the appropriate log every time maintenance is performed (no matter the extent). The entry in the log must include:

(a) The date of maintenance
(b) Who did the maintenance
(c) Description of the maintenance
(d) Proof that the maintenance activity was successful

The extent of the maintenance is not important, however, it is important that a notation be included for each maintenance activity such as changing a column or cleaning the detector. A notation of a successful continuing calibration or initial calibration that accompanies the data shall serve as proof that the maintenance is complete and the instrument is in working order.

10.2 Gas Chromatograph

10.2.1 Column Over time, the column will exhibit a poor overall performance, as contaminated sample matrices are analyzed. The length of time for this to occur will depend on the samples analyzed. When a noticeable decrease in column performance is evident and other maintenance options do not result in improvement, the column should be replaced. This is especially evident in calibration difficulties. Whenever GC maintenance is performed, care should be taken to minimize the introduction of air or oxygen into the column.

Clipping off a small portion of the head of the column often improves chromatographic performance. When cutting off any portion of the column, make sure the cut is straight and “clean” (uniform, without fragmentation) by using the proper column-cutting tool.

Poor performance can also be due to ineffective column ferrules, which should be replaced when a tight seal around the column is no longer possible. This can be detected with the use of a leak detector.

10.2.2 Injection Port Injection port maintenance includes changing the injection port liner, and column ferrule as needed. Liners should be changed when recent sample analyses predict a problem with chromatographic performance.

10.2.3 In-Line Purifiers shall be changed and maintained as recommended by the supplier.

10.2.4 Injector Septa Septa should be changed periodically, whenever there is a noticeable change in peak definition.

10.2.5 Detectors Clean detectors when needed or whenever there is a noticeable change in the background interference and peak definition.

11) Procedure

11.1 Data System and Analytical Sequence

11.1.1 Data System Load the appropriate method for the GC temperature program. Also, load the appropriate analytical sequence (example: J:\GC10\Sequence\rskboth.s) and enter the analytical sequence information in the table window, including sample/standard name, volume and method file. Load the appropriate analytical method (J:\GC10\Methods\"current ICAL file"). Run the sequence and inject the standards and samples in the appropriate order detailed in Section 11.1.2.

11.1.2 Analytical Sequence The number of samples in an analytical batch shall not exceed 20. Matrix spikes (MS), duplicate matrix spikes (DMS), laboratory duplicates (LD), and sample dilutions are not considered separate samples. Matrix spikes, matrix spike duplicates and duplicate field samples must be analyzed at the request of the client. Whenever possible, the analysis of the laboratory duplicate (LD), matrix spike (MS) and duplicate matrix spike (DMS) shall be rotated among clients. A client may request to have one or more of these batch QC samples run at each sample submission.

Batch QC samples may be analyzed anywhere in the analytical sequence; i.e., it is not necessary to analyze the batch QC samples in the exact order or position shown in this section. This analysis shall be run as a "closed" batch (beginning and ending with a CCV).

Analytical Sequence Guidelines

Sequence Position	*Sample Type*	*Sample Description / Detector*[1]
1	QC	CCV (FID &/or TCD)[7]
2	QC	ICV (FID &/or TCD)[2]
3	QC	RB (Helium – FID &/or TCD)[3]
4	Batch QC	MCS (FID &/or TCD)[4]
5	Batch QC	LCS (FID &/or TCD)[5]
6	Batch QC	LCS Duplicate (FID &/or TCD)[6]
7-15	Field	Samples 1-8 (FID &/or TCD)
16	Batch QC	MS (FID &/or TCD)[9]
17	Batch QC	LD (FID &/or TCD)[8]
18	QC	CCV (FID &/or TCD)[7]
19-28	Field	Samples 9-18 (FID &/or TCD)
29	QC	CCV (FID &/or TCD)[7]

[1]The reportable analytes associated with the FID (or TCD) need only be evaluated if one or more field samples are to be reported for those analytes. In addition, only a single injection is necessary for analysis on both detectors.
[2]The ICV is an optional daily standard.
[3]The reagent blank (RB) should be analyzed daily as a system check.
[4]The method control sample (MCS) must be prepared and analyzed with each batch of 20 or fewer samples. Refer to Section 3.11 for the complete definition.

[5]An LCS must be prepared and analyzed at a frequency of 1 in 20 or fewer samples.
[6]The LCSD must be analyzed as a check of method precision (including preparation) and is especially necessary since the LD is only a duplicate manual injection.
[7]An acceptable CCV must be analyzed initially, every ten sample injections (or every 12 hours, whichever is more frequent) and at the completion of the analytical sequence. Refer to Section 11.7 for additional information.
[8]A laboratory duplicate (LD) should be analyzed at a frequency of 1 in 20 or fewer samples.
[9]A matrix spike (MS) must be prepared and analyzed as requested by the client.

11.2 Sample Submission

A minimum of one 40mL VOA vial will be held as a "back up" for every sample submission if provided. Whenever required, other vials may be used as LD, MS and DMS.

11.3 Chromatographic Conditions

The settings and system parameters are as follows:

HP 5890 GC Instrument Control Parameters

Sample Inlet: GC
Injection Source: Manual
Injection Location: Front
Run Time: ~10.0 min (refer to Section 11.12.2, #3)

OVEN

Initial Temperature: 55˚C
Initial Time: 2.0min
Maximum Temperature: 250˚C
Equilibration Time: 0.0min

Ramps: Rate: 20˚/min
Final Temp.: 205˚C
Final Time: 0.5min

INJECTOR

Mode: Packed
Temp.: 100˚C
Pressure: 20psi at 55˚C oven temperature

COLUMN 1

Model No.: Supelco Carboxen 1010 PLOT
Max. Temp.: 250˚C
Nominal Length: 30.0m
Nominal Diameter: 0.53mm ID
Initial Flow: 10 mL/min

COLUMN 2

Model No.: Restek MXT-QPLOT
Max. Temperature: 250˚C
Nominal Length: 30.0m
Nominal Diameter: 0.53mm ID
Initial Flow: 10 mL/min

DETECTORS

FID
Temperature: 280˚C
H_2 Flow: 30 mL/min
Air: 350 mL/min
N2 Make up: 30 mL/min

TCD
Temperature: 250˚C
Reference Flow: 45 mL/min
He Make up: 20 mL/min

11.4 Initial Calibration

Introduce each initial calibration concentration by direct injection using a gastight syringe. The ICAL concentrations may change as long as the low standard analyzed is at

or below the reporting limit for each analyte. Refer to Section 13.2 for calculations and Section 12.3 for the acceptance criteria. If an initial calibration is not used (did not pass criteria), it must be noted in the run logbook.

11.4.1 Initial Calibration Analysis Requirements These requirements apply to both detectors/columns for this method.

1. An initial calibration (ICAL) can be used as long as the continuing calibration verification standard (CCV) analysis at the beginning of and throughout the analytical sequence meets the analysis' criteria. Once a set of ICAL standards is analyzed and found to be acceptable, the previous ICAL can no longer be used to analyze new samples and it is to be archived. The only time an archived ICAL can be used thereafter is to review or re-evaluate sample(s) previously processed using that ICAL. *The practice of evaluating a CCV versus historical ICALs is not permitted.*

2. If a CCV analysis at the beginning of an analytical sequence fails to meet the analysis' criteria, a second CCV may be analyzed. If the second CCV meets the analysis' criteria, the analysis may continue. If the second CCV fails to meet the analysis' criteria, the analysis is to be stopped, corrective action is to be taken and documented (for example, in the maintenance logbook). *Analysis of more than two CCVs in succession without documented corrective action is not permitted.* Refer to Section 12.5.2 for DoD QSM CCV requirements.

   - Initial calibration requirements

     a. A minimum of five concentrations
     b. The concentration of the lowest calibration standard must be at or below the MRL for each reportable analyte.
     c. The highest concentration, together with the lowest concentration, defines the calibration range.
     d. An instrument blank should be analyzed prior to beginning the analysis of the calibration standards and each analyte concentration in it should be <MRL.
     e. All the ICAL analyses must be completed within 48 hours.
     f. The initial calibration event must not be interrupted by maintenance.
     g. Only one value per concentration is to be used.
     h. Multiple analyses of a calibration standard and use of all the analyses in the ICAL or picking-and-choosing responses from one analysis or the other to use in the analyte's ICAL is not permitted. Once the ICAL has been used on a sample, it is not to be changed.
     i. One ICAL standard may be re-analyzed as long as the requirements of the point dropping policy are met.
     j. The ICAL must be verified by analysis of an ICV standard (i.e., a second-source standard) prior to the analysis of samples.
     k. Point dropping policy:
        - Minimum of five consecutive concentrations is required.
        - Lowest concentration must be at or below the MRL and is not to be dropped unless the MRL is changed to the concentration of the remaining lowest standard.
        - Points may be dropped from the high end, but doing so lowers the calibration range.
        - Points must not be dropped from the "interior" of a curve unless there is an assignable cause* for doing so that affects many (if not all) the analytes in the calibration standard. If a calibration standard is to be dropped from the interior of the curve, all the analytes in the calibration standard must be dropped from all the analytes' calibration curves.

- If a point or a calibration standard is dropped, the reason must be documented.
- One calibration standard may be re-analyzed if the first analysis of the standard has been dropped and the other requirements in this policy are met (e.g., still within 48 hours). The replacement standard must be analyzed within 24 hours of the original calibration standard analysis for the particular calibration level.

  * Assignable causes include

    - Standard preparation error
    - Instrument malfunction (e.g., acquisition halts during the analysis)
    - Bad injection or purge
    - If ≥25% of the analytes in a multi-analyte calibration standard have a response that is <50% of the expected response based on the other calibration standards

11.4.2 ICAL Update Procedure

1. Open most recent method.
2. Save to new ICAL method ID. The date used in method ID is the date files were analyzed.
3. Clear all responses prior to update initiation and/or clear levels if different concentrations are to be used (Initial Calibration → Clear All Calibration Responses; Initial Calibration → Clear All Calibration Levels).
4. Quantitate standard
5. Review all peaks for retention time, integration, etc.
6. Update responses for standard
7. Repeat for all standards
8. If necessary load midpoint standard and update retention times.
9. Save method.
10. Verify Calibration Files listed on Response Factor Report are correct (Both Primary and Secondary Reviewer).
11. Verify responses of Page 3 of Edit Compounds are correct (Both Primary and Secondary Reviewer).
12. Verify file ID, acquisition time, quant time, update time, and last update information is correct on the Calibration Status Report (Both Primary and Secondary Reviewer).
13. Save Method. Confirm that no other copies of the method are open on other computer workstations.

Note: It is also acceptable to quantitate all standards and review all peaks before updating responses but steps 1-2 still must be completed initially. Step 3 also must be done prior to beginning ICAL update.

11.4.3 Initial Calibration File

An ICAL file is to be created for each initial calibration performed per instrument into which is placed the following ICAL documents. The file shall remain in the laboratory and be filed by instrument and date.

- Injection log (optional)
- ICAL Checklist filled out, reviewed and approved
- Blank analysis quantitation report
- Calibration status report (aka Calibration History)
- Relative Response Factor Report / Percent Relative Standard Deviation

- Quantitation report for each calibration standard (including manual integration documentation – before and after manual integration)
- ICV quantitation report and evaluate continuing calibration report (aka Percent Difference Report-either automated or through manual calculations)

11.4.4 Initial Calibration Review

Analyst's calculation and assessment along with a peer review of all ICAL data and documentation is required before the ICAL may be used to analyze samples. Sample results may only be reported if the ICAL is reviewed and found to be acceptable. The ICAL checklist in Attachment B must be properly completed to document the review and approval process and filed with the ICAL raw data.

11.4.5 Directions for ICAL

Inject the ICAL standard (Section 9.4.1) at a minimum of five levels (refer to Section 11.4.1). The following are the analytes and their associated detectors from which the results are reported.

Carbon dioxide..... TCD
Methane ..... FID
Ethylene (Ethene) ..... FID
Ethane..... FID
Propylene (Propene)..... FID
Propane..... FID

1. Purge standard cylinder valve at least three times using a 10mL syringe.
2. Take an appropriate size syringe and purge the standard cylinder valve with the standard gas a minimum of three times to prevent contamination.
3. Fill the syringe with greater than the amount to inject and adjust to the appropriate volume immediately before injection into the GC.
4. Allow chromatogram to run until all of the analytes have eluted.
5. Repeat steps 1-4 for each of the remaining standard volumes using the appropriate size syringe and dilution of the standard.

11.5 Initial Calibration Verification (ICV)

When an ICAL is performed it must always be followed by an ICV standard (second source standard) prior to the analysis of submitted samples. Refer to Section 12.4 for the acceptance criteria.

Directions for ICV Determination (FID)

1. Purge cylinder valve at least three times using a 10mL syringe.
2. Take a 500µL syringe and purge the cylinder valve with the standard gas a minimum of three times to prevent contamination.
3. Fill the syringe with >100µL and adjust to 100µL immediately before injection into the GC.
4. Allow chromatogram to run until all of the analytes have eluted.

The actual syringe listed and the injection volume may change with the desired concentration to be analyzed.

Directions for ICV Determination (TCD)

1. Purge cylinder valve at least three times using a 10mL syringe.
2. Take a 500µL syringe and purge the cylinder valve with the standard gas a minimum of three times to prevent contamination.
3. Fill the syringe with >100µL and adjust to 100µL immediately before injection into the GC.
4. Allow chromatogram to run until all of the analytes have eluted.

The actual syringe listed and the injection volume may change with the desired concentration to be analyzed.

11.6 LOQ Establishment, Verification, and Acceptance Criteria

1. The LOQ must be set within the calibration range (≥ low std. of the current passing ICAL) prior to sample analysis.
2. The LOQ for each analyte must be ≥ the analyte's LOD.
3. Initially a passing demonstration of precision and bias must be performed at the LOQ
4. Run CCV 2 times at LOQ and:
   - Evaluate the LOQ for precision and bias using current control chart limits or fixed limits of 70-130% until enough points have been generated.
   - Check the signal to noise ratio (S/N) using the software. The S/N ratio must be at least 3:1 for each analyte.
   - If anything fails, verify at higher level and notify reporting. Also, make a note in the ICAL documentation.
   - Turn in all LOQ verification data (quant reports and software reports/checks) to QA (regardless of pass/fail).
5. Verify the LOQ on each instrument quarterly by running the CCV at the LOQ and verifying that ongoing precision and bias requirements are met.

11.7 Continuing Calibration Verification (CCV)

Reportable results must be bracketed by CCV results that meet the QC requirements for the verification of the calibration. Also, sample concentrations must be quantitated from the current initial multi-point calibration and may not be quantitated from any continuing calibration verification standard. A continuing calibration check is performed at the beginning and end of every sequence and after every ten sample injections or every 12 hours, whichever is more frequent. The concentrations of the CCV should be varied within the established calibration range.

Directions for CCV Determination

The continuing calibration check shall be performed with the injection of a known amount of the ICAL/CCV standard (Section 9.4.1).

1. Purge cylinder valve at least three times using a 10mL syringe.
2. Take an appropriate size syringe and purge the cylinder valve with the standard gas a minimum of three times to prevent contamination.
3. Fill the syringe with a volume greater than the required amount and adjust to the proposed volume immediately before injection.
4. Allow chromatogram to run until all of the analytes have eluted.

The actual syringe listed and the injection volume may change with the desired concentration to be analyzed.

11.8 Reagent Blank (RB)

A RB is to be analyzed daily and follow the CCV standard or ICV standard (if analyzed).

Directions for RB Determination

The RB check is performed with the injection of 100µL of high purity helium.

1. Purge cylinder valve at least three times using a 10mL syringe.
2. Take a 500µL syringe and purge the cylinder valve with the standard gas a minimum of three times to prevent contamination.
3. Fill the syringe with >100µL and adjust to 100µL immediately before injection into the GC.
4. Allow chromatogram to run until all of the analytes have eluted.

The actual syringe listed and the injection volume may change with the desired concentration to be analyzed.

11.9 Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD)

The LCS and LCSD must be both prepared and analyzed with the corresponding field samples. The purpose of these batch QC samples is to evaluate analyst specific precision and bias or to assess the performance of all or a portion of the procedure (preparation and analysis). A LCS and LCSD are prepared with either the ICV or ICAL standard and are analyzed for each detector during the analytical sequence. The standard used must be noted on the run log for both the LCS and LCSD.

1. Fill a 40mL VOA vial with Sparkletts crystal water or equivalent and cap it with a Teflon-lined septum producing zero headspace.
2. LCS headspace generation inject 8mL of the LCS (FID) standard (Section 9.4.2) into the vial by following step 3 Section 11.12.1.
3. Complete steps 4-9 of Section 11.12.1.
4. Analyze sample per steps 1-3 of Section 11.12.2.
5. Repeat steps 1-4 of this section for the LCSD (FID), LCS (TCD) and LCSD (TCD)

11.10 Matrix Spike (MS)/Matrix Spike Duplicate (MSD) Analysis

Matrix spikes and matrix spike duplicates should be analyzed whenever possible. The MS and MSD must be both prepared and analyzed with the corresponding field samples. The purpose of these batch QC samples is to evaluate the effect of the matrix on a method's recovery efficiency and the precision of the recovery for each analyte.

Matrix spiking should only be performed on samples received in four (one for a back-up) separate vials, or at the specific request of the client. Matrix spikes shall be prepared and analyzed as outlined in Section 11.12 except the CCV standard is used in place of the helium.

11.11 Method Control Sample (MCS)

The MCS must be prepared and analyzed with the corresponding field and batch QC samples.

1. Fill a 40mL VOA vial with Sparkletts crystal water or equivalent and cap it with a teflon-lined septum producing zero headspace.
2. MCS headspace generation - inject 8mL of helium into the vial by following step 3 of Section 11.12.1.
3. Complete steps 4-9 of Section 11.12.1.
4. Analyze sample per steps 1-3 of Section 11.12.2.
5. Refer to Section 12.9 for quality control requirements including acceptance and rejection of the MCS.

11.12 Sample Preparation and Analysis

All samples must be prepared and analyzed with the MCS and LCS and LCSD for each detector. In addition, the time between sample preparation completion (after shaking) and the beginning of the associated analytical sequence should not exceed five hours but all samples (including standards and batch QC) must be analyzed the same day they are prepped.

Note: It is unacceptable to prepare batch QC samples at a separate time than the field samples.

11.12.1 Instructions for Headspace Generation

1. Remove the sample from storage (refrigerator).
2. Purge the headspace gas through a 10mL gastight syringe equipped with a sidehole needle (gauge 22) for approximately 30 seconds prior to beginning sample preparation.
3. Place the end of the waste sample overflow line into a graduated cylinder and insert the needle of the waste sample overflow through the Teflon faced septum of the sample.

4. Flush the 10mL gastight syringe with the headspace gas a minimum of 2-3 times to eliminate ambient air. Draw an aliquot of the headspace gas greater than what is needed, and adjust the syringe plunger to the appropriate volume *immediately* before injecting. Fill with a volume aliquot of gas equivalent to 20 % of the sample volume. For example, if the sample is taken in a 40mL VOA vial then 8.0mL of the headspace gas is added.
5. Introduce the headspace gas by slowly pushing the plunger of the gas tight syringe into the sample container. Once the desired volume of headspace gas is injected, remove the syringe quickly.
6. Allow approximately 2 minutes for the sample overflow to complete and quickly remove the waste sample overflow needle.
7. Verify that the volume in the graduated cylinder is equal to the volume of displaced gas introduced to the sample prior to proceeding to the next step.
8. Shake sample container to agitate.
9. Allow the sample to equilibrate at ~20°C for 2-4 hours (see Section 11.12.2 below).

11.12.2 Sample Analysis is performed by a direct injection technique using a gastight syringe. The samples are allowed to equilibrate according to the analytes requested by the client. Refer to the table below for the correct equilibration time for each sample type.

Reporting Compounds	Equilibration Time
Methane, Propane, Ethane, Ethene, Propene	2 hours minimum
Carbon Dioxide	4 hours minimum
Methane, Propane, Ethane, Ethene, Propene, and Carbon Dioxide	4 hours minimum

A sample volume of 100µL is used unless the detector response requires a smaller sample volume. The sample concentration of any identified analyte must be calculated from the current initial multi-point calibration. The response for the analyte must be within the range of responses of that analyte from the lowest to the highest initial calibration standards. If the response is greater than the highest standard, it must be reanalyzed (see Section 11.12.3).

Note: All samples, including batch QC, must be analyzed together the same day they are prepared. This is required in order to minimize the loss of sample integrity. The preparation and analysis of the LCS and LCSD with the corresponding field samples adds to this evaluation of sample integrity.

1. Take a 500µL syringe and puncture the Teflon septa and pump the syringe within the sample headspace a minimum of three times to get a representative sample.
2. Fill the syringe with greater than the amount to inject and adjust to the appropriate volume *immediately* before injection into the GC.
3. If methane, ethene and/or ethane concentrations are being evaluated, the run may be cut short after the ethane peak has eluted. However, after every third or fourth sample, the chromatogram must be run to the end in order to evaluate carry-over. In addition, if carbon dioxide is being evaluated, allow the chromatogram to run until all of the analytes have eluted.

Identification of peaks: Retention time windows are generated in accordance with the procedure described in Section 11.17. The retention time for each

sample peak (from each column) shall be compared to the retention times in the continuing calibration verification standard in order to confirm qualitative analysis.

Refer to Section 13.10 for calculations.

11.12.3 Sample Dilution Samples require dilution if peak saturation occurs or if the quantified concentration is above the upper calibration range. Dilute the sample by injecting a smaller volume. Make sure that the correct injection volumes are recorded on the run log as well as the quantitation report. Guidance in performing dilutions and exceptions to this requirement are given below.

1. Use results from the original analysis to determine the approximate dilution factor required and get the largest analyte peak within the calibration range.
2. The dilution factor chosen should keep the response of the analyte peak for a reported target compound in the upper half of the calibration range of the instrument. Additional compounds may be reported as long as they are within the calibration range.

Refer to Section 13.10 for calculations.

11.13 Laboratory Duplicate

Analyze two separate aliquots from the same sample vial. Refer to Section 13.8 for the required calculations.

11.14 Duplicate Field Samples

Duplicate field samples may be analyzed when they are submitted and shall be reported as separate samples. Replicate samples must be analyzed following all the field sample guidelines detailed in this SOP.

11.15 Manual Integration

If manual integration is necessary the guidelines described in the *SOP for Manual Integration* shall be followed. This includes the criteria for performing a manual integration, defining unacceptable data file manipulation, required documentation and review, as well as guidelines to follow when performing a manual integration.

11.16 Method Detection and Reporting Limits

The detection limit for this method is determined by following the guidelines in the *SOP for Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation.* Detection limits must be determined each time there is a change in the test method that affects how the test is performed, or when a change in instrumentation is such that it affects the sensitivity of the analysis. The method detection limit (MDL) must be verified at a minimum annually. Quarterly verifications as detailed below are required for DoD accredited analytes. All sample processing steps shall be included in the determination of the detection limit and all supporting data retained.

Method reporting limits (MRL) are the minimum quantities of a target analyte, for a given method, which are reported to the client. The low standard concentration for each analyte must be at or below the set MRL. The quantitation (reporting) limit for each analyte is defined as greater than the MDL to meet laboratory requirements. Refer to Section 5.5 for information on the MDL for methane.

The MDL should be verified with a standard analyzed at 1-4x the previously determined MDL. If each peak has a signal to noise ratio of at least 3:1, the MDL is considered verified. Otherwise, analyze at a higher concentration until the sensitivity is determined and raise the MDLs and method reporting limits (MRLs) as specified in this section.

The detection limit shall be used to determine the LOD for each analyte. Once determined on each instrument, the highest LOD (for each analyte from all instrument determinations) shall be used as the uniform LOD.

11.16.1 Performance and Acceptance Criteria

1. Perform Limit of Detection (LOD) verification on all instruments (performing this method) immediately following the MDL study. Spike the LOD at 2-4x the MDL; the spike level establishes the LOD.
2. LOD Acceptance
   - Analyte must be detected reliably and identified by the method-specific criteria and produce a signal that is at least 3 times the instrument's noise level (3:1 signal to noise ratio).
   - It is specific to each combination of analyte, matrix, method and instrument configuration.
   - The LOD must be verified quarterly on each instrument (spiked at LOD) using the criteria listed above.
3. If the LOD verification fails (per #2), repeat the detection limit determination and LOD verification at a higher concentration or perform and pass two consecutive LOD verifications at a higher concentration and set the LOD at the higher concentration.
4. The laboratory shall maintain documentation for all detection limit determinations and LOD verifications (regardless of pass or fail).

11.17 Retention Time Windows

Retention time windows for each target analyte must be generated whenever there is a major change in instrument conditions including flow rates or when standard analyses result in analyte retention times outside the established windows. The procedure for determining the retention time windows for this method is as follows. However, other approaches may be employed, providing that the analyst can demonstrate that they provide performance appropriate for the intended application. For example, the analyst may use the corresponding retention times from the initial calibration as they may show shifts in RTs due to the volume injected (higher concentrations lead to wider peaks).

1. Make sure that the system is operating reliably and that the system conditions have been optimized for the target analytes in the sample matrix to be analyzed.
2. Make four injections of all applicable standard mixes over a 72-hour period. Make the injections cover the entire 72-hour period or the end result could be windows, which are too tight.
3. Record the retention time for each single component analyte to three decimal places. Calculate the mean and standard deviation of the four absolute retention times for each single component analyte.
4. If the standard deviation of the retention times for the target compound is 0.000, then additional injections may be included or the use of a default standard deviation of 0.01 minutes.
5. The width of the retention time window for each analyte is defined as ±3 times the standard deviation of the mean absolute retention time established during the 72-hour period. If the default standard deviation of 0.01 is used, the width of the window will be 0.03 minutes.
6. Establish the center of the retention time window for each analyte by using the absolute retention time for each analyte in the continuing calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.
7. Retention time windows must be calculated for each analyte on each column and instrument. New retention time windows must be established when a new column is installed or if analysis parameters are changed.

12) Quality Control Requirements and Corrective Action

12.1 This section of the standard operating procedure contains technical acceptance criteria and preferred corrective actions to data nonconformities. Corrective actions shall follow the procedures outlined in the *SOP for Nonconformance and Corrective Action*, where appropriate.

12.2 To the extent possible, samples shall be reported only if all of the quality control measures are acceptable. If a quality control measure is found to be out of control and the data must be reported, all samples associated with the out of control quality control measure shall be reported with the appropriate data qualifier(s).

12.3 Initial Calibration

The Instrument must be recalibrated initially, whenever the laboratory takes corrective action (i.e. maintenance, which may change or affect the initial calibration criteria), or if the continuing calibration acceptance criteria have not been met.

12.3.1 Acceptance Criteria

- The percent relative standard deviation (% RSD) of the analytes of each of the levels must be less than 20% for the calibration to be considered acceptable.
- All initial instrument calibrations must be verified with a standard obtained from a second manufacturer or lot (see Section 9.4.2).
- The retention time for each analyte (at each calibration level) must within 0.10 minutes of the mean RT over the ICAL range. However it must be noted that higher injection volumes and/or higher concentrations of any analyte may not meet this criteria, which is acceptable.

12.3.2 Corrective Action

If the initial calibration technical acceptance criteria are not met, inspect the system for possible sources. It may be necessary to replace the syringe needle, column, Teflon tip on the syringe plunger or take other corrective actions such as clean or replace the detector to meet the initial calibration technical acceptance criteria. A demonstration of an in-control system is required before proceeding with the analysis. Refer to Section 11.4 for the initial calibration requirements as it includes information on dropping points. Also, check standards for a bad injection and re-analyze standard. If a bad injection is not evident, perform maintenance and attempt another initial calibration (make notation in maintenance logbook regarding any steps taken). Note in the run log that the initial ICAL was not used. Upon the completion of another unacceptable ICAL, the expiration date of the standards will be evaluated and new standards prepared if necessary.

12.4 Initial Calibration Verification (ICV) Standard

12.4.1 Acceptance Criteria

The percent difference of each calculated analyte concentration (per detector) must be within ±15% of the actual concentration of the standard.

12.4.2 Corrective Action If the initial calibration verification fails to meet the acceptance criteria, it must be reanalyzed. A second failed ICV must initiate corrective action and two consecutive standards must pass in order for the ICAL to be deemed acceptable. It may be necessary to prepare either new ICAL or ICV standards, perform maintenance or reanalyze the initial calibration. A demonstration of an in-control system is required before proceeding with the analysis.

12.5 Continuing Calibration Verification (CCV) Standard

12.5.1 Acceptance Criteria

All continuing calibration verification standards within an analytical sequence must be evaluated against the following acceptance criteria.

- The percent difference (%D) for each calculated target analyte must be within ≤15%.
- The RT of each analyte in the CCV must fall within 0.33 minutes of the mean RT from the ICAL.

12.5.2 Corrective Action

If the criteria are not met a second continuing calibration standard shall be analyzed. If the result is still unacceptable per this SOP, then the analyst must demonstrate performance after corrective action with a successful calibration verification or initial calibration. If there has not been evidence of acceptable performance then samples may not be analyzed until a successful ICAL is established and verified. However, sample data associated with unacceptable calibration verification may be reported as qualified data under the following special conditions:

1. When the acceptance criteria for the continuing calibration verification are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then any non-detects may be reported. Otherwise the samples affected by the unacceptable calibration verification shall be reanalyzed after a new calibration curve has been established, evaluated and accepted.
2. When the acceptance criteria for the CCV are exceeded low, i.e., low bias, those sample results may be reported if they exceed a known maximum regulatory limit. Otherwise the samples affected by the unacceptable calibration verification shall be reanalyzed after a new calibration curve has been established, evaluated and accepted.

Note: No greater than two consecutive CCV standards may be analyzed before corrective action is initiated.

DoD QSM Requirement: If a CCV fails, the laboratory must immediately analyze two additional consecutive CCVs (immediately is defined as within one hour).

- Both of these CCVs must meet acceptance criteria in order for samples to be reported without reanalysis.
- If either of these two CCVs fail or if the laboratory cannot immediately analyze two CCVs, the associated samples cannot be reported and must be reanalyzed.
- Corrective action(s) and recalibration must occur if the above scenario fails. All affected samples since the last acceptable CCV must be reanalyzed.
- Flagging data for a failed CCV is only appropriate when the affected samples cannot be reanalyzed. The laboratory must notify the client prior to reporting data associated with a failed CCV.

12.6 Reagent Blank (RB)

12.6.1 Acceptance Criteria

The main purpose for analyzing the reagent blank is to verify the zero point of the analytical system and to evaluate carryover. Review Section 5.5 for information on methane interference. The analyte concentrations (in ppm) for

the RB (He) must not be greater than the reporting limit. Typically, the only analyte with a concentration close to the criteria is the methane interference peak. It is not necessary to run the integrated concentrations through the worksheet to evaluate the acceptance criteria. The action limit for this peak is considered to be approximately 0.15ppm (without putting it through the worksheet calculations) and it must be reanalyzed.

12.6.2 Corrective Action

If the analyte results in the RB do not meet the acceptance criteria determine whether the cause is instrumentation problems or the result of a poor injection. If the problem is with the injection, re-analyze the RB. However, if the cause is due to an instrumentation problem, maintenance must be performed, along with the proper logbook documentation, and the RB re-analyzed.

12.7 Laboratory Control/Laboratory Control Sample Duplicate (LCS/LCSD) Analysis

12.7.1 Acceptance Criteria

- The LCS and LCSD percent recovery must fall within the laboratory generated limits where available. If limits are not available the percent recovery must fall within 70% to 130% for all analytes except CO2. The LCS/LCSD percent recovery for CO2 shall be 50-150%.
- The reproducibility of the LCS/LCSD are considered acceptable when the results agree within the laboratory generated limits where available. If limits are not available, the RPD must be ±15% for all analytes except CO2 which shall be ±30%.
- DoD Requirement: Refer to Attachment 4 for DoD QSM acceptance criteria.

12.7.2 Corrective Action

An out of control LCS may be an indication of a problem with the sample preparation or analysis portions of the procedure. It is important to evaluate the cause to determine if the samples have been affected in the same or similar manner and therefore, will be reported either bias high or bias low depending on the percent recovery of the LCS/LCSD. If the LCS criteria are not met, determine whether the cause is instrumentation problems, result of poor injection or a problem with sample preparation. If necessary, perform maintenance and if the problem is with the injection re-analyze the sample. All samples processed with an out of control LCS will require to be re-prepared/analyzed if sufficient backup samples are available or have data qualifiers attached to the analytical results.

12.8 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Analysis

12.8.1 Acceptance Criteria

- The percent recovery must fall within fixed control limits of 50%-150%.
- Analytes must have a RPD of ±30%.
- DoD Requirement: Refer to Attachment 4 for DoD QSM Acceptance Criteria.

12.8.2 Corrective Action

If the criteria are not met, determine if there was an injection problem. If this is the case then reanalyze one or both of the samples. If they are still unacceptable and there is an assignable cause such as matrix interferences the results should be qualified.

12.9 Method Control Sample

12.9.1 Acceptance Criteria

Due to the nature of water, there is no true blank for carbon dioxide. Therefore, results for the MCS are reported to the client. However, any other detected analytes must not exceed the method reporting limit.

For DoD samples, the method control sample will be considered to be contaminated if:

1. The concentration of any target analyte in the blank exceeds 1/2 the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater);
2. The concentration of any common laboratory contaminant in the blank exceeds the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater); or
3. The blank result otherwise affects the samples results as per the test method requirements or the project-specific objectives.

The laboratory shall evaluate whether reprocessing of the samples is necessary based on the above criteria.

12.9.2 Corrective Action

If the analyte results in the MCS do not meet the acceptance criteria the source of the problem must be investigated and measures taken to eliminate the source. Determine whether the contamination is from the instrument or due to contamination in the helium, nitrogen, syringe, or other source. Regardless, appropriate corrective measures must be taken and documented. If the result in the MCS has been determined to originate from the previous sample the MCS may be reanalyzed. If the results are the same, the MCS along with all associated samples must be reported to the client with the appropriate qualifiers.

12.10 Sample Analysis

Sample results must be quantitated from the current instrument initial calibration and may not be quantitated from any continuing calibration verification standard.

12.10.1 Acceptance Criteria

- The field samples must be analyzed along with a laboratory method control sample that met the MCS criteria in Section 12.9.
- All target analyte peaks must be within the initial calibration range.
- All analytes must be within the retention time windows, utilizing the CCV (or midpoint concentration, if analyzing samples during the same sequence as the ICAL) as the absolute RT.
- All analytes must be within 0.33 minutes of the mean RT of the ICAL.
- Once the samples have been prepared they must be analyzed the same day in order to prevent loss of sample integrity.
- All batch QC samples must be prepared and analyzed with submitted samples so that sample integrity may be further evaluated and the results reported accordingly.

12.10.2 Corrective Action

To the extent possible, samples shall be reported only if all of the quality control measures are acceptable. If a quality control measure is found to be out of control, and the data must be reported, all samples associated with the out of control quality control measure shall be reported with the appropriate data qualifier(s). When corrective actions are made, samples analyzed while the system was not functioning properly must be reanalyzed.

- Results not bracketed by initial instrument calibration standards (within calibration range) must be analyzed with a smaller injection volume or reported as having less certainty, e.g., defined qualifiers or flags.
- The retention time of the analyte must meet the criteria to be considered a reportable result.
- If the pH reading indicated that the sample was preserved and CO_2 is to be reported the result must be reported as estimated.
- Field and batch QC samples exceeding the same day hold time requirement between preparation and analysis must be re-prepared and analyzed.

12.11 Laboratory Duplicate

12.11.1 Acceptance Criteria

The results must meet all of the criteria stated in Section 12.10 and be within the laboratory generated limits where available. If these limits are not available for a particular analyte the RPD must be ±15%. This is required provided that the analytes are at least 10 times the method reporting limit.

12.11.2 Corrective Action

If the replicate results do not fall within the technical acceptance window, the sample should be re-analyzed. If the results are still unacceptable and there does not appear to be any matrix effects, interfering peaks, or instrument problems, the results for both injections shall be reported to the client.

12.12 Replicate Field Sample

Due to the variation in analyte concentrations (this is especially true for methane and carbon dioxide) for replicate sample submissions, results will be reported to the client as separate samples.

13) Data Reduction and Reporting

13.1 Quantitation

The headspace result for each analyte (in ppm) from the Hewlett Packard Chemstation data system shall be entered into a Microsoft Excel worksheet. The worksheet calculates the final concentration of dissolved gas in the liquid sample for each target analyte based on the calculations specified in this section.

Each chromatogram must be carefully scrutinized for errors in integration performed by the Enviroquant Chromatography Data Processing Program (CDPP). If it is determined that an analyte peak was incorrectly integrated or if a peak was misidentified the peak must be manually integrated in accordance with the *SOP for Manual Integration.*

13.2 Initial Calibration

The initial calibration curve must be saved with a two letter identification followed by the date of the analysis (mm,dd,yy). No curve may be overwritten at any time to ensure a complete and accurate audit trail.

- Tabulate the peak area along with standard concentration injected to determine the response factor (RF) for each analyte at each concentration using equation number 10.
- Calculate the percent relative standard deviation (%RSD) of the mean RF (equation number 11) for each analyte using equation numbers 7 and 8.
- Determine the mean retention time of each analyte spanning the initial calibration range using equation number 5.

13.3 Initial Calibration Verification

- Calculate the concentration for each analyte using equation numbers 1-4.

- Calculate the % difference between calculated concentration (see above) and the actual concentration using equation number 9.
- Determine the retention time difference for each analyte between the initial calibration and the ICV using equation number 6.

13.4 Continuing Calibration Verification

- Calculate the concentration for each analyte using equation numbers 1-4 for each standard analyzed within a given analytical sequence.
- Calculate the % difference between the calculated concentration (for each CCV in a sequence, see above) and the actual concentration using equation number 9.
- Determine the retention time difference for each analyte between the initial calibration and the each CCV in the sequence using equation number 6.

13.5 Laboratory Control Sample / Duplicate Laboratory Control Sample

- Calculate the concentration for each analyte using equation numbers 1-4.
- Calculate the percent recovery (%R) for all analytes in both the LCS and LCSD (for both detectors, if applicable) using equation number 12.
- Calculate the relative percent difference in the LCS and LCSD, for each detector (if applicable) for each of the target analytes using equation number 13.

13.6 Matrix Spike / Matrix Spike Duplicate (if applicable)

- Calculate the concentration for each analyte using equation numbers 1-4.
- Calculate the relative percent difference in the MS and MSD for each of the target analytes using equation number 13, if applicable.
- Calculate the percent recovery (%R) for all analytes in both the MS and MSD (if applicable) using equation number 12.

13.7 Sample Analysis

Quantitative Analysis - Calculate the concentration for each analyte using equation numbers 1-4.

13.8 Laboratory Duplicate

- Calculate the concentration for each analyte using equation numbers 1-4.
- Determine the relative percent difference calculated using equation number 13.

13.9 Duplicate Field Samples

- Calculate the concentration for each analyte using equation numbers 1-4.

13.10 Calculations

13.10.1 Equation Number 1

Headspace Concentration (ppm)

$H_p = [(D)(1)/V_i]DF$

where:

D is the concentration in ppm from the HP Chemstation data system

1 is the default injection volume (1 ml) as required by the data system

V_i is the actual headspace injection volume in milliliters

DF is any applicable dilution factor

H_p is the concentration in ppm in the headspace

13.10.2 Equation Number 2

Headspace Concentration (µg/L)

$$H_m = H_p \times \frac{1}{10^6} \times \frac{1\ \text{mole}}{24.06\text{L}} \times \frac{MW_{(g)}}{1\ \text{mole}} \times \frac{10^6 \text{ug}}{1\text{g}}$$

where:

H_p is the concentration in ppm in the headspace

MW is the molecular weight in grams of the analyte in question

24.06 is the gas constant at 1 atm pressure and 20°C

$(1/10^6)$ coverts ppm to a decimal (ppm to Atm)

H_m is the concentration in µg/L in the headspace

13.10.3 Equation Number 3

Equilibrated Water Concentration (µg /L)

$$E_w = \frac{(H_p)(M_w)(MW)(1 \times 10^3)\ (1 \times 10^3)}{(1 \times 10^6)(C)}$$

the units in the above equation cancel as follows:

$$\mu g/L = \frac{(ppm)(moles/L)(g/mole)(mg/g)(\mu g/mg)}{(ppm/atm)(atm/mole\ fraction)}$$

where:

E_w is the concentration of dissolved gas in mg/L in the equilibrated water (liquid phase)

H_p is the concentration in ppm in the headspace

M_w is the number of moles of water in one liter (55.51 moles/liter)

MW is the molecular weight of the analyte of interest in g/mole

1×10^3 mg/g is the factor used to convert from grams to milligrams

1×10^3 µg/mg is the factor used to convert from milligrams to micrograms

1×10^6 ppm/atm is the factor used to convert from ppm to partial pressure

C is the Henry's law constant* for the analyte in question in atm/mole fraction

Henry's Law Constants at 20°C (atm/mole fraction)

Methane 3.76×10^4
Ethane 2.63×10^4
Ethylene (Ethene) ..... 1.02×10^4
Propylene (Propene)..... 6.00×10^3
Propane 7.06×10^4
Carbon dioxide..... 1.42×10^3

13.10.4 Equation Number 4

Dissolved Gas Concentration (µg/L)

$$W = \frac{(H_m)(V_h)}{(V_s)} + E_w$$

where:
W is the concentration of dissolved gas in mg/L in the zero headspace sample;
H_m is the concentration in mg/m³ in the headspace;
V_h is the volume of headspace in milliliters added to the sample;
V_s is the volume of sample in milliliters remaining after displacement.

13.10.5 Equation Number 5

Mean Retention Times ($\overline{RT}$)

$$\overline{RT} = \sum_{i=1}^{n} \frac{RT_i}{n}$$

Where:

$\overline{RT}$ Mean retention time, minutes
RT_i Retention time for the analyte in the standard, minutes
n number of standards

13.10.6 Equation Number 6

Retention Time Difference (RTD)

$$\left| RT_c - RT_s \right|$$

where:

RT_C Retention time of the target compound in the CCV, minutes.
RT_S Retention time of the compound in the standard, minutes.

13.10.7 Equation Number 7

Standard Deviation, SD

$$SD = \sqrt{\sum_{i=1}^{N} \frac{\left(RF_i - \overline{RF}\right)^2}{N-1}}$$

where:

RF_i are the individual RFs from each concentration level in the initial calibration curve

$\overline{RF}$ Average (or Mean) RF of all concentration levels in the initial calibration curve
N total number of calibration concentration levels

13.10.8 Equation Number 8

Percent Relative Standard Deviation, %RSD

$$\%RSD = \frac{SD}{\overline{RF}}(100)$$

where:

SD Standard Deviation calculated in equation number 3
$\overline{RF}$ Average or Mean RF

13.10.9 Equation Number 9

Percent Difference, %D

The %D is used for evaluating ICV and CCV vs. the initial calibration

$$\%D = \frac{C_{CCVorICV} - C_{std}}{C_{std}}(100)$$

where, for any given analyte:

$C_{CCVorICV}$ is the concentration being evaluated.
C_{std} is the concentration from the current calibration curve;
C_{std} actual concentration x injection volume.

13.10.10 Equation Number 10

Response Factor (RF)

The response factor, for analyte *x* is given by:

$$RF = \frac{A_x}{C_x}$$

where:

A_x = Area of the analyte in the standard
C_x = Concentration of the analyte in the standard, in ppm

13.10.11 Equation Number 11

Average (or Mean) RF

$$\overline{RF} = \frac{\sum_{i=1}^{N} RF_i}{N}$$

where:

RF_i are the individual RFs from each concentration level in the initial calibration curve.
N is the number of calibration concentration levels.

13.10.12 Equation Number 12

Percent Recovery (%R)

$$\%R = \frac{C}{S} x100$$

where:

C = Concentration of the analyte recovered
S = Spiked amount

13.10.13 Equation Number 13

Relative Percent Difference (RPD)

$$\frac{|R_1 - R_2|}{\left(\frac{R_1 + R_2}{2}\right)} x100$$

where:

R_1 First measurement value
R_2 Second measurement value

13.11 Data Review

The analyst must review data on a real time basis for all calibration and QC data. Any samples, QC samples or batch QC found to be unacceptable will require to be handled according to the guidelines described in this procedure. Also, the results must not be reported until they are appropriately reviewed and approved according to this SOP. The QC data must be evaluated by analytical sequence following the data review checklist in Attachment C. In order to access batch precision, the laboratory duplicate must be checked against the acceptance criteria detailed in this document for all reported samples. Since matrices differ, matrix spikes or matrix spike duplicates are not used to evaluate batch performance. They are utilized to access the ability of the method to produce acceptable results for particular sample matrices.

The data shall be reviewed and the sample results calculated and assessed by one analyst and reviewed by a second qualified analyst. The data review checklist must be used to document the reviews and once it has been completed, initialed and dated it is to be filed with each job file. In addition, the data review process shall be conducted in accordance with both the *SOP for Data Review and Reporting* and the *SOP for Laboratory Ethics and Data Integrity*.

Initial calibrations must be reviewed with all ICAL documentation retained in a separate file organized by instrument and date. Refer to the initial calibration checklist in Attachment B for the review guideline. The ICAL file must contain all the pertinent information stated in Section 11.4.3.

13.12 Reporting

The results of each test shall be reported clearly, unambiguously and objectively, and shall include all the information necessary for the interpretation of the test results and all information required by this SOP and the *SOP for Data Review and Reporting.*

If reporting carbon dioxide, and the pH reading indicated that the sample was acid preserved, the report shall include a qualifier (refer to Section 16.8.3).

If the laboratory recommended hold time of 14 days is exceeded for propane, propene, or carbon dioxide a notation in the case narrative is required (no data flags are required).

13.13 Sample Preparation and Analysis Observations / Case Narrative Summary Form

This form, which is included in the *SOP for Laboratory Storage, Analysis and Tracking*, must be generated when there are specific sample composition information or analysis issues and/or observations. In addition, during the analysis, specific identification information or problems, interferences, calibration issues, flags, and additional/expanded explanation of flags should be added to the form. This form may be modified as long as the sections and basic concepts are reserved.

This form is necessary as a means for documentation. This form, among other information, will be reviewed when compiling the final report and case narrative. All information regarding the job shall remain in the file, in order that sufficient documentation is available to recreate the job from sample receipt through analysis, data reduction, and reporting.

13.14 Sufficient raw data records must be retained of the analysis (field samples, calibration standards and batch QC), instrument calibrations and method detection limit studies. This includes analysis/calibration date, test method, instrument, sample identification, each analyte name, analyst's initials, concentration and response, and standards used for the analysis and calibrations as well as any manual integrations. All information entered and reported on the quantitation reports must be complete and accurate.

13.15 The essential information to be associated with analysis, such as computer data files, run logs, etc. shall include: Sample ID code, date and time of analysis, instrument operating conditions/parameters (or reference to such data), analysis type, all manual calculations including dilutions and manual integrations, analyst's initials, sample preparation, standard and reagent origin, receipt, preparation, and use; calibration criteria, frequency and acceptance criteria, data and statistical calculations, review, confirmation, interpretation, assessment and reporting conventions.

14) Method Performance

14.1 An on-going assessment of method performance is conducted in order to ensure that the laboratory is capable of reporting results which are acceptable for its intended use. Validation of the method is confirmed by the examination and provision of objective evidence that these requirements are met.

14.2 Method Detection Limit (MDL)

The procedure used to determine the method detection limits are as stated in the *Code of Federal Regulations* (40 CFR 136 Appendix B) as defined in the *SOP for Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation.* The MDL is defined as the minimum concentration of a substance that can be measured

and reported with 99% confidence that the value is above zero or blank concentration. MDLs can be obtained using standards at a concentration of about 0.3ug/L to 0.9ug/L and making at least seven replicate measurements of the compounds of interest, computing the standard deviation, and multiplying this value by the appropriate Student's t value for 99 percent confidence.

The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects. Refer to Section 11.16.1 for the LOD verification criteria.

14.3 Accuracy and Precision

Refer to Section 12.11 for information on replicate precision criteria for method performance. Single laboratory accuracy is presented as the second source initial calibration verification standard, which meets the method performance criteria of 15%. Additionally, laboratory generated control limit data for LCSs are presented for the analytes of interest and may be referenced in Attachment D. Refer to Section 11.6 for the accuracy and precision LOQ requirements.

14.4 Demonstration of Capability

This laboratory has continuously performed this method since before July 1999. Ongoing demonstration of capability shall be performed and documented; however, the initial demonstration of method capability is not required.

14.5 Proficiency Testing (PT) Program

Proficiency testing samples are not available from a third party for this method. Repeatability studies will be performed biannually to meet the DoD QSM proficiency testing requirements. A minimum of eight QC analyses performed over multiple days or on the same day will be compiled. Statistical validity will be assessed by evaluating results against LCS control limits and an RSD of 15%.

15) Pollution Prevention and Waste Management

15.1 The following wastes are generated during the analysis of groundwater samples by RSK 175 method: liquid samples (neutral or pH 2), displaced sample volume (8 mL), intermediate gaseous standards and purchased intermediate and stock gaseous standards. All of the waste shall be disposed of in accordance with the *Simi Valley Lab Waste Management Plan.*

16) Contingencies for Handling Out-of-Control or Unacceptable Data

16.1 All results that are out of control must be qualified on the corresponding final reports. It is important to provide the client with all of the appropriate information regarding the sample analysis, QC and batch QC.

16.2 Initial Calibration/Initial Calibration Verification

No data shall be reported which are associated with an out of control ICAL or ICV.

16.3 Continuing Calibration Verification

Refer to Section 12.5.2 for sample reporting criteria associated with an unacceptable CCV value.

16.4 Reagent Blank

No samples may be analyzed or data reported which are associated with an out of control RB/system.

16.5 Laboratory Control Sample/Laboratory Control Sample Duplicate

All samples processed with an out of control LCS will require to be re-prepared/analyzed if sufficient backup samples are available or have data qualifiers attached to the analytical results.

16.6 Matrix Spike/Matrix Spike Duplicate

If the client requests the MS or MS/MSD results, they must either have a data qualifier or a discussion in the case narrative.

16.7 Method Control Sample

Results for carbon dioxide are not considered a contamination and shall be reported to the client. However, all other sample results associated with a "contaminated" method control sample must be "flagged" in the report and/or discussed in the case narrative.

16.8 Field Samples

When sample quality control results are out-of-control: examine the sample results for matrix interferences and for carry-over. Re-analyze the samples and/or re-analyze the sample(s) at a lower aliquot. If the out-of-control results are due to matrix interferences, report the results with a matrix interference qualifier.

16.8.1 Sample Preparation and Analysis Holding Times

A statement dictating all holding time occurrences (most specifically, the same day requirement between preparation and analysis) must accompany the sample results in the final report. However, if all samples including QC samples are prepared and analyzed together, the LCS/LCSD results may be evaluated in order to determine the estimated loss of sample integrity, especially if this time limit has been exceeded. If the results for the LCS/LCSD do not meet the acceptance criteria all results shall be flagged, noted as being estimated and the reason included in the case narrative.

16.8.2 ICAL Dynamic Range

Results not bracketed by initial instrument calibration standards (within calibration range) must be reported as having less certainty, e.g., defined qualifiers or flags or explained in the case narrative.

16.8.3 pH for Carbon Dioxide

If the pH reading indicated that the sample was preserved and CO_2 is to be reported the result must be reported as estimated.

16.8.4 Thermal Preservation

A comment must be included in the case narrative or a reference to the Sample Acceptance Check form for samples that are received outside of the required temperature.

16.9 Laboratory Duplicate

The appropriate data qualifier or a discussion in the case narrative must be included with an out of control LD result. The LD may be accessed with the LCS/LCSD and reported accordingly.

17) Training

17.1 Demonstration of Capability

Training demonstrations shall be conducted in accordance with the *SOP for Training Policy,* DoD QSM, and TNI requirements. An initial demonstration of proficiency must be

performed prior to independent analyses of samples. In addition, ongoing demonstration must be performed annually.

Once performance is found to be acceptable, a required certification statement must be completed by the QA Manager and either the immediate supervisor or Laboratory Director and retained on file as a demonstration of compliance.

17.1.1 Quarterly Demonstration A demonstration of method sensitivity must be performed *quarterly on each instrument* performing this method.

1) A spike at the current LOD must be analyzed.
2) Verification of precision and bias at the LOQ must be performed.

Refer to Section 11.6 (LOQ) and 11.16.1 (LOD) for additional information on how these demonstrations are to be performed as well as the acceptance criteria.

17.1.2 Annual Demonstration Each analyst must perform this demonstration both initially and annually. Analyze four LCS standards at 1-4x the MRL (LOQ) either concurrently or over a period of days as a verification of precision and bias of the quantitation range. The standard deviation (n-1) and average percent recovery of the four replicates are compared against current laboratory control limits for precision and bias. See Attachment E.

17.1.3 Change in Personnel, Instruments, Method and/or Matrix The requirements in Sections 17.1.1 and 17.1.2 must be performed per the schedule noted and when there is a change in personnel, instruments, method or matrix. "Change" refers to any change in personnel, instrument, test method, or sample matrix that potentially affects the precision and bias, sensitivity, or selectivity of the output (e.g., a change in the detector, column type, matrix, or other components of the sample analytical system, or a method revision).

All attempts at this demonstration must be completed and turned into the QA department for retention.

18) Summary of Changes

Table 18.1 Summary of Revision Changes

Revision Number	Effective Date	Document Editor	Description of Changes
18.0	03/14/2020	C. Arend	Cover Page – updated Laboratory Director name
			2.1 – updated 3rd sentence to align with current procedure
			3.24 – removed last sentence
			5.5 – revised to align with current MDL procedure
			8.3.1 – removed last bullet (Sonicator)
			9.4.1.1 – updated 1st and 2nd SOP titles
			11.12 – replaced "(after sonication)" with "(after shaking)"
			11.12.1 – #8 revised to align with current procedure
			11.15 – updated SOP title
			11.16 – 2nd paragraph last sentence corrected MRL to MDL
			13.1 – updated SOP title
			13.10.2 – reformatted equation
			19.6 – updated reference
			19.7 – updated reference

			Attachment 1 - #4 updated 3rd SOP title
			Attachment 2 - #11 updated SOP title
			Attachment 4 – updated control limits and removed Note on MDL Table (no longer applicable)

19) References and Related Documents

19.1 D. H. Kampbell, J. T. Wilson and S. A. Vandegrift, *Dissolved Oxygen and Methane in Water by GC Headspace Equilibration Technique*, Intern. J. Environ. Anal. Chem., Vol. 36, pp. 249-257, Gordon and Breach, Science Publishers. Inc., 1989.

19.2 *CRC Handbook of Chemistry and Physics*, 66th edition.

19.3 *Hawley's Condensed Chemical Dictionary*, 11th edition.

19.4 *Wastewater Engineering*, Metcalf and Eddy, Inc. McGraw-Hill, 1972.

19.5 Perry, J. H., *Chemical Engineer's Handbook*, McGraw-Hill, New York, 1978, 5th ed.

19.6 DoD/DoE QSM, *Department of Defense (DoD), Department of Energy (DoE) Quality Systems Manual (QSM) for Environmental Laboratories*, Current Version.

19.7 TNI Standard 2009 and 2016, Volume 1, *Management and Technical Requirements for Laboratories Performing Environmental Analysis.*

20) Attachments

20.1 <u>Attachments</u>

Attachment 1 – Training Plan

Attachment 2 – Initial Calibration Checklist

Attachment 3 – Data Review Checklist

Attachment 4 – MDLs, LODs, MRLs, and Control Limits

Attachment 1

Training Plan

Training Plan for Analysis of Dissolved Gases by GC/FID/TCD

Trainee _____ Trainer _____ Instrument _____

1. Read SOP Trainer ____ Trainee ____ Date _____

2. Read Article: "Dissolved Oxygen and Methane in Water by GC Headspace Equilibration Technique" Trainer ____ Trainee ____ Date _____

3. Demonstrated understanding of the scientific basis of analysis Trainer ____ Trainee ____ Date _____

   Gas chromatography Thermal Conductivity Detector
   Henry's Constant Flame Ionization Detector

4. Demonstrated familiarity with related SOPs Trainer ____ Trainee ____ Date _____

   SOP for Batches and Sequences
   SOP for Making Entries onto Analytical Records
   SOP for Manual Integration
   SOP for Significant Figures
   SOP for Nonconformance and Corrective Action
   SOP for Performing MDL Studies and Establishing Limits of Detection and Quantitation

5. Observe performance of SOP Trainer ____ Trainee ____ Date _____

   ___standard preparation
   ___sample preparation
   ___analytical sequence setup
   ___initial calibration and initial calibration verification
   ___continuing calibration verification
   ___batch QC sample setup
   ___sample analysis
   ___EnviroQuant introduction
   ___data reduction and reporting

6. Perform SOP with supervision Trainer ____ Trainee ____ Date _____

   ___standard preparation
   ___sample preparation
   ___analytical sequence setup
   ___initial calibration and initial calibration verification
   ___continuing calibration verification
   ___batch QC sample setup
   ___sample analysis
   ___EnviroQuant use
   ___data reduction and reporting

7. Independent performance of the SOP Trainer ____ Trainee ____ Date _____

   ___standard preparation
   ___sample preparation and sample analysis
   ___analytical sequence setup including batch QA sample preparation
   ___initial calibration, initial calibration verification, and continuing calibration verification
   ___EnviroQuant proficiency
   ___data reduction and reporting
   ___initial demonstration of competency
   ___ Four consecutive laboratory control samples

8. Instrument operation and maintenance Trainer ____ Trainee ____ Date _____

   ___gas chromatograph and capillary column installation
   ___detector (FID) setup and maintenance
   ___detector (TCD) setup and maintenance ____data system

Attachment 2

Initial Calibration Checklist

Initial Calibration Checklist (Dissolved Gases in Water by RSK-175)

Analysis: RSK-175

ICAL Date _____ Instrument ☐ GC10 ☐ GC _____

Analyst **Reviewer**

☐ 1. Is the required documentation in the ICAL file? ☐
- ☐ Sequence report
- ☐ Blank analysis Quantitation Report
- ☐ Calibration Status Report (aka Calibration History) – Initial
- ☐ Response Factor Report
- ☐ Quantitation Report for each calibration standard (including manual integration documentation – before and after printouts)
- ☐ ICV Quantitation Report and Evaluate Continuing Calibration Report (aka % Diff. report)

☐ 2. ICAL performed continuously (i.e., not interrupted for maintenance or sample analysis)? ☐

☐ 3. Was the ICAL, including any re-analysis, performed within a 48 hour period? ☐

☐ 4. Were the standards analyzed from low concentration to high concentration? ☐

☐ 5. For each analyte, is the lowest standard's concentration at or below the MRL? ☐

☐ 6. Does each analyte's ICAL include a minimum of 5 consecutive concentrations? ☐

☐ 7. For each analyte, is there only one value used for each calibration level? ☐

☐ 8. If a point is dropped, is information noted in the ICAL explaining the reason? ☐

☐ 9. If a point was dropped from the interior was there a proper assignable cause? ☐

☐ 10. For each analyte, are there no levels skipped? ☐

☐ 11. Are all peak integrations including manual integrations (per *SOP for Manual Integration*) acceptable? *If so, initial and date the appropriate pages.* ☐

Quality Control

☐ 12. The %RSD for each analyte is ≤20%? ☐

☐ 13. For the ICV analysis, is the percent recovery for each analyte 85-115%? ☐

☐ 14. The RT for each target compound at each level within the generated retention time window (using the midpoint as the absolute RT) and within 0.1min of the mean RT? ☐

☐ 15. All analytes in the MB are ≤MRL (as long as low standard from the ICAL is ≤MRL)? ☐

COMMENTS:

_____

_____

_____

_____

Analyst _____ Secondary Reviewer _____

Date _____ Date _____

Attachment 3

Data Review Checklist

Dissolved Gases in Water by RSK-175
Data Review Checklist
(Note exceptions and include Sample Preparation and Analysis Observations / Case Narrative Summary Form as appropriate)

Analysis Date _____ Instrument ☐ GC10 ☐ GC ___ Analyst _____

QC Level _____ Project # _____ Due Date _____

Analyst **Reviewer**

Initial Calibration

☐ 1. Is the referenced ICAL the most recent ICAL performed? ..... NA

Continuing Calibration

☐ 2. Does each CCV in the sequence have a %difference of ≤15%? ..... ☐

☐ 3. RT for each analyte for each CCV fall within 0.33min of the mean RT from the ICAL? ..... ☐

Batch QC

☐ 4. Is the laboratory duplicate within 15% of their average (for all hits 10x the RL)? ..... ☐

☐ 5. LCS/LCSD RPD within lab generated limits (where available), RPD±15% others (CO2 30%)? ..... ☐

☐ 6. LCS/LCSD recovery within lab generated limits (where available), 70-130% others (CO2 50-150%)? ..... ☐

DoD: Must meet DoD QSM LCS/DLCS limits

☐ 7. Is the MS/MSD (RPD) within ±30%?; Is the recovery within 50-150%? ..... ☐

DoD: MS/MSD must meet DoD QSM LCS/DLCS limits

☐ 8. Are all the analytes in the Method Control Sample (MCS) < the MDL? ..... ☐

Sample Data

☐ 9. All target analyte responses are within calibration range? ..... ☐

☐ 10. Are peak integration are acceptable? ..... ☐

☐ 11. All manual integrations flagged and documented (before and after)? If so, initial and date. ..... ☐

☐ 12. All analyte peaks are within corresponding RT window using the CCV as the absolute RT? ..... ☐

☐ 13. All analyte peaks within 0.33min of the mean RT from the ICAL? ..... ☐

☐ 14. All calculations correct? ..... ☐

☐ 15. First quantitation report initialed and dated by analyst? ..... ☐

☐ 16. **DOD:** Are manual integrations notated in the case narrative? ..... ☐

Documents Included

☐ 17. Injection Log (optional) ..... ☐

☐ 18. Sample raw data ..... ☐

☐ 19. CCV Analysis Quantitation Report and Evaluate Continuing Calibration Report (%D report) ..... ☐

☐ 20. LCS/LCSD Analysis Quantitation Report ..... ☐

☐ 21. MCS Analysis Quantitation Report ..... ☐

☐ 22. MS/MSD Analysis Quantitation Report, if applicable ..... ☐

☐ 23. Laboratory Duplicate Analysis Quantitation Report, if applicable ..... ☐

☐ 24. Quantitation Report for each sample (including manual integration documentation) ..... ☐

COMMENTS:

_____

_____

☐ LIMS Run Approval ☐ LIMS Supervisor Approval

Analyst _____ Secondary Reviewer _____

Date _____ Date _____

Attachment 4

Method Detection Limits, Limits of Detection, Method Reporting Limits, and Control Limits

Method Detection Limits, Limits of Detection, and Method Reporting Limits

Analyte	MDL	LOD	MRL	Units	Comments
Methane	0.51	1.0	1.3	ug/L	DoD Certified
Ethylene (Ethene)	0.24	0.55	1.0	ug/L	DoD Certified
Ethane	0.16	0.47	0.60	ug/L	DoD Certified
Propane	0.26	-	1.0	ug/L	
Propylene	0.45	-	1.0	ug/L	
Carbon dioxide	370	860	1000	ug/L	DoD Certified

The method detection and reporting limits may change with each new MDL study and ICAL performed, check the current documentation for verification.

Laboratory Control Sample / Laboratory Control Sample Duplicate / Relative Percent Difference

Analyte	LCS - LCL (%R)	LCS - UCL (%R)	LD (RPD)
Methane	66	120	20
Ethylene (Ethene)	62	139	16
Ethane	65	122	15
Propane	60	113	17
Propylene	67	173	15
Carbon dioxide	59	113	12

Note 1: These limits are calculated annually and may change when new limits are determined. Therefore, refer to current documentation for verification. DoD Requirement: LCS/DLCS must meet DoD QSM LCS/DLCS limits.
Note 2: All Matrix Spikes and Matrix Spike Duplicates will be fixed at 50-150 with an RPD of 30. DoD Requirement: MS/MSD must meet DoD QSM LCS/DLCS limits.

DoD QSM Requirements

Analyte	LCS - LCL (%R)	LCS - UCL (%R)	MS – LCL (%R)	MS – UCL (%R)
Methane	73	125	73	125
Ethylene (Ethene)	72	133	72	133
Ethane	74	131	74	131
Carbon dioxide	80	122	80	122

Appendix C EHS Support Standard Field Sampling SOPs

SOP-04 Field Documentation

Purpose

The purpose of this SOP is to provide guidance to ensure that field documentation for any field activity is correct, complete, and adequate. Logbooks and field documentation forms are used for keeping a record of field activities and identifying, locating, labeling, and tracking samples. A field logbook should document any deviations from the applicable work plan, quality assurance project plans, and health and safety plans. A complete and accurate field logbook and field documentation aids in maintaining good quality control. All field records must be factual, objective, and legible.

Relevant EHS Support SOPs

- SOP-05 Sample Management and Shipping
- SOP-07 Investigation Derived Waste
- SOP-08 Field Equipment Operation and Calibration
- SOP-09 Equipment Decontamination
- SOP-21 Soil Sample Collection Methods
- SOP-22 Soil Sampling for Chemical Analysis
- SOP-23 Soil Sampling for Physical Analysis
- SOP-24 Hand Auger
- SOP-25 Drilling Methods using Direct Push Technology
- SOP-26 Drilling Methods using Hollow Stem Auger
- SOP-27 Drilling Methods using Sonic
- SOP-28 Drilling Methods using Rotary (Air, Mud, Water)
- SOP-29 Rock Coring
- SOP-30 Field Classification and Description of Soil
- SOP-31 Field Classification and Description of Rock
- SOP-32 Borehole and Well Abandonment
- SOP-40 Groundwater Monitoring Well Design and Installation
- SOP-42 Groundwater Monitoring Well Development
- SOP-43 Groundwater Sampling Using Low Flow Sampling
- SOP-44 Groundwater Sampling Using Volume Purge Techniques

Attachments

- Attachment A Examples of Chain of Custody
  - Environmental/Chemical
  - Physical

Required Materials

- Project work plan or instruction
- Field logbook and field documentation
- Black waterproof and/or indelible ink pens

1 Field Documentation

Field documentation serves as the primary record of collected data and activities used to support a given project. Subject to the requirements of the applicable work plan, documentation may include field logbooks, field documentation forms, or reports for the various field activities. Minimum expectations for field documentation are as follows:

- Field documentation must be accurate, legible, and written in indelible ink.
- Field documentation will be recorded and maintained on a daily basis as the work progresses, and should contain enough information to allow the activities to be reconstructed so that the work conducted and timeline are understood.
- The date, project name, and number of pages (e.g., 1/1, 2/3) will be written at the top of each page of the field document.
- Mistakes will be crossed out with one line, dated, and initialed. Any corrections/additions made to documentation will be dated and initialed.
- Materials that obliterate the original information (e.g., erasures, correction fluids, mark-out tapes) are prohibited.
- Skipped pages or blank sections at the end of a page in a field logbook should be crossed out with an "X" covering the entire page or blank section, dated, and initialed.
- The responsible field team member should sign and log the date at the bottom of each page in the field logbook and after the last entry for the day.
- Field logbooks and/or field documentation (e.g., boring logs, sampling forms) will contain all information of the field investigation. Use of approved field documentation forms for recording field data are at the discretion of the Project Manager.
- Original field documentation forms should have the date, project name, technician's name, and project activity at the top of the field document.
- The responsible field team member will sign and log the date at the bottom of each page of the field documentation form.
- Photographic documentation descriptions will be included in the field logbook during field investigations.
- All field documentation will be included with the project files. The location of the electronic project files will be confirmed with the Project Manager. The original hard copy field documentation will be scanned as an electronic copy and then placed in the project file folder, or sent to the Project Manager. The field logbook will be kept with the project file folder, Project Manager, or responsible field team leader.

1.1 Field Logbooks

A field logbook serves as the primary record for a field investigation. A field logbook will be maintained for every field investigation or operation undertaken during an investigation. The field logbook should contain detailed records of the field activities in as much detail as possible so personnel can accurately reconstruct the activities and events that have taken place during field assignments. Field logbooks are considered accountable documents in legal proceedings and may be subject to review. Therefore, the entries in the logbook must be accurate, detailed, and reflect the importance of the field events.

Field logbooks, generally in a 4⅝ by 7¼ inches or 8½ by 11 inches in format, should be bound with water resistant and acid-proof covers and have preprinted lines and wide columns. An indelible ink pen should be used to document the activities in the field logbook.

Various field tasks require observations pertaining to that task/activity. Documentation that should be provided in the field logbook for various field tasks is outlined below. The information may or may not be inclusive of the task performed, but is intended to provide an overview of the type of information and level of detail required for accurate and accountable record keeping.

1.1.1 General Field Logbook Requirements

All field personnel or field sampling teams are responsible for completing and providing a field logbook. Information that should generally be recorded in the field log includes

- Project and site name
- Site location (e.g. city and state)
- Health and safety activities
  - Record of tailgate meetings, topics discussed, attendees, company name of the attendees
  - Site contaminants of concern and/or other relevant hazards and steps to avoid, mitigate or remove hazards
  - Required personal protective equipment and decontamination procedures
  - Utility locate (one-call locate service, sketch, photographs), if applicable
- Time (24-hour clock)
- Personnel and subcontractors present for work activity and time spent on job site
- Weather, or changes in weather during the day
- Field operations and personnel assigned to the activities
- A documentary of the timeline detailing daily activities and operations, and summary of daily operations
- Problems encountered and corrective actions
- Quality control activities: e.g., decontamination procedures, quality assurance/quality control (QA/QC) samples taken, calibration of field equipment
- Deviations from the project work plan
- Visitors to the work area/site (date, time, name, company and contact information)
- Records of communications: discussions of job-related activities with the client, subcontractor, field team members, project manager, and/or visitors
- Records or documentation of equipment, supplies, or materials received or shipped invoices; copies of waste manifests or bill of lading, shipping information
- Field observations for inspections, monitoring, sampling, etc.
- Description and photographic log

1.1.2 Calibration Logs

Calibration will be conducted in accordance with SOP-08 Field Equipment Operation and Calibration. Calibration documentation logs are included as attachments to SOP-08. The following information should be provided in the field logbook or approved field documentation as applicable to the work:

- Calibration date and time for all equipment used for the project
- Type of equipment (e.g., photoionization detector (PID), pH meter, dust monitor, noise dosimeter, groundwater monitoring equipment) Serial number and model of equipment calibrated
- Calibration standard (gas or standard solution),concentration, and expiration
- Equipment response to calibration standard
- Adjustments made and recalibration
- Person performing calibration
- Manufacturer/vendor calibration sheet (for most recent maintenance calibration)

1.1.3 Drilling Log

Drilling activities will be conducted in accordance with subsurface borehole advancement SOPs (SOP-24 to SOP-29), SOP-21 Soil Sample Collection Methods, various media-specific sampling SOPs, SOP-40 Well Design/Construction, SOP-09 Equipment Decontamination, and/or SOP-32 Borehole and Well Abandonment. The following information should be provided in the field logbook or applicable field documentation:

- Borehole, well, or sample location (sketch)
- Borehole, well, or sample location identification
- Drilling activities
  - Name of drilling company and driller
  - Field geologist, hydrogeologist, engineer, or appropriate scientist logging the soil/bedrock
  - Time and date of drilling, stoppage, completion, and/or backfilling
  - Drilling method and equipment used (including soil sampler type and diameter)
  - Borehole and drill casing diameter
  - Reference elevation for depth measurements
  - Monitoring readings (e.g., PID readings)
  - Depth interval and recovery
  - Geologic information
  - Total drilling depth.
- Encountered obstructions or refusal
- Well construction information (e.g., materials used, total depth, screen interval, surface completion)
- Method of abandonment
- Type and amount of material used to abandon boreholes
- Sampling performed (soil, groundwater, waste, etc.)
  - Date and time of sample collection
  - Sample type (media) and method (e.g., grab, composite)
  - Sample interval

  - Number of samples collected, sample IDs/nomenclature used
  - Quality control samples collected (e.g., duplicates, equipment blanks)
  - Analyses to be performed on collected samples.
- Equipment decontamination procedures
- Investigation derived waste (IDW) containerization (number of drums, roll off-bins, etc.)
- Disposal of IDW (shipping/transport records or temporary storage details)
- Field observations
- Problems encountered and corrective action
- Signature and date of party generating log

1.1.4 Geologic Log

The preparation of geologic logs is the responsibility of the field geologist(s). A detailed description of unconsolidated soil logging is provided in SOP-30 Field Classification and Description of Soil and SOP-31 Field Classification and Description of Rock. A drilling log template is provided as an attachment to SOP-30 and SOP-31. The field logbook or approved field documentation forms for geologic logging should include:

- Type and volume of drilling fluids (e.g., mud, water, etc.)
- Depth, volume, and rate of drilling fluid loss, if applicable
- Blow counts, if applicable
- Geologic/Lithologic description of unconsolidated materials–Color, Unified Soil Classifications System (USCS) description, penetration resistance (consistency or density), moisture content, grain size information, minor lithologic information, miscellaneous information (e.g., odor, fractures, visible contamination, etc.)
- Geologic/Rock description of consolidated materials—Color, rock type, relative hardness, density, texture, weathering, bedding, structures (e.g., fractures, joints, bedding, etc.), minor lithologic information, miscellaneous information (e.g., presence of odor, visible contamination, etc.)
- Depth of stratigraphic/lithologic changes
- Depth to groundwater (first encountered, at completion, stabilized, absence of groundwater)
- Product description, if present (depth, thickness, visual and odor characteristics)
- Depth, type, and volume of grouting, grout mixes, sealing materials
- Field observations
- Problems encountered and corrective action
- Signature and date at the bottom of each page

1.1.5 Well Construction Log

The preparation of well construction diagrams is the responsibility of the field leader, geologist, technician, or engineer. Well construction is further discussed in the SOP-40 Groundwater Monitoring Well Design and Installation. A well construction form is provided as an attachment to SOP-40. The field logbook or approved field documentation form for well construction would include:

- Drilling and well installation dates
- Type, length, and diameter of well screening and casing

- Well screen perforation size
- Well screen and casing depths
- Depth, type, and volume of grouting, grouting mixes, and sealing materials
- Other construction details (e.g., depth and type of sumps, centralizers, multichannel tubing, permanent pumps, etc.)
- Surface construction details (e.g., flush mount, protective covers, concrete pads, weep hole)
- Surface elevation and reference elevation
- Problems encountered and corrective action
- Signature and date at the bottom of each page

1.1.6 Well Development and Groundwater Sampling Log

These topics are further discussed in SOP-42 Well Development, SOP-43 Groundwater Sampling Using Low Flow, and/or SOP-44 Groundwater Sampling Using Volume Purge Techniques. Respective field documentation forms are provided as attachments in each SOP. Basic information that is recorded in the field logbook or on approved field documentation forms for well development and groundwater sampling include:

- Calibration records (refer to Calibration Log documentation above)
- Date and time of well development or groundwater sampling
- Borehole, well, or sample location identification
- Water level and total depth of well
- Depth to product and product thickness, if present
- Reference elevation, if required
- Additional well information (e.g., casing diameter, filter pack thickness)
- Volume of water to be purged, if applicable
- Type of purging and sampling equipment
- Consistent time interval measurements of groundwater field parameters (e.g., pH, turbidity, conductivity, temperature, depth to water, etc.)
- Groundwater sampling details
  - Sample identification
  - Date and time of sample collection
  - Sample interval, if required
  - Quality control samples (e.g., duplicates, equipment blanks), if collected
  - Number of samples collected
  - Analyses to be performed on collected samples.
- Equipment decontamination procedures
- IDW containerization (volume, placement)
- Disposal of IDW (shipping/transport records or temporary storage details)
- Field observations
- Problems encountered and corrective action
- Signature and date at the bottom of each page.

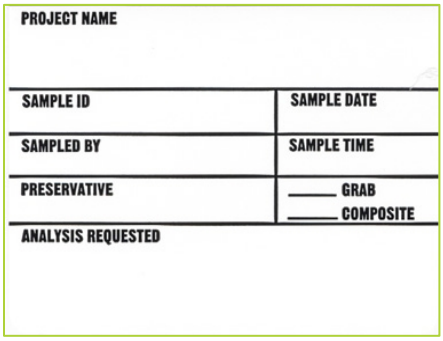
1.2 Documentation of Sampling Activities

Field documentation also includes sample labels, sample seals, chain of custody (COC) records, and the shipping airbill. Management of samples from collection to shipment to laboratory is further discussed in SOP-05 Sample Management and Shipping.

1.2.1 Sample Labels

Sample identification should be completed in accordance with the project work plan or sampling plan. A sample label will be completed using waterproof indelible marker. A sample label will be affixed to all sample containers and contain the:

- Sample identification
- Project location, project name, and/or project number
- Type of sample (grab or composite)
- Type of preservative, if applicable
- Date and time of collection
- Analytical method
- Initials of sampling personnel.



PROJECT NAME	
SAMPLE ID	SAMPLE DATE
SAMPLED BY	SAMPLE TIME
PRESERVATIVE	_____ GRAB _____ COMPOSITE
ANALYSIS REQUESTED	

Figure 1 Example of a Sample Label

1.2.2 Custody Seals

Custody seals consist of an initialed/signed and dated security tape covered with clear packing tape. The custody seal is to provide a line of evidence that sample coolers or containers have not been tampered since the cooler was packed and sealed. Custody seals will be placed on coolers prior to the sampling team's release to a second or third party (e.g., shipment to the laboratory).

Figure 2 Example of a Custody Seal

1.2.3 Chain-of-Custody Records

A COC record is the legal record that tracks the possession and handling of samples from the time of field collection through laboratory analysis and provides information on the sample condition and integrity as received by the laboratory. A sample is considered in custody if it meets any of the following criteria:

- Is in an individual's possession
- Is in view after being in an individual's physical possession
- Is locked or sealed so that no one can tamper with it after it has been in an individual's physical custody
- Is in a secured area that is restricted to authorized personnel.

The COC is documented through a record that lists each sample and the individuals responsible for sample collection, shipment, and receipt. Information recorded on the COC includes:

- Project name and project number
- Time and date of sample collection
- Sample identification number
- Sample matrix
- Sampler's signature
- Required analysis
- Number and type of containers and preservatives
- Other additional notations (e.g., sheen, odor, turnaround time, regulatory standards for analysis).

A copy of the COC record will be retained by the sampler prior to release to a second or third party. Prior to release the COC record will be properly signed, dated, and checked for completeness. Examples of COCs for chemical testing and physical testing are included as **Attachment A**.

1.2.4 Shipping Airbills

Samples shipped from the field to the laboratory or vendor via a commercial carrier (e.g., Federal Express) may require an airbill or receipt. Upon completion of the field sampling event, the sampling team or field leader will be responsible for submitting the sender's copy of the shipping airbills to be copied. While airbills may differ, the general shipping information includes:

- The date of shipment:
- The sender's mailing address and phone number
- The recipient's mailing address and phone number
- The EHS support shipping number
- The project number
- Shipping requirements.

A copy of the airbill or tracking number will be kept to verify sample shipment arrives as scheduled to the appropriate vendor or laboratory.

1.3 Photographs

Photographs provide the most accurate demonstration of the field worker's observations. Photographs can be significant to the project team during future inspections, data evaluation, report preparation, informal meetings, and hearings. Photographs should be taken with a camera-lens system having a perspective similar to that afforded by the naked eye. Telephoto or wide-angle shots cannot be used in enforcement proceedings. Video coverage of a sampling episode can be equally (or even more) valuable than photographs because the coverage can be used to prove that the investigation or sampling process was conducted properly as well as where they were taken.

A photograph must be documented by the photographer in the field logbook if it is to be a valid representation of an existing situation. The following information will be recorded in the field logbook for photographs taken:

- Site name and location
- Photographer
- Sequential photographic number
- Date and time photograph taken
- Directional reference or GPS coordinate of the photograph
- Subject of photographs and description.

Table 1 Example Format for Photographic Log

Site Name and Location:
Photographer:

Photo #	Date	Time	Photo Direction	Location/GPS Location	Subject	Subject Description

General Photographic Suggestions

- Some clients do not permit photographs. Confirm with the project manager or site manager that photographs are allowed.
- Take photographs before, during, and after to convey a timeline. Photographs should be taken for investigations, emergencies, incidents, and as appropriate.
- Be aware of the goal(s) of the project and capturing images that clearly demonstrate progress towards achieving the goal(s).
- The photographer should be prepared to take a variety of shots, from long range to close-up. Many shots will be repetitive in nature or format, especially close-up site feature photographs.
- Photographs taken to document sampling locations should include two or more reference points or include landscape features that are unlikely to change over several years (buildings, other structures, etc.) as to facilitate relocating the point at a later date.
- Consider the angle of light, cloud cover, background, shadows, and contrasts. Medium and long view photos are best shot with the sun at the photographer's back.
- Capture seasonal features such as foliage, stream flow, cloud cover, and site access as these features may help demonstrate passage of time.
- Use a ruler, person, farm animal, automobile, etc. when possible to convey the scale of the image. The angle (e.g., overhead, elevated shot from a bridge, peak, etc.) may provide better perspective of the intended subject.
- Photographs of soil or rock cores should have a location and depth interval label, as well as the boring/well ID and an "up" indicator.

Attachment A Examples of Chain of Custody

>>> Select a Laboratory <<<

#N/A
#N/A
#N/A
#N/A

Chain of Custody Record

Regulatory Program: ☐ DW ☐ NPDES ☐ RCRA ☐ Other:

Client Contact	Project Manager:	Site Contact:	Date:	COC No:
Your Company Name here	Tel/Fax:	Lab Contact:	Carrier:	_____ of _____ COCs
Address	**Analysis Turnaround Time**			Sampler:
City/State/Zip	☐ CALENDAR DAYS ☐ WORKING DAYS			**For Lab Use Only:**
(xxx) xxx-xxxx Phone	TAT if different from Below _____			Walk-in Client:
(xxx) xxx-xxxx FAX	☐ 2 weeks			Lab Sampling:
Project Name:	☐ 1 week			
Site:	☐ 2 days			Job / SDG No.:
P O #	☐ 1 day			

Sample Identification	Sample Date	Sample Time	Sample Type (C=Comp, G=Grab)	Matrix	# of Cont.	Filtered Sample (Y / N)	Perform MS / MSD (Y / N)																	Sample Specific Notes:

Preservation Used: 1= Ice, 2= HCl; 3= H2SO4; 4=HNO3; 5=NaOH; 6= Other _____

Possible Hazard Identification:
Are any samples from a listed EPA Hazardous Waste? Please List any EPA Waste Codes for the sample in the Comments Section if the lab is to dispose of the sample.

☐ Non-Hazard ☐ Flammable ☐ Skin Irritant ☐ Poison B ☐ Unknown

Sample Disposal (A fee may be assessed if samples are retained longer than 1 month)

☐ Return to Client ☐ Disposal by Lab ☐ Archive for_____ Months

Special Instructions/QC Requirements & Comments:

Custody Seals Intact: ☐ Yes ☐ No | Custody Seal No.: | Cooler Temp. (°C): Obs'd:_____ Corr'd:_____ Therm ID No.:_____

Relinquished by:	Company:	Date/Time:	Received by:	Company:	Date/Time:
Relinquished by:	Company:	Date/Time:	Received by:	Company:	Date/Time:
Relinquished by:	Company:	Date/Time:	Received in Laboratory by:	Company:	Date/Time:

PTS Laboratories, Inc.

CHAIN OF CUSTODY RECORD

PAGE OF

COMPANY

ADDRESS CITY ZIP CODE

PROJECT MANAGER

PROJECT NAME PHONE NUMBER

PROJECT NUMBER FAX NUMBER

SITE LOCATION

SAMPLER SIGNATURE

PO#

TURNAROUND TIME

24 HOURS ☐ 5 DAYS ☐
48 HOURS ☐ NORMAL ☐
72 HOURS ☐

OTHER: _____

SAMPLE INTEGRITY (CHECK):

INTACT _____ ON ICE _____

PTS QUOTE NO.

PTS FILE:

ANALYSIS REQUEST

SAMPLE ID NUMBER	DATE	TIME	DEPTH, FT	NUMBER OF SAMPLES	SOIL PROPERTIES PACKAGE	HYDRAULIC CONDUCTIVITY PACKAGE	PORE FLUID SATURATIONS PACKAGE	TCEQ/TNRCC PROPERTIES PACKAGE	CAPILLARITY PACKAGE	FLUID PROPERTIES PACKAGE	PHOTOLOG: CORE PHOTOGRAPHY	MOISTURE CONTENT, ASTM D2216	POROSITY: TOTAL, API RP40	POROSITY: EFFECTIVE, ASTM D425M	SPECIFIC GRAVITY, ASTM D854	BULK DENSITY (DRY), API RP40 or ASTM D2937	AIR PERMEABILITY, API RP40	HYDRAULIC CONDUCTIVITY, EPA9100, API RP40, D5084	GRAIN SIZE DISTRIBUTION, ASTM D422/4464M	TOC: WALKLEY-BLACK	ATTERBERG LIMITS, ASTM D4318					COMMENTS

1. RELINQUISHED BY	2. RECEIVED BY	3. RELINQUISHED BY	4. RECEIVED BY
COMPANY	COMPANY	COMPANY	COMPANY
DATE TIME	DATE TIME	DATE TIME	DATE TIME

PTS Laboratories, Inc. • 8100 Secura Way • Santa Fe Springs, CA 90670 • Phone (562) 347-2500 • Fax (562) 907-3610
PTS Laboratories, Inc. • 4342 W. 12th St. • Houston, TX 77055 • Phone (713) 316-1800 • Fax (713) 316-1882

SOP-05 Sample Management and Shipping

Purpose

The purpose of this SOP is to provide a general reference for ensuring the integrity of samples from collection to their final disposition (e.g., laboratory) is met. This SOP considers general shipping of environmental (chemical) or geotechnical (physical) samples.

Shipping under this SOP includes direct delivery, courier, and/or air transport. Regulations for sample labeling, packing, and shipping of dangerous goods by air transport are promulgated by U.S. Department of Transportation (DOT) under Code of Federal Regulations, Title 49 [49 Code of Federal Regulations (CFR)], Subchapter C, Hazardous Materials Regulations, and the International Air Transport Authority (IATA).

Relevant EHS Support SOPs

- SOP-04 Field Documentation

Attachments

- Attachment A Example of Laboratory Holding Times

Required Materials

- Field logbook and field documentation
- Site maps, site layouts, site plans
- Health and Safety Plan
- Appropriate personal protective equipment (PPE)
- Black waterproof and/or indelible ink pens
- Sample labels
- Chain of Custody
- Custody seals
- Coolers
- Clear packing and duct tape
- Plastic baggies
- Trash bags, or drum liners
- Bubble wrap
- Ice
- Federal Express form (with EHS Support account)

1 Shipping of Hazardous Substances or Dangerous Goods

Shipment of hazardous substances and dangerous goods including non-aqueous phase liquids (quantity regulated), compressed gas, biological hazards, radioactive substances require special shipping procedures and training. Shipment of hazardous substances and dangerous goods requires additional training and regulatory-approved packaging if sent by common carrier. The shipment of hazardous substances and dangerous goods, their packaging, labeling, and shipping are regulated by the United States Department of Transportation (DOT) Hazardous Material Regulation (HMR), 49 CFR, Parts 106 through 180 and the IATA Dangerous Goods Regulation (DGR).

Shipment of a potentially hazardous substance or dangerous goods will be discussed with the Project Manager and the EHS Support Health and Safety Manger. Dangerous goods must not be offered for air transport by any personnel except for personnel trained and certified by IATA in dangerous goods shipment.

1.1 Definitions

Dangerous goods: Dangerous goods are articles or substances that can pose a significant risk to health, safety, or property when transported by air; they are classified as defined in Section 3 of the DGR (IATA 2007).

Environmental samples: Environmental samples include but are not limited to drinking water, groundwater, surface water, soil, sediment, mixed waste samples, treated municipal and industrial wastewater effluent, biological specimens, or any samples not expected to be contaminated with high levels of hazardous materials.

Hazardous Materials Regulations: The HMR are DOT regulations for the shipment of hazardous materials by air, water, and land; they are located in 49 CFR 106 through 180.

Hazardous samples: Hazardous samples include dangerous goods and hazardous substances. Hazardous samples shipped by air should be packaged and labeled in accordance with procedures specified by the DGR. Ground shipments should be packaged and labeled in accordance with the HMR.

Hazardous substance: A hazardous substance is any material, including its mixtures and solutions, that is listed in Attachment A of 49 CFR 172.101 and its quantity, in one package, equals or exceeds the reportable quantity listed in the attachment.

IATA Dangerous Goods Regulations: The DGR are regulations that govern the international transport of dangerous goods by air. The DGR are based on the International Civil Aviation Organization (ICAO) Technical Instructions. The DGR contain all of the requirements of the ICAO Technical Instructions and are more restrictive in some instances.

Nonhazardous samples: Nonhazardous samples are those samples that do not meet the definition of a hazardous sample and do not need to be packaged and shipped in accordance with the DGR or HMR.

1.2 Non-Hazardous Sample Management and Shipping

1.2.1 General Requirements

- Samples will be placed in contaminant-free containers stored in cool, dry, clean areas to prevent exposure to fuels, solvents, and other non-site related impacts.
- Sample containers will not be used if held for an extended period on the job site (some states dictate this time limit) or exposed to extreme heat conditions.
- Sample container will be kept out of the sun.

Samples will be shipped in an expeditious time to ensure samples are received by the laboratory within the holding time of the sample method. An example of sample container, preservative and holding times is included as **Attachment A**.

1.2.2 Sample Labels

Sample labels will be completed using black waterproof indelible marker. One sample label will be affixed to each sample container. The sample identification will be written as specified in the project work plan. Pre-printed sample labels should be used when available. Documentation for sample labeling can be referenced in SOP-04 Field Documentation.

1.2.3 Sample Packing

Protocols for sample temperature maintenance and sample packing are applicable to collection of samples year-round or as otherwise specified. The intent is to ensure samples arrive at the laboratory in good condition—both physically intact and appropriately preserved.

- Place each sample container in a re-sealable plastic baggie or similar
- Squeeze as much air as possible from the plastic baggie and seal
- Glass containers should be wrapped in bubble wrap

1.2.4 Cooler Packing for Samples on Ice

Determine the maximum allowable weight of each cooler (for example, the FedEx limit is 150 pounds. Most shippers will not accept a shipment for transportation when it appears if the shipment is:

- Improperly packed or packaged
- Of a kind or type likely to incur damage from high or low temperature under normal air transportation conditions
- Of an inherent nature or contains defects that may indicate transportation could not be furnished without loss or damage to the shipment or damage to the shippers facilities or equipment

Cooler Packing Instructions for Samples on Ice:

1. Tape the drain plug on the inside and outside of the cooler.
2. Place cushioning material (e.g., bubblewrap) in the bottom and around the sides of the cooler.
3. Place a large plastic bag (e.g., trash bag) in the bottom of cooler to contain samples. Allow the top edges of the plastic bag to hang over the outside of the cooler while filling.
4. Place the wrapped bottles upright in the cooler allowing enough room for ice bags and cushioning material to be placed between and around the containers.
5. If required, place a temperature blank in the cooler with the samples.
6. Insulate the samples with additional cushioning to deter breakage.
7. If using wet ice, place the ice in a plastic bags and seal (considered a double bagging to protect against possible leakage).
8. Distribute ice substitute bags (such as gel ice) or plastic bags containing wet ice between samples and over the containers to preserve them at approximately 4 degrees Celsius (°C).
9. Fill the remaining space in the cooler with additional ice and/or cushioning material to prevent the contents from shifting during shipment.
10. Pull the top edges of the large plastic bag up and together, force out any extra air, and twist the top of the plastic bag several times. Secure the twisted portion of the bag with a tie strap or tape.
11. If the cooler is being couriered or hand delivered to the laboratory, a signature will be required from the party releasing the cooler(s) and the party accepting responsibility for the cooler and its contents. If the cooler is being shipped via air carrier, a signature will be required from the party releasing the cooler (following the air carriers delivery to the laboratory, the laboratory will append their signature).
12. Place the chain of custody (COC) in a plastic baggie outside, and on top of the large plastic bag containing the samples and ice. The baggie containing the COC may be taped to the underside of the cooler top.
13. Retain an original carbon copy or photocopy of the completed COC.
14. Complete two custody seals.
15. Seal the cooler by placing the one custody seal on the front and the other custody seal on the rear of the cooler across the edge where the cooler and cooler lid meet.
16. Use clear packing tape and encircle the tape around the cooler. The packing tape should cover the custody seals and should secure the lid.

1.2.5 Packing for Samples (not on ice)

1. Place cushioning material (e.g., bubblewrap) around the sample container.
2. Fill the remaining spaces of the container with additional packing material to secure the sample from movement.
3. If the container is being couriered or hand delivered to the laboratory, a signature will be required from the party releasing the cooler(s) and the party accepting responsibility for the cooler and its contents. If the cooler is being shipped via air carrier; a signature will be required from the party releasing the cooler (following the air carriers delivery to the laboratory, the laboratory will append their signature).
4. Place the COC in a plastic bag and place in container.
5. Retain an original carbon copy or photocopy of the completed COC.

6. Complete a custody seal and attach along an opening of the container (e.g., the edge of a box).
7. Using clear packing tape, tape the container shut.

1.2.6 Shipping Airbills

1. Complete the shipping or airbill form.
2. It is recommended to ship coolers certified to ensure samples are received within a sample's required holding time.
3. Ship the samples. If necessary, notify the laboratory the samples have been shipped.
4. Retain a copy of the shipment airbill to use for tracking of the package.

1.2.7 Records

The documentation for sample packaging and shipping will consist of chain-of-custody records and shipper's records. Documentation should be kept and placed in with the project files.

Attachment A Example of Laboratory Holding Times

RECOMMENDED HOLDING TIMES FOR ENVIRONMENTAL SAMPLES

Parameters	Method*	Container	Recommended Quantity (mL)	Preservative	Holding Time
Acidity	305.1, 2310B	P,G	100	4^0C	14 days
Alkalinity	310.1, 310.2, 2320B	P,G	100	4^0C	14 days
Ammonia-N	4500NH3BE, 350.3	P,G	500	4^0C, H_2SO_4 to pH <2	28 days
Biochemical Oxygen Demand (BOD)	405.1, 5210B	P,G	1000	4^0C	48 hours
Bromide	300.0, 9056	P,G	200	None	28 days
Chemical Oxygen Demand (COD)	HACH 8000	P,G	100	4^0C, H_2SO_4 to pH <2	28 days
Chloride	325.3, 9251, 9056	P,G	200	None	28 days
Chlorine, Residual	330.3, 4500 CLG	P,G	200	None	Immediately
Coliform, Fecal	9222D	P,G (sterile)	100	4^0C, $Na_2S_2O_3$	6 hours
Color	2120C, 110.3	P,G	100	4^0C	48 hours
Cyanide	335.1, 335.2, 335.3 9012A	P,G	1000	4^0C, ascorbic acid, NaOH to pH > 12	14 days
Ferrous Iron	3500FED	P,G	100	2mHCl/100mL	Immediately
Flashpoint	1010	P,G	100	None	Not specified
Fluoride	300.0, 9056, 340.2	P	500	None	28 days
Hardness	130.2 2340B	P,G	100	HNO_3 to pH < 2	6 months
Nitrogen, Kjeldahl (TKN)	4500NH, 351.4	P,G	500	4^0C, H_2SO_4 to pH <2	28 days
Nitrate-N	353.2	P,G	100	4^0C	48 hours
Nitrate-Nitrite as N	353.2	P,G	200	4^0C, H_2SO_4 to pH <2	28 days
Oil and Grease	1664A	G	1000	4^0C, H_2SO_4 or HCl to pH < 2	28 days
Phenols	420.1, 420.2, 9066	P,G	1000	4^0C, H_2SO_4 to pH <2	28 days
Phosphorus, Total	365.1	P,G	200	4^0C, H_2SO_4 to pH <2	28 days
Phosphorus, Ortho	365.2, 4500PE	P,G	200	4^0C	48 hours
pH	150.1, 9040B, 9045C	P,G	100	None	Immediately
Radiochemisrty Alpha, Beta, Radium Tritium Radon, I-131	900 & 9000 series	 P,G P,G P,G	 2000 100 1000	 HNO_3 to pH < 2 None HNO_3 to pH < 2	 6 months 6 months 14 days
Reactivity	SW846 7.3.3.2, 7.3.4.2	G	100g	4^0C	Not Specified
Silica	370.1, 4500Si D	P, PFTE, Quartz	100	4^0C	28 days
Solids, Dissolved (TDS)	160.1, 2540C	P,G	100	4^0C	7 days
Solids, Suspended (TSS)	160.2, 2540D	P,G	500	4^0C	7 days
Solids, Volatile (TVS)	160.4, 2540E	P,G	100	4^0C	7 days
Solids, Total (TS)	160.3, 2.540B	P,G	100	4^0C	7 days
Specific Conductance	120.1, 9050	P,G	100	4^0C	28 days
Specific Gravity	2710F	P,G	100	4^0C	28 days
Sulfate	375.4, 9056, 9038	P,G	200	4^0C	28 days
Sulfide	376.1, 376.2, 9034	P,G	500	4^0C, Zn acetate, NaOH to pH > 9	7 days
Sulfite	4500S03B	P,G	200	None	Immediately
Surfactants (MBAS)	425.1, 5540C	P,G	250	4^0C	48 hours
Total Organic Carbon (TOC)	415.1, 9060	P,G	100	4^0C, HCl to pH < 2	28 days
Total Organic Halogens (TOX)	9020B	G-TLC (amber)	100	4^0C, H_2SO_4 to pH <2	28 days
Total Petroleum Hydrocarbon (TPH)	418.1	G-TLC	1000	4^0C, H_2SO_4 or HCl to pH < 2	28 days
Turbidity	180.1, 2130B	P,G	100	4^0C	48 hours
Viscosity	D2196	P,G	500	None	Not Specified

*The methods listed are from typical EPA references.
#Solid and waste samples: Quantity 1-100g, preservative 4 ° C
**Holding time for solids and samples is not defined
Organic Nitrogen = TKN – Ammonia-N

RECOMMENDED HOLDING TIMES FOR ENVIRONMENTAL SAMPLES

Metals

Parameters	Method*	Container	Recommended Quantity (mL)	Preservative	Holding Time
Metals (except Hexavalent Chromium and Mercury):					
Aqueous					
Total	6010B, 200.0, 7000 series	P,G	500	HNO_3 to pH < 2	6 months
Dissolved	6010B, 200.0, 7000 series	P,G	500	Filter on site HNO_3 to pH < 2	6 months
Solid					
Total	6010B, 200.0, 7000 series	P,G	100g	4^0C	6 months
Hexavalent Chromium					
Aqueous	7196A	P,G	500	4^0C	24 hours
Solid	3060A/7196A	P,G	100g	4^0C	30/7 days
Mercury					
Aqueous					
Total	245.2/7470	P,G	500	HNO_3 to pH < 2	28 days
Dissolved	245.2/7470	P,G	500	Filter on site HNO_3 to pH < 2	28 days
Solid					
Total	7471	P,G	100g	4^0C	28 days

Metals – Boron must be collected in a polyethylene container.

*The methods listed are from typical EPA references.
CrIII=Total Cr-Hexavalent Cr

Organic Parameters

Volatile Organics

Sample Matrix	Method*	Container	Minimum Quantity	Preservative	Holding Time
Concentrated Waste Samples	8021B, 8260B, 8015M	G-TLC or G-TLS	2 x 40mL vials or 4-oz wide mouth	4^0C	14 days
Aqueous Samples	8021B, 8260B, 8015M, 624, VPH	G-TLS	2 x 40mL vials	4^0C, HCl to pH < 2 , $Na_2S_2O_3$ if residual chlorine present	14 days, 7 days if not acid preserved
Solid Samples	8021B,8260B, 8015M, VPH	G-TLS or G-TLC	4-oz wide mouth and/or Terracore Kit	4^0C	14 days **

*The methods listed are from typical EPA references.

Semivolatile Organics, Pesticides/PCBs, Herbicides, PAHs, Petroleum

Hydrocarbons

Sample Matrix	Method*	Container	Minimum Quantity	Preservative	Holding Time
Concentrated Waste Samples	8270C, 8081, 8082, 8015M, 8151A, 8141A, FL-PRO	G-TLC (Amber)	1 Liter	None	14 days until extraction, 40 days after extraction
Aqueous Samples	8270C, 8081, 8082, 8015M, 8151A, 8141A, 8310,608, 625, FL-PRO,EPH ***	G-TLC (Amber)	2 x 1 Liter	4^0C	7 days until extraction, 40 days after extraction
Solid Samples	8270C, 8081, 8082,	G-TLC	8 oz.	4^0C	14 days until

RECOMMENDED HOLDING TIMES FOR ENVIRONMENTAL SAMPLES

	8015M, 8151A, 8141A, 8310,EPH FL-PRO ***				extraction, 40 days after extraction
Parameters	**Method***	**Container**	**Recommended Quantity (mL)**	**Preservative**	**Holding Time**
Dioxins and Furans**	613, 8280A, 8290, 1613	G-TLC(Amber)	2 x 1 Liter	4^0C	30 days until extraction, 45 days after extraction

*The methods listed are from typical EPA references.
**Concentrated wastes and soil samples are collected in 2 oz. to 1 Liter amber glass jars with TLC.
***1005/1006, Petroleum Hydrocarbons –14 days after extraction

TCLP/SPLP Parameters

Parameters	Holding Time from Collection to TCLP Extraction (days)	Holding Time from TCLP Extaction tor Preparative Extraction (days)	Holding Time from TCLP/Preparative Extraction to Analysis (days)	Total Time
Volatiles	14	NA	14	28
Semivolatiles	14	7	40	61
Mercury	28	NA	28	56
Metals	180	NA	180	360

Reference: 40CFR Part 136 Tables IA, IB, IC, ID & IE and Table II., SW846 Table 4-1 and Table 3-1, SW846 Method 1311 8.5,
*The methods listed are from typical EPA references
Acronymn Definitions: (Teflon is a registered trademark of E.I. DuPont)
CLP: EPA Contract Laboratory Program
G-TLC: Glass with Teflonâ-lined cap
NA: Not Applicable
G: Glass
G-TLS: Glass with Teflonâ-lined septrum
P: Polyethylene

SOP-08 Field Equipment Operation and Calibration

Purpose

The purpose of this SOP is to provide general procedures for the calibration of field instruments used during field investigations for field screening and measurements. This SOP applies to calibration for equipment used during field investigations with additional focus on the more commonly used field instruments - a multi-parameter water quality indicator and a photo-ionization detector (PID).

The manufacturer's manual should be referred to for calibration and standard operating procedures as well as operating instructions for the various field equipment. It is beyond the scope of this SOP to describe all alternatives to equipment type, calibration procedures, and maintenance.

Relevant EHS Support SOPs

- SOP-04 Filed Documentation

Attachments

- **Attachment A** Examples of Instrument Calibrations Forms
  - Multi-probe Water Quality Meter Calibration Form
  - Photoionization Detector or Single Gas Meter Calibration Form
  - Bump Test Form
- **Attachment B** Water Quality Meter
  - Calibration and Maintenance of a Portable Multi-Probe Water Quality Meter (YSI 556)
- **Attachment C** Portable Gas Meter
  - Calibration and Maintenance of a Photo-ionization Detector (Rae System 2000)

Required Materials

- Field logbook or field documentation
- Black waterproof and/or indelible ink pens
- Appropriate personal protective equipment (PPE)
- Field equipment and supplies necessary to perform the task

1 Field Equipment Calibration

Calibration of field equipment is conducted to ensure observations obtained in the field obtain a level of accuracy. Calibrate field monitoring equipment within calibration acceptance criteria, based on contaminants of concern potentially encountered, and within the instruments operational limits. Equipment calibration is only as good as the quality and accuracy of the calibration standard used. Therefore, verify that the calibration standards meet the minimum requirements for source and purity recommended by the instrument manufacturer.

Field monitoring equipment will be properly calibrated and remain operable in the field. All field equipment will be thoroughly inspected for functionality and calibrated prior to use.

1.1 General Field Equipment Calibration Procedures

- The type of field equipment used should be consistent for the activities performed to ensure the variability when monitoring/sampling is minimized.
- Instruments used during the field activities will be checked for possible malfunctions, cleaned, and calibrated prior to use.
- A calibration log will be completed for all equipment requiring calibration. Examples of a water quality meter calibration, a portable gas meter calibration, and a bump test form are included as **Attachment A**.
- Common field equipment includes a multi-probe water quality meter and a photo-ionization meter. Field equipment calibration and maintenance for a multi-probe water quality meter, specifically a YSI 556, is included as **Attachment B**. Field equipment calibration and maintenance for a portable gas meter, specifically a RAE System 2000 PID, is included as **Attachment C**. Included in **Attachment C** is the function of a bump test on a multi-gas detector.
- Calibration verification will be performed on field instruments prior to their initial use, at least once daily, as specified in the work plan, and/or whenever indications of instrument malfunction or questions in the instrument's readings are observed. The calibration schedule is outlined in **Table 1**.

Table 1 Calibration Schedule

Equipment	Calibration Standard	Frequency
Water quality meter	As required for project	Daily
Photoionization Detector	Isobutylene	Daily

- Project-specific requirements may require calibration of field monitoring equipment at a greater frequency (e.g., mid-day, end of day).
- Attempt to recalibrate instruments before collecting additional data if instrument readings appear to be irregular or drifting.
- Calibrate sensors in a controlled environment such as in the designated field preparation room. Avoid calibrating units in the field since it can introduce error.

In general, instrument identification and calibration should include the following steps:

1. Determine which instruments are needed for the specific field tasks.
2. Obtain the necessary instruments and associated calibration gases and/or reference standards for calibration.
3. Check expiration dates on calibration gases and/or standard solutions. Replace the standard if out of date.
4. Assemble the instrument and turn it on, allowing the instrument to warm up.
5. Check the battery charge. Charge or replace if necessary.
6. Clean the instrument (if necessary).
7. Calibrate the instrument prior to field use in accordance with manufacturer's procedures, and if necessary adjust the instrument to meet calibration specifications.
8. If the instrument malfunctions and the malfunction cannot be corrected, obtain another instrument, and have the malfunctioning instrument repaired or returned.
9. For an instrument to be considered calibrated and ready for use, the instrument must read within at least 10% of the calibration standard, or as outlined in the project work plan.
10. If the instrument reads within 10% of the reference standard value upon first testing, the instrument will be considered calibrated. If the instrument reads >10% difference from the reference standard value it will be calibrated, recalibrated, or taken out of service. Consult the manufacturer's instruction manual for more specific details on the instrument in use.
11. Document calibration activities and results on the Instrument Calibration Log (**Attachment A**) and record the activity in the Field Log Book.
12. Recharge batteries and add carrier gases (if applicable) at the end of each day or as needed.

2 Records

A record will be maintained of the calibration, and/or calibration verification. The records will include the following information, where applicable:

- Date and time of calibration activity
- Project name and number
- Personnel conducting the calibration
- Serial number and/or meter numbers
- Instrument name and model number
- Calibration gases or reference standard used, concentration of the gases and solutions used, and the associated units (if applicable), and lot numbers of calibration intervals
- Instrument readings after calibration
- Instrument readings of calibration verification data.

Additional documentation that will be retained include:

- Equipment rental shipping and calibration documents (provided by the Rental Company)
- Service and repair records
- Certificates of traceability for reference standards.

The calibration activity will be recorded in the field logbook. Calibration data will be recorded in the Instrument Calibration Log and/or the field logbook. Examples of Instrument Calibration Log are included in **Attachment A.**

3 Corrective Action

Field instruments can be affected by changes in temperature, humidity, and barometric pressure. Instrument calibration should be checked when significant changes in weather occur. In addition, instrument calibration should be checked if maintenance activities (e.g. battery replacement, lamp replacement, or refueling) are required, if instrument malfunctions occur, or when questionable readings are observed.

Corrections and reviews of calibration records will be completed in accordance with the SOP for Field Notes and Documentation. Errors will be corrected by drawing a single line through the error, entering the correct information, initialing, and dating the change. Materials that obliterate the original information, such as correction fluids and/or mark-out tapes, are prohibited. All corrections will be initialed and dated.

Attachment A Examples of Instrument Calibration Forms

003 EHS Field Form
Instrument Calibration Log

Multi-Parameter Water Meter	
Project Name	Equipment Type
Project Location	Make/Model/Serial No.
Project Number	Page _____ of _____

Calibration Reference Solution					
	Parameter	Standard	Units	Buffer Expiration Date	
	pH	4.01	S.U.		
		7			
		10.01			
	Conductivity				
	ORP				

Date/Time	Calibrated By	Temp	pH Standard 1	pH Standard 2	pH Standard 3	Conductivity	ORP (Redox)	Dissolved Oxygen	Comment
		C°	*7*			*___ S/cm*	*mV*	*mg/L*	

004 EHS Field Form
PID Instrument Calibration Log

Photoionization Detector or Single Gas Meter	
Project Name	Equipment Type
Project Location	Make/Model/Serial No.
Project Number	Page _____ of _____
Calibration	
Calibration Gas Type	Calibration Standard Concentration

Date/Time	Calibrated By	Calibration Results	Comments

005 EHS Field Form
Bump Test Form

Multi-Gas Meter Bump Test Log	
Project Name	Equipment Type
Project Location	Make/Model/Serial No.
Project Number	Page _____ of _____
Calibration	
Calibration Gas Type	Calibration Standard Concentration

Bump Test

Date/Time	Calibrated By	Did Bump Test Pass?	Comments

Attachment B Calibration and Maintenance – Portable Multi-Probe Water Quality Meter

ATT B SOP-08 Field Equipment Operation and Calibration Attachment B – Water Quality Meter

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1 Portable Multi-Parameter Water Quality Probe Calibration

Water quality meters and instruments vary by manufacturer and model number. Instructions for maintenance and operation of all these field instruments are described in the operation manuals provided by the manufacturer. The manufacturer's manual should take precedent over the procedures described herein. The procedures described below are for portable multi-parameter water quality probes such as the YSI 556 or AquaProbe. Additional probes, such as a total dissolved solid or salinity, are available and should be used as directed by the Project Plan and calibrated according to the manufacturer's manual.

Figure 1 Example of AquaProbe® AP-5000 Multi-parameter Probe and Multi-parameter Readout Instrument (YSI 556).

If a "RapidCal" or "QuickCal" option is available for the instrument, initiate the calibration and follow the calibration prompts. The volume of the calibration solutions must be sufficient to cover both the probe and temperature sensor (see manufacturer's instructions for additional information). While calibrating or measuring, make sure there are no air bubbles lodged between the probe and the probe guard.

1.1 pH

Calibrate daily using at minimum a 2-point calibration method. A 2-point calibration uses two pH reference standard solutions (for example, pH 4 and pH 7 or pH 7 and pH 10) and is valuable only if the water being monitored is known to be either basic or acidic. For example, if the pH is known to vary between 5.5 and 7, a 2-point calibration with a pH 7 and pH 4 reference standard solution is sufficient.

If the pH of water being measured is unknown, a 3-point calibration method is preferred. Using this calibration, the pH sensor is calibrated with a pH 7 standard and two additional reference standards (such as pH 4 and pH 10). The 3-point calibration method accounts for the full pH range and assures maximum accuracy when the pH of the media to be monitored cannot be anticipated. Typically, the procedure for a 3-point calibration is the same as for a 2-point calibration, but the instrument may prompt you to select a third pH reference standard.

1.1.1 pH Calibration Procedure

1. Allow the reference standards to equilibrate to the ambient temperature.

2. The calibration container should be filled with the reference standard solution, so the pH probe and temperature sensor are immersed in the reference standard.
3. Record reference standard solution information and temperature on the Instrument Calibration Log (Attachment A). Temperature can affect the pH, therefore enter the pH calibration values based on the appropriate temperature as labeled on the pH calibration solutions used or according to **Table 1**, below.
4. Record the final pH calibration reading, with the corresponding temperature, on the Field Calibration Sheet.
5. Remove probe from its storage container and rinse with a small amount of reference standard.
6. Select monitoring/run mode for pH calibration on the data logger or screen prompt. Immerse probe into the initial reference standard (e.g., pH 7).
7. Enter the reference standard value (e.g., 7) into the instrument. The readings should remain within manufacturer's specifications. If they change, re-calibrate. If readings continue to change after re-calibration, consult manufacturer.
8. Remove probe from the reference standard and rinse with a small amount of initial standard.
9. Immerse probe into the second standard (e.g., pH 4). Repeat step 5
10. If instrument only accepts two standards, the calibration is complete. Go to step 10.
11. Immerse probe in third buffered standard (e.g., pH 10) and repeat steps 5 to 7.
12. Remove probe from the third standard and record results.
13. Toggle from Calibration Mode to Monitoring/Run mode. To ensure the initial calibration standard (e.g., pH 7) has not changed, immerse the probe into the initial standard. Wait for the readings to stabilize. The reading should read the initial standard. If not, recalibrate.

Table 1 pH Buffer Solution Values Based on Temperature

Temperature	pH Buffer			Temperature	pH Buffer		
°C	4.01	7.0	10.01	°C	4.01	7.0	10.01
0	4	7.11	10.32	24	4.01	7	10.02
1	4	7.11	10.31	25	4.01	7	10.01
2	4	7.1	10.29	26	4.01	6.99	10
3	4	7.09	10.28	27	4.01	6.99	9.99
4	4	7.09	10.26	28	4.01	6.99	9.98
5	4	7.08	10.25	29	4.01	6.99	9.98
6	4	7.08	10.23	30	4.02	6.98	9.97
7	4	7.07	10.22	31	4.02	6.98	9.96
8	4	7.07	10.21	32	4.02	6.98	9.95
9	4	7.06	10.2	33	4.02	6.98	9.94
10	4	7.06	10.18	34	4.02	6.98	9.93
11	4	7.05	10.17	35	4.02	6.97	9.93
12	4	7.05	10.16	36	4.03	6.97	9.92
13	4	7.04	10.14	37	4.03	6.97	9.91
14	4	7.04	10.13	38	4.03	6.97	9.9

Temperature	pH Buffer			Temperature	pH Buffer		
15	4	7.03	10.12	39	4.03	6.97	9.9
16	4	7.03	10.11	40	4.03	6.97	9.89
17	4	7.02	10.10	41	4.04	6.97	9.88
18	4	7.02	10.09	42	4.04	6.97	9.88
19	4	7.02	10.08	43	4.04	6.96	9.87
20	4	7.01	10.06	44	4.04	6.96	9.86
21	4.01	7.01	10.05	45	4.04	6.96	9.86
22	4.01	7.01	10.04	46	4.05	6.96	9.85
23	4.01	7	10.03	47	4.05	6.96	9.85

1.1.2 pH Probe Storage and Maintenance

A pH meter with a glass probe needs to be stored wet. It is best to use an "electrode storage solution" or a pH 4 or 7 buffer but tap water will sometimes work for short storage periods. Never use distilled or deionized water for storage; this will ruin the probe. During storage, the probe can be immersed in the storage solution or in contact with a soaked sponge or paper towel, the cap for the probe will typically have a sponge or a reservoir to fill with solution. If a probe dries out, usually it can be reconditioned by soaking in a storage or buffer solution for a few hours.

Electrodes with glass membranes can get dirty after heavy use, which affects the sensitivity of the electrode. Soaking the electrode in an “electrode cleaner solution” will help. The typical lifetime of a glass pH probe is about 6 months to 2 years, dependent upon if the pH probe is used correctly and is properly maintained. Most meters will allow you to change out the electrode when it is time for replacement.

1.2 Conductivity

Perform calibration for conductivity according to the recommended manufacturer’s calibration instructions. Conductivity is generally calibrated for Specific Conductance and entered as milliSiemens per centimeter (mS/cm) at 25 degrees Celsius (°C). Conductivity standard solution at 25°C has a specific conductance value of 1.413 mS/cm (also 1413 microSiemens per centimeter (µS/cm) or 1413 µmho/cm) when at a temperature of 25°C. If the temperature varies from 25°C, the conductivity will vary from the standard. Record the reference standard solution information and conductivity reading with the corresponding temperature on the Instrument Calibration Log.

1.2.1 Conductivity Calibration Procedure

1. Allow the calibration standard to equilibrate to the ambient temperature.
2. Remove probe from its storage container, rinse the probe with a small amount of the conductivity reference standard (discard the rinsate), and place the probe into the reference standard.
3. Select the Monitoring/Run mode. Allow the probe temperature to stabilize.

4. Look up the conductivity value at this temperature from the conductivity versus temperature correction table (**Table 2**). Select Calibration Mode, then Conductivity. Enter the temperature corrected conductivity value into the instrument.

Table 2 Value Relationship of a 1,413 µS/cm (1.413 mS/cm) Reference Standard to Temperature

Temperature	Conductivity Standard	Temperature	Conductivity Standard
°C	**1413 µS/cm**	**°C**	**1413 µS/cm**
0	776	24	1386
1	799	25	1413
2	822	26	1441
3	846	27	1468
4	870	28	1496
5	894	29	1524
6	918	30	1552
7	943	31	1580
8	968	32	1608
9	992	33	1636
10	1017	34	1665
11	1043	35	1693
12	1068	36	1722
13	1094	37	1751
14	1119	38	1780
15	1145	39	1808
16	1171	40	1837
17	1198	41	1866
18	1224	42	1896
19	1251	43	1925
20	1277	44	1954
21	1304	45	1983
22	1331	46	2013
23	1358	47	2042

5. Select Monitoring/Run Mode. The reading should remain within manufacturer's specifications. If it does not, recalibrate.

Read the conductivity value on the instrument and compare the value to the specific conductance value on Table 2. The instrument value should agree with the standard within the manufacturer's specifications. If not, re-calibrate. If the re-calibration does not correct the problem, the probe may need to be cleaned or serviced by the instrument manufacturer.

1.2.2 Conductivity Probe Storage and Maintenance

These probes can usually be stored dry. Conductivity probes can get dirty over time, which interferes with the flow of electricity and can skew measurements. Clean the probes as recommended in the manufacturer's manual.

1.3 Oxygen Reduction Potential (ORP)

Most ORP meters are pre-calibrated in the factory and do not need to be calibrated before use. If verification of accuracy is needed there are "validation solutions" which show if a meter is reading correctly. A calibration check of the ORP probe can be performed by placing it into a Zobell™ solution that is within approximately 10°C of the expected groundwater temperature, or as close to groundwater or surface water temperature as practical.

1.3.1 ORP Calibration Procedures

1. If the instrument instruction manual states that the instrument is factory calibrated, then verify the factory calibration against the standard. If they do not agree within the specifications of the instrument, the instrument will need to be re-calibrated by the manufacturer.
2. Remove the probe from its storage container and place it into the standard.
3. Select Monitoring/Run Mode.
4. Wait for the probe temperature to stabilize, then record the temperature.
5. Look up the millivolt (mv) value at this temperature from the millivolt versus temperature correction table usually found on the standard bottle, on the standard instruction sheet, or in the manufacturer's manual. You may need to interpolate millivolt value between temperatures.
6. Select Calibration Mode, then "ORP". Enter the temperature-corrected ORP value into the instrument.

Select Monitoring/Run Mode. The readings should remain unchanged within manufacturer's specifications. If they change, recalibrate.

1.3.2 ORP Probe Storage and Maintenance

ORP meters are stored wet in a storage or buffer solution, and not in deionized/distilled water. If left dry, the probe can be reconditioned by soaking in a storage or buffer solution for about one hour. Electrode cleaning solutions should be used as needed to keep the probe clean and working correctly.

1.4 Dissolved Oxygen

Most meters allow calibration of the DO meter in air or against a wet sponge or paper towel, which gives a "saturated air" calibration. The only solution typically used for calibrating a DO meter is a "zero-oxygen" solution. This solution is used only if the samples being measured have very low oxygen concentrations.

There are two primary types of dissolved oxygen sensing technologies available: the optical based sensing method, which is commonly referred to as luminescent, and the Clark electrochemical or membrane-covered electrode. Within these two types of technologies, there are slight variations to calibration and measurement. Check the manufacturer's manual to ascertain the requirements of the probe being used.

1.4.1 DO Calibration Procedure

1. Place a wet piece of cloth or paper towel in the cap that covers the probe. The probe should not come in contact with the wet cloth or towel. The probe must fit tightly into the container to prevent the escape of moisture evaporating from the sponge or towel.
2. Turn on the instrument to allow the DO probe to warm up.
3. Allow the confined air to become saturated with water vapor (saturation occurs in approximately 10 to 15 minutes). Select Monitoring/Run Mode. Check temperature. Readings must stabilize before continuing to the next step.
4. Select Calibration Mode; then select "DO %".
5. Enter the local barometric pressure (usually in millimeters of mercury) for the sampling location into the instrument. This measurement must be determined from a local barometer. Do not use barometric pressure obtained from the local weather services unless the pressure is corrected for the elevation of the sampling location. [Note: inches of mercury times 25.4 mm/inch equals mm of mercury or consult Oxygen Solubility at Indicated Pressure chart attached to the SOP for conversion at selected pressures].
6. The instrument should indicate that the calibration is in progress. The instrument will take one minute or more to calibrate. After calibration, the instrument should display %-saturated DO.
7. Record the result in the Instrument Calibration Log.
8. Select Monitoring/Run Mode. Compare the DO (mg/L) reading to the Oxygen Solubility at Indicated Pressure chart as provided in the Equipment Manual. The numbers should agree. If they do not agree to the accuracy of the instrument (usually ± 0.2 mg/L), repeat calibration. If this does not work, change the membrane and electrolyte solution.
9. If a DO reference standard is used, remove the probe from the container and place it into a 0.0 mg/L DO standard. The standard must be filled to the top of its container and the DO probe must fit tightly into the standard's container (no headspace). Check temperature readings, as they must stabilize before continuing.
10. Wait until the "mg/L DO" readings have stabilized. The instrument should read 0.0 mg/L or to the accuracy of the instrument (usually ± 0.2 mg/L). If the instrument cannot reach these values, it will be necessary to clean the probe, and change the membrane and electrolyte solution. If this does not work, prepare a new 0.0 mg/L DO standard. If these measures do not work, contact manufacturer.
11. Record the result in the Instrument Calibration Log.

Check the dissolved oxygen reading against the theoretical value of saturated oxygen at different elevations. If the instrument is not reading in the proper range, it should be recalibrated, or the dissolved oxygen probe membrane should be replaced.

1.4.2 DO Probe Storage and Maintenance

Dissolved oxygen meters that use membranes should be stored wet to prevent the electrolyte solution and membrane from drying out. This can be done by submerging the probe in tap water or placing it against a moistened sponge, which many meters include for storage. If the probe dries out, the electrolyte solution and membrane may have to be changed.

Dissolved oxygen probes with membranes should have the membrane and electrolyte solution changed about every 2 months with normal use. Continual use may also result in deposits accumulating on the metal cathode. The deposits can be removed by removing the membrane from the DO sensor tip, and lightly brushing the metal end with very fine sandpaper (400 grit). Multi-parameter meters typically come with a maintenance kit that includes membranes, electrolyte solution, and a sanding disk.

Optical DO meters do not contain electrolyte solution or membranes, so they can be stored dry. Optical DO meters do not need any maintenance except for changing the sensing element, typically once a year with normal use.

1.5 Turbidity

Turbidity meters have calibration standards that are usually between 0 and 1000 nephelometric units (NTU). Most turbidity meter kits come with a set of these standards. When choosing which calibration standards to use, choose a reference standard that is near the anticipated turbidity of the water sample. The more reference standards used during the calibration, the better the accuracy.

1.5.1 Turbidity Calibration Procedures

1. Using a standard in the range of 5 to 20 NTUs, calibrate according to manufacturer's instructions or verify calibration if instrument will not accept a second standard. If verifying, the instrument should read standard value to within the specifications of the instrument. If the instrument has range of scales, check each range that will be used during the sampling event with a standard that falls within that range.
2. Record the results in the Instrument Calibration Log.

1.5.2 Turbidity Probe Storage and Maintenance

There are no storage requirements. The only maintenance involves the glass cuvettes. Light must be able to pass through the cuvettes, so if there are scratches, dirt or even oils from fingers on the sides of the cuvettes, it could skew the measurements. Make sure the cuvettes are clean, dry, and free of scratches before placed in the turbidity meter.

Attachment C Portable Gas Meters

ATT C SOP-08 Field Equipment Operation and Calibration Attachment B – Portable Gas Meter

EHS Support

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1 Portable Gas Meter

Many instruments are available for organic vapor monitoring, as well as monitoring of explosive atmosphere, oxygen levels, toxic gas, and airborne dust. Because it is beyond the scope of this SOP to describe all these alternatives, this SOP will focus on conducting air monitoring using a PID. In addition, the purpose of a function check (also known as a bump test) will be discussed; however, the calibration of a multi-gas meters (e.g., 4-gas meters, oxygen, hydrogen sulfide) will not be included in this SOP. Calibration of a multi-gas meters should follow recommended instructions in the manufacturer's manual.

All field air monitoring equipment will be calibrated onsite.

1.1 Function Check (Bump Test)

The function check (bump test) is a qualitative function check in which a challenge gas is passed over the sensor(s) at a concentration and exposure time sufficient to activate all alarm settings. The purpose of this check is to confirm that gas can get to the sensor(s) and that all the instrument's alarms are functional. The bump test or function check verifies that audible and visual alarms are activated and does not provide a measure of the instrument's accuracy.

Figure 1 Examples of Multi-Gas Meters (Rae System, BW Honeywell)

1.1.1 Bump Test Procedure

The bump test procedure is simple and easy, usually taking less than a minute to perform.

1. Turn on the equipment and allow the temperature of the unit to equilibrate to its surrounding.
2. Connect the tubing from the challenge gas to the gas monitor intake.
3. If tubing contains an in-line balloon, pinch off the middle of the tubing.
4. Turn on or open the challenge gas valve. If tubing contains an in-line balloon, allow balloon to inflate slightly, but not burst. If balloon bursts, replace balloon.
5. If visual and audible alarms come one, the bump test is successful. Turn off the challenge gas and remove the tubing from the meter.
6. If alarms do not come on, trouble shoot to assess cause (e.g., is challenge gas valve open, does the meter require calibration or repair).
7. Document the bump test results.
8. Return the PID to a secure area. Clean the instrument.

9. Connect the instrument to charger and plug in the charger. The probe must be connected to the readout unit to ensure that the unit accepts a charge.

1.2 Photoionization Detector

The PID is generally set to factory defaults for alarm limits, and unless directed, shipped to the renter with alarm limits specific to isobutylene (100 ppm). Calibrating the PID is a two-point process using "fresh air "and a standard reference gas (also known as span gas). First, a "Fresh air" calibration that contains no detectable volatile organic compounds (0.0 ppm) is used to set the zero point for the sensor. Then a standard reference gas that contains a known concentration of a given gas is used to set the second point of reference.

Figure 2 Examples of hand-held PIDs (RAE Systems, PhoCheck)

1.2.1 PID Calibration Procedures

1. Allow the temperature of the unit to equilibrate to its surrounding.
2. Verify the alarm limits are input correctly for the span gas (e.g., isobutylene). If the span gas or alarm limits on monitor do not match the span gas being used, consult with the manufacturer's manual, and change the limits as appropriate.
3. To perform a fresh air calibration, use the calibration adapter to connect to the PID to a "fresh" air source such as a "zero-gas" cylinder or "zero-gas" transferred into a Tedlar® bag. The "fresh" air is clean dry air without any organic impurities. If such an air cylinder is not available, any clean ambient air without detectable contaminants can be used.
4. Chose the "Fresh Air Cal" or similar under the menu prompt.
5. Open the Tedlar® bag valve or cylinder valve to initiate flow through the tubing into the instrument sensor. There can be a 3 to 5-second delay in read-out depending upon the instruments sensitivity.
6. Allow instrument to run during the test until prompted to accept the test result.
7. Turn off any flow of gas.
8. Record the reference standard and result in the Instrument Calibration Log.
9. To perform the span gas calibration, attach a flow-limiting regulator to span gas cylinder. The regulator flow must match or exceed the intake pump of the meter. Alternatively, the span gas can be transferred to a Tedlar® bag.
10. Chose the "Span Gas Cal" or similar under the menu prompt.
11. Open the Tedlar® bag valve containing the span gas or the span gas cylinder valve to initiate flow through the tubing into the instrument sensor.

12. Allow the instrument to run during the calibration test until prompted to accept the test results. The calibration results should be very close to the span gas concentration. If within 10% of the span gas concentration, the calibration is considered complete.
13. Turn off any flow of gas.
14. Record the reference standard and result in the Instrument Calibration Log.
15. Return to the "Ready" prompt and press "Yes" button to use the instrument during the day.
16. At the end of the day or work shift, turn the instrument to OFF.
17. Return the PID to a secure area. Clean the instrument.
18. Connect the instrument to charger and plug in the charger. The probe must be connected to the readout unit to ensure that the unit accepts a charge.

1.2.2 PID Equipment Maintenance

Daily maintenance generally includes cleaning of the outside of the equipment and ensuring the PID lamp remains free of moisture. The white filter tip used to protect the PID lamp should be discarded and replaced if it becomes soiled or wet. If the PID lamp needs to be cleaned or replaced, consult the manufacturer's manual. In many cases, a replacement or backup PID should be used so the malfunctioning instrument can be repaired.

SOP-09 Field Equipment Decontamination

Purpose

The purpose of this SOP is to provide procedures for field decontamination of environmental sampling equipment and personal protective equipment (PPE). Decontamination of equipment and PPE is designed to ensure that sample cross-contamination, human-health exposure, and contamination transport is minimized.

This SOP covers field decontamination of small re-useable equipment using a manual cleaning application. Procedural modifications may be warranted depending on field conditions, equipment limitations, or limitations imposed by the procedure. Construction of a decontamination station, use of a high-pressure spray washer, and decontamination of heavy equipment and machinery is addressed under SOP-10 Drill Rig and Heavy Equipment Decontamination.

Relevant EHS Support SOPs

- SOP-04 Field Documentation
- SOP-06 Pre-Field Mobilization
- SOP-07 Investigative Derived Waste
- SOP-10 Drill Rig and Heavy Machinery Decontamination
- SOP-12 Quality Assurance/Quality Control Samples
- Any SOP that references using small equipment or re-used equipment

Attachments

Attachment A Soluble Contaminants and Recommended Solvent Rinse

Required Materials

- Field logbook and field documentation
- Site maps, site layouts, site plans
- Health and Safety Plan (HASP)
- Appropriate personal protective equipment (PPE)
- Brushes and flat-blade scrapers
- Hand-held spray bottles
- Water - potable water, rinsate water
- Laboratory-grade non-phosphate detergent
- Additional cleaning agents, as specified in the project work plan, with appropriate safety data sheets
- Plastic waste bags or sheeting
- Waste containers (55-gallon drum or similar)

- Wash basins, buckets, pails, or tubs
- Paper towels and/or disposable drying cloths
- Drying shelves, as needed

1 Small Field Equipment Decontamination Guidelines

Decontamination is performed as a quality assurance measure. Improperly decontaminated sampling equipment can lead to misinterpretation of environmental data due to interference caused by cross-contamination between samples or sample locations through use of contaminated equipment. Decontamination also protects field personnel from potential exposure to hazardous materials on equipment. Proper PPE will be worn when conducting decontamination procedures.

1.1 Decontamination Area

The decontamination area should be located, if possible, where decontamination fluids and soil wastes can be easily discarded or discharged in accordance with the project plan or waste management plan. Select the decontamination area so decontamination investigative derived wastes (IDW) can be managed in a controlled area with minimal risk to the surrounding environment. The decontamination area should be large enough to allow temporary storage of equipment and materials, drum or waste storage, and if required to contain a large area for decontamination of large equipment (e.g., for heavy equipment or hollow-stem auger). Large equipment decontamination and decontamination pad construction for large equipment decontamination procedures can be referenced in SOP-10 Drill Rig and Heavy Machinery Decontamination.

Smaller decontamination areas, such as equipment decontamination between groundwater or surface water sample locations, may take place at the sampling location. In this case, required decontamination supplies and equipment must be mobilized to the location. Bucket and decontamination stations may be placed on plastic sheeting, or in basins, or tubs to capture decontamination IDW. Decontamination materials, including wastes, should be stored in central location(s) to maintain control over the materials used or produced throughout the investigation program.

1.2 Decontamination Considerations

- No hand to mouth contact (e.g., eating, smoking, drinking, chewing) shall be permitted during decontamination activities.
- All contaminated equipment shall be disassembled to the extent practical to allow for thorough decontamination procedures.
- If heavy residuals (e.g., petroleum, creosote) are encountered during field activities, an appropriate solvent (e.g., methanol) should be considered to remove any residues from equipment. If additional solvents are required and approved per the project plan or Project Manager, the solvent must be properly used, collected, stored, and disposed of according to the investigative derived waste plan, health and safety plan, and/or material safety data sheet. Take care that materials and solutions used for decontamination procedures are not hazardous themselves or could potentially contaminate samples (that is, are acids and solvents). Necessary precautions should be used if handling detergents and reagents, if used. A generalized solvent or reagent summary for few contaminants is included in Attachment A.
- Personal protective equipment (PPE) shall be worn to avoid splashing, skin contact, and incidental ingestion during decontamination procedures.

- Necessary precautions shall be used when handling detergents and reagents, if used.
- Quality assurance/quality control measures, if required, will be specified in the Project's Work Plan.

1.3 General Decontamination Procedures

Field equipment for decontamination may include a variety of items used in the field for monitoring and/or for collection of soil, sediment, and/or water samples, such as water level meters, certain water quality monitoring meters (check with manufacturer for suggested decontamination procedure), split-spoon samplers, trowels, scoops, spoons, and pumps. Dedicated equipment is not usually decontaminated, as a general rule. Disposable equipment (e.g., bailers, rope, EnCore™ samplers, and filters) will be properly discarded after use.

Decontamination will occur before use, between sample locations, and prior to transporting off-site for re-used or non-disposable equipment. Rental equipment used in the field, which is being returned to the respective vendor, will be decontaminated prior to shipment. Conduct consistent decontamination of sampling equipment to ensure the quality of the samples collected.

Equipment decontamination is comprised of four general steps.

1. Removal of gross (visible) contamination
2. Removal of residual contamination
3. Prevention of recontamination
4. Disposal of wastes associated with the decontamination

Decontamination Caution: Some types of decontamination procedures require the use of solvents or rinsates which may be chemical specific. A general Soluble Contaminants and Recommended Solvent Rinse (EPA, 1994) is provided in **Attachment A**; however, the table may be limiting and not appropriate for the scope of work. Safety Data Sheets should be included in the project Health and Safety Plan or available for reference.

1.4 Small Equipment Decontamination Procedures

Small equipment generally includes soil sampling equipment (e.g., trowels, split spoon samplers, hand augers, water interface probes). Small equipment decontamination procedures will be generally conducted as follows:

1. Remove any gross contamination from the equipment. Gross contamination generally applies to soil sampling equipment that may have residue clinging to the equipment. The clinging residual soil can usually be removed by dry brushing or scraping, or in some cases using a high-pressure sprayer. Removal of gross contamination should be done close to the source of contamination.
2. Remove residual contamination including film or other particles. This generally consists of a series of sprayers, buckets, or basins used to wash and rinse the equipment.

3. Wash equipment vigorously with a bristle brush or similar in a bucket containing potable water with non-phosphate lab-grade detergent such as Liquinox®, Alconox®, or equivalent.
4. Rinse equipment thoroughly in a second bucket containing potable water (1st rinse).
5. Rinse equipment thoroughly with distilled or deionized water (2nd rinse).
6. In few instances, such as decontaminant of sensitive field instruments, it may be necessary to rinse equipment with distilled, deionized, or American Society for Testing and Materials International (ASTM) reagent grade water (3rd rinse).
7. Allow equipment to air dry in an area free from contact with contaminants. All decontaminated equipment should be dry prior to use. A decontaminated metal drying rack may be used to aid in the drying process.
8. Decontamination equipment should be stored to preserve the clean status. This step will vary on the nature of the equipment. Protection measures may include covering or wrapping the equipment in plastic or aluminum foil. Only personnel wearing clean protective gloves (e.g., nitrile, latex) should handle the decontaminated equipment to prevent re-contamination.
9. If the decontaminated equipment is not to be used immediately after cleaning, it should be covered or wrapped to protect the equipment from contaminants.
10. Replace dirty detergent water solution and rinsate(s) between borings, sample locations, or as deemed appropriate to limit cross-contamination.
11. Document the procedure used, fluids used, and any changes into a bound field notebook or on project-specific forms.
12. Waste decontamination materials such as spent liquids and solids will be collected and managed in accordance with SOP-07 Investigative Derived Waste.

1.5 Groundwater Sampling Decontamination Procedures

Proper decontamination between monitoring wells is essential on equipment such as submersible or bladder pumps in which mechanisms of the pump come in direct contact with potentially contaminated water. This SOP does not address decontamination of re-useable bailers. The following steps shall be used for contaminated pumps:

1. Disassemble the equipment to the extent practical.
2. Wash any small mechanism of the pump assembly (e.g., check valve, tube adapter)
3. Wash the exterior of the pump casing vigorously with a bristle brush or equivalent in a bucket containing potable water with non-phosphate lab-grade detergent such as Liquinox®, Alconox®, or equivalent. A bottle brush may be used to clean the interior of pump casing.
4. If decontaminating a pump in which sample water comes in contact with internal mechanisms of the pump system, place the pump into a potable water wash container containing non-phosphate lab-grade detergent. Ensure the pump intake is fully submerged and the pump outlet is allowed to flow directly back into the wash container. Energize the pump at a very low flow rate to allow the wash water to recirculate through the pump mechanism for 2 to 5 minutes.
5. Rinse the external portion of the pump using potable water (1st rinse). Submerge the pump intake into potable water (1st rinse) and energize the pump to recirculate the rinse water through the pump mechanism.
6. Use distilled, deionized, or ASTM reagent grade water (2nd rinse) as necessary to the external and internal portions of the pump and pump mechanisms.

7. Dry off excess water with a clean paper towel or disposable cloth.
8. Reassemble the pump.
9. Replace dirty detergent water solution and rinsate(s) between sample locations or as deemed appropriate to limit cross-contamination.
10. Document the procedure used, fluids used, and any changes into a bound field notebook or on project-specific forms.

2 Records

Field logbook and field documentation will be completed in accordance with SOP-04 Field Documentation. Detailed records will be maintained about decontamination procedures. Required records may include details about:

- Decontamination personnel
- Decontamination solutions types and methods
- Date and time of decontamination
- Decontamination station location
- Equipment type or identification numbers
- Decontamination solution Lot numbers
- Any problems encountered, observations, or alterations
- Safety Data Sheets for any specialized chemicals used in the decontamination process
- Volume of decontamination materials generated (IDW log)

Attachment A Soluble Contaminants and Recommended Solvent Rinse

APPENDIX A

Table

Table 1. Soluble Contaminants and Recommended Solvent Rinse

TABLE 1 Soluble Contaminants and Recommended Solvent Rinse		
SOLVENT[1]	EXAMPLES OF SOLVENTS	SOLUBLE CONTAMINANTS
Water	Deionized water Tap water	Low-chain hydrocarbons Inorganic compounds Salts Some organic acids and other polar compounds
Dilute Acids	Nitric acid Acetic acid Boric acid	Basic (caustic) compounds (e.g., amines and hydrazines)
Dilute Bases	Sodium bicarbonate (e.g., soap detergent)	Acidic compounds Phenol Thiols Some nitro and sulfonic compounds
Organic Solvents [2]	Alcohols Ethers Ketones Aromatics Straight chain alkalines (e.g., hexane) Common petroleum products (e.g., fuel, oil, kerosene)	Nonpolar compounds (e.g., some organic compounds)
Organic Solvent[2]	Hexane	PCBs

[1] - Material safety data sheets are required for all decontamination solvents or solutions as required by the Hazard Communication Standard

[2] - WARNING: Some organic solvents can permeate and/or degrade the protective clothing

SOP-12 Quality Assurance/Quality Control Samples

Purpose

The purpose of this SOP is to give details to the quality control (QC) measures taken to ensure the integrity of the samples collected, and to establish the guidelines for the collection of QC samples. The objective of the QC program is to ensure that quality data of known and reliable quality are developed.

Documentation of representative data is essential to site investigations; therefore, the data must be validated though the performance of QC sampling. Verification performance sampling is necessary to evaluate and identify contradictory or suspect data. The project manager must determine the QC sampling requirements. Data validation measures must be specified as part of all environmental investigations. The collection of field QC samples serves to ensure proper field procedures, but can also serve as a mechanism for the laboratory to perform their quality assurance/quality control (QA/QC) program [such as collecting sufficient sample volume to allow the laboratory to perform a matrix spike (MS)/matrix spike duplicate (MSD) on their equipment or method].

Relevant EHS Support SOPs

- SOP-04 Field Documentation
- SOP-05 Sample Management and Shipping
- SOP-09 Equipment Decontamination
- SOP-22 Soil Sampling for Chemical Analysis
- SOP-42 Groundwater Sampling for Chemical Analysis
- SOP-61 Surface Water Sampling
- SOP-62 Sediment Sampling

Required Materials

Equipment used during collection of QC samples will be the same equipment utilized to collect the primary or parent sample, which may include a wide variety of tools depending upon the media sampled, type of sampling, and methods used.

- Field logbook and field documentation
- Site maps, site layouts, site plans
- Health and Safety Plan
- Appropriate personal protective equipment (PPE)
- Black waterproof and/or indelible ink pens
- Quality control bottle sets
- Other laboratory-supplied quality control bottle types (e.g., trip blanks, temperature blanks)
- Appropriate sample containers, sampling kits, labels, coolers and ice, Chain of Custody forms

1 Quality Assurance/Quality Control Samples

In order to assess the accuracy and precision of the field methods and laboratory analytical procedures, QA/QC samples are collected during the sampling program according to the project work plan. The QA/QC samples may be labeled with QA/QC identification numbers or fictitious identification numbers (if blind submittal is desired) and are sent to the laboratory with the other samples for analyses. The frequency, types, and locations of QC (field-specific) samples will be specified in the project work plan or the site specific quality assurance project plan (QAPP). Types of quality control samples may include duplicate, trip blank, equipment blank, field blank, matrix spike and matrix spike duplicate, and temperature blank.

The QA/QC samples could be sampled on any sample media such as soil, groundwater, surface water, sediments (SOP 22, SOP-42, SOP-61, and SOP-62) or project-specific media. Field documentation (SOP-04) and sample management and shipping (SOP-05) will be used for any QA/QC samples generated during the investigation process. Naming of QA/QC samples should be provided in the project work plan or QAPP.

1.1 Duplicate Samples

Duplicate sample analysis evaluates the precision of field and laboratory components of field samples and matrix heterogeneity. Duplicate samples are two physical samples collected simultaneously from the same location under identical conditions. The project work plan will determine if the duplicate sample is homogenized. A duplicate sample should be:

- Collected for any media sampled in the field.
- Collected in accordance with the sample collection procedures identified in the project work plan.
- The work plan should identify the ratio of duplicate sample collection per primary samples; however, if the ratio is not addressed in the project work plan, duplicate samples will be collected at a rate of 1 duplicate sampled per 20 samples (5%).
- Submitted for laboratory analysis for the same or a subset of the analysis requested for the primary (or parent) sample.
- Handled and preserved in the same manner as the primary sample.

To collect duplicate samples:

1. Collect the duplicate sample concurrently with the primary (or parent) sample (e.g., water, surface water, air) or in the next consecutive sample (e.g., soil, sediment). For soil or sediment samples collected in an 18-inch long split barrel that contains three 6-inch long (brass or stainless steel) sleeves of soil, the middle sleeve is designated as the primary sample, then the next sleeve (either the top or bottom sleeve) will be the duplicate sample.
2. Record the duplicate sample name in the field logbook or field documentation, including the chain of custody.

3. Record the duplicate sample location in the field logbook or field documentation. Do not indicate the duplicate location in the chain of custody if the sample will be considered a “blind duplicate.”

1.2 Trip Blank

A trip blank sample is a sample of distilled or de-ionized water prepared in the laboratory, which accompanies the samples to and from the field, never opened, until all samples are ready for analysis. The trip blank assesses the potential for in-transit contamination of samples. The trip blank is later opened in the laboratory and analyzed along with field samples for constituent(s) of interest to ascertain whether cross-contamination has occurred during field handling, shipment, or in the laboratory.

- One trip blank (generally one or two 40-milliliter volatile organic analytical vials) should accompany each cooler containing volatile organic compound samples that are being submitted for lab analysis.
- The sample name convention should be dictated in the project work plan. If the nomenclature is not provided in the project work plan, the trip blank should be labeled with the date (e.g., TB-20140531) and/or sequence (TB-2-201405301). The addition of the date streamlines identification of the potentially affected samples in case cross-contamination is suspected during container or sample shipment.
- The trip blank is recorded on the chain of custody, at a minimum, and can be included in the field logbook or field documentation.

1.3 Equipment Blank

The collection of an equipment blank evaluates field decontamination procedures. To collect an equipment blank:

1. Decontaminate the reusable sample equipment (e.g., pump, split spoon sampler, bailer) in accordance with the project work plan or SOP-09 Field Decontamination. If equipment blank is being collected off a supplied material (e.g., tubing, disposable bailer), the supplied material will be unused (new).
2. Run "clean" (e.g., distilled/de-ionized/demonstrated analyte free) water through or down the equipment and into the appropriately labeled sample set.
3. The equipment blank sample set is identical to the sample set being analyzed. (For instance, if the project requires analysis for volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs), the equipment blank sample set will include a bottle set and analysis for VOCs and SVOCs.)
4. In some situations, one equipment blank will be required for each type of sampling procedure (e.g., bailer, soil sampling equipment, etc.).
5. Record the equipment blank sample name in the field logbook or field documentation, including the chain of custody.
6. Record the equipment blank sample location, type of equipment, etc. in the field logbook or field documentation.

7. The equipment blank can be collected one per equipment type, one per borehole, one per day, or as outlined in the project work plan or QAPP.

1.4 Field Blank

A field blank might be necessary where ambient air quality is poor. Taking this field blank would determine if airborne contaminants interfere with constituent identification or quantification.

- The field blank will be collected as outlined in the project work plan or QAPP.
- The field blank sample set is identical to the sample set being analyzed. (For instance, if the project work plan requires analysis for VOCs and SVOCs, the equipment blank sample set will include a bottle set and analysis for VOCs and SVOCs).

To collect a field blank:

1. The "clean" (e.g., distilled/de-ionized/demonstrated analyte free) water container will remain unopened until collection of the field blank sample occurs at the designated location.
2. Fill the sample bottle set with "clean" water. Pour clean water directly in to the sample bottles at the designated sample location. The clean water is exposed to the air as it travels from the “clean” water container to the sample container.
3. Record the field blank sample name in the field logbook or field documentation, including the chain of custody.
4. Record the field blank sample location in the field logbook or field documentation.

1.5 Matrix Spike and Matrix Spike Duplicates

An extra volume of sample media may be collected during the sampling event for performance of MS/MSD analyses by the laboratory to assess laboratory accuracy, precision, and matrix interference. The laboratory adds spikes of compounds (e.g., standard compound, test substance, etc.) to the additional sample volume to determine if the matrix is interfering with constituent identification or quantification. In addition, MS/MSD samples perform as a check for systematic errors and lack of sensitivity of analytical equipment.

Results of the laboratory analyses are compared with the results of the primary sample and the known concentrations of the spike compounds. The percent recovery and relative percent difference are calculated, and results are used to evaluate the precision and accuracy of the analytical method for various labeled "extra volume samples for MS/MSD." The MS/MSD sample should be:

- Collected for any media sampled in the field.
- Collected in accordance with the sample collection procedures identified in the project work plan.
- The work plan should identify the ratio of MS/MSD sample collection per primary samples; however, if the ratio is not addressed in the project work plan, MS/MSD samples will be collected at a rate of 1 MS/MSD sampled per 20 samples (5%).

- Submitted for laboratory analysis for the same or a subset of the analysis requested for the primary (or parent) sample.
- Handled and preserved in the same manner as the primary sample.

To collect a MS/MSD sample:

1. Collect the duplicate sample concurrently with the primary (or parent) sample (e.g., water, surface water, air) or in the next consecutive sample (e.g., soil, sediment). For soil or sediment samples collected in an 18-inch long split barrel that contains three 6-inch long (brass or stainless steel) sleeves of soil, the middle sleeve is designated as the primary sample, and the top and bottom sleeve will be the designated as the MS/MSD sample.
2. Generally, two to three times the volume of primary sample is required in an MS/MSD sample (or, the sample is collected in triplicate).
3. Identify the MS/MSD is on the chain of custody by indicating the extra volume or number of sample jars, and include a sample identifier or note to indicate the sample is an MS/MSD sample.
4. Record the MS/MSD sample name in the field logbook or field documentation, including the chain of custody.

1.6 Temperature Blank

A temperature blank is a vial of water that accompanies a sample cooler that will be opened and tested upon arrival at the laboratory to ensure the temperature of the contents of the sampling shipping container are within the required 4 degrees (°) Celsius ± 2°. Temperature blanks are generally included for chemical analysis samples that have a temperature requirement.

- The temperature blank requires little attention except to ensure one is in each cooler containing ice.
- Check with the laboratory if a temperature blank is not included in the cooler shipped to the site. A few laboratories are moving to temperature sensors (e.g., infrared sensors) to monitor cooler temperature upon arrival to the laboratory.
- Temperature blanks are generally required for those samples required to be preserved to 4° C ± 2°.
- No documentation is required on temperature blanks by the field staff.

2 Records

Field notes will be kept in a bound field logbook or approved field documentation following the format specified in SOP-04 Field Documentation. Detailed records will be maintained during sampling activities, particularly with respect to the location of QA/QC samples. The following information should be recorded:

- Location of QA/QC sample
- QA/QC sample name
- Type of QA/QC sample
- Sample analysis
- If needed, equipment type the QC sample was collected from
- “Clean” water type (laboratory supplied, grocery store)
- If applicable, weather conditions (e.g., air quality for field blanks)

SOP-41 Fluid Measurement

Purpose

This SOP provides personnel procedures to use in measuring the depth to water, the depth to non-aqueous phase liquids, and the total depths in monitoring wells, piezometers, water bores, or other wells or access points (extraction wells, injection wells, etc.). For this SOP, the term "well," "monitoring well," or "water bore" will be used as the generic term for a water monitoring point.

Relevant EHS Support SOPs

- SOP-04 Field Documentation
- SOP-09 Equipment Decontamination
- SOP-42 Well Development
- SOP-43 to SOP-47 Groundwater Sampling SOPs
- SOP-48 to SOP-50 Aquifer Testing SOPs

Attachments

- Attachment A Fluid Level Monitoring Forms

Required Materials

- Air monitoring instrumentation (e.g., PID) and supplies
- Field logbook and field documentation
- Site plan showing borehole locations
- Health and Safety Plan (HASP)
- Indelible ink pens and waterproof marking pen
- Fluid measurement device (e.g., water level indicator, interface probe)
- Extra batteries
- Paper towels and trash bags
- Decontamination supplies
- Information about the well or borehole including well construction details, previous well gauging data, if available.

1 Fluid Level Monitoring

Water level data is generally used for several purposes during a site investigation, including:

- Determination of horizontal and vertical hydraulic gradients
- Monitoring of changes in groundwater levels over time
- Assessment of surface water/groundwater interaction that occurs during various flow conditions
- Estimation of aquifer properties after aquifer testing
- Calculation of purge volume of standing water in the well for well development or water sampling
- Monitoring recharge during and after purging and aquifer testing.

A water level meter will typically be used to measure the groundwater levels and total depths. If non-aqueous phase liquid (NAPL) is present in the well, an oil-water interface probe will be used. NAPL level data is generally used for purposes of estimating NAPL volume, extent, or properties; and NAPL stabilization or stability.
A number of devices are available for the collection of fluid level measurements in monitoring wells. The most commonly used (and covered in this SOP) include an electric water level sounder and an interface probe (often times called a membrane interface probe or an oil-water interface probe). Other types of water level indicators and recorders include weighted steel tape, chalked tape, sliding float method, airline pressure method, and automatic recording methods (data loggers). These methods are primarily used for closed systems or permanent monitoring wells.

1.1 General Well Monitoring Considerations

General knowledge of the well construction, former fluid levels, and groundwater analytical data is helpful before field mobilization. This data can be useful in determining the monitoring order of the well (less contaminated to more contamination), and can be used to confirm or deny that current measurements comply (within a certain level of accuracy) with historical measurements.

Fluid levels and well depth measurements should be made relative to an established reference point on the well casing and should be documented in the field records. This reference point is usually identified by a permanent marker marking on the top of a polyvinyl chloride (PVC) well riser or by notching the top of casing with a chisel for stainless steel wells. Whether a marking is present or not, the north side of the top of casing is considered the general convention reference point.

Fluid levels should be allowed to equilibrate to atmospheric conditions after removing the sealing caps. Changes in fluid levels generally occur due to:

- Atmospheric pressure changes
- Tidal influences
- Changes in river stage, impoundments levels, or flow in unlined ditches
- Pumping of nearby wells
- Precipitation.

There are no set guidelines and appropriate equilibration times can range from minutes to hours depending on well recharge, local geology and topography, and project objectives. If fluid levels appear to rise or fall during the measurement process, allow at least three to five minutes to assess if levels have stabilized. If levels appear to change, a best determination should be made (i.e., allow more stabilization time) when to collect the water level.

1.2 Water Level Monitoring

Water level meters use a battery-powered probe assembly attached to a cable marked in 0.01-foot (5 millimeters) increments. These types of instruments consist of a spool of dual conductor wire and a probe attached to the end and an indicator. When the probe comes in contact with a fluid, the circuit is closed and a meter light and/or audible buzzer attached to the spool will signal contact. Note: A water level indicator is not capable of distinguishing between water and other fluids with a density close to that of water. Commonly used water level indicators are shown in **Figure 1**.

Figure 1 Water Level Indicators (Solinst and Heron)

Water level measurements are commonly taken in each monitoring well immediately prior to, during, and following well development (SOP-42 Well Development), prior to, during, after well purging and sampling depending on the sampling method (SOP-43 to SOP-47), and for any aquifer testing (SOP-48 to SOP-50). Water level measurements may also be taken to monitor or generate water table or piezometric surfaces. When measuring wells for monitoring potentiometric surface, and if the analytical concentrations in groundwater is known for each of the wells, it is advisable to collect water levels beginning with the least contaminated well(s) and progressing to the most contaminated well(s).

1.2.1 Water Level Measurement Procedures

1. Decontaminate the water level indicator in accordance with the procedures described in SOP-09 Equipment Decontamination.
2. Note well ID, time of day, and date in site logbook or the appropriate field form.
3. Open well and remove well cap.
4. If required in the project work plan, monitor headspace of well with a PID or plan-specified detector to assess presence of volatile organic compounds. Record results.
5. Turn on the indicator. Depress the “test button” to ensure the indicator is operating correctly. When the “test button” is depressed, the meter light should illuminate, and the audible buzzer should emit a tone. If not, assess problem.
6. Ensure the indicator’s reel is not “locked.” If it is, loosen the lock.

7. Slowly lower the water level indicator probe down the monitoring well until the probe contacts the water surface, as indicated by the audible alarm. Do not let the probe tip and tape free-fall down the well. Always hold onto the meter's reel handle.
8. Raise the probe slowly out of the water until the audible alarm stops. Continue raising and lowering the probe until a precise level is determined within 0.01 foot or 5 millimeters.
9. Record the water level in the field logbook or approved field documentation.
10. Decontaminate the water level indicator for measurement at the following well.

1.2.2 Total Well Depth Measurements Procedures

Total depth measurements should be routinely conducted on wells as part of routine maintenance (i.e., ensuring the well has not been compromised or is filling with sediment). Collection of total depths for this SOP refers to wells or boreholes that do not have dedicated pumps or extraction equipment (e.g., monitoring wells, piezometers). If total depths are requested on wells that have dedicated equipment, construction, operation, and extraction equipment details should be made available to assess the ability to collect a total depth reading, if a system needs to be de-energized, etc.

A water level indicator should be used to measure the total depths of wells that do not a separate-phase liquid.

Use the following procedures to measure the total depth of a monitoring well:

1. Visually inspect the probe tip. Confirm the zero-measurement point **(Figure 2)**.
2. Slowly lower the water level meter until the cable goes slack (assume to be the bottom of the well). Do not let the probe tip and tape free-fall down the well. Always hold onto the meter's reel handle.
3. Gently raise and lower the water level meter probe to tap the bottom of the well.
4. Record the reading on the cable at the established reference point to the nearest 0.01 foot or 5 millimeters.
5. If there is an offset [.g., 0.3 feet (9 cm) for some Solinst or Heron indicators] between the bottom of the probe and the water level sensor **(Figure 2)**, adjust the total depth measurement accordingly (i.e., add the additional length from the zero-measurement point).
6. Record the total depth measurement in the field logbook or approved field documentation.

Figure 2 Comparison of Zero Measurement Points at the Top of the Probe and 0.3 Feet (9 cm) Above the Tip of the Probe

1.3 NAPL Monitoring and Procedures

The interface probe device is very similar to a water level indicator in that the probe is operated from a 9-volt battery, is connected to a measuring tape that measures to the nearest 0.01 foot or 5 millimeters, and contains a receiver with an audio and/or visual signal that indicates when phase changes occur. The difference from the water level indicator is that the device detects the difference in conductivity or specific gravity between the aqueous and nonaqueous phases in the well. The device detects the presence of both light NAPL (LNAPL) (floating) and dense NAPL (DNAPL) (sinking) in water wells.

1. Decontaminate the interface probe in accordance with the decontamination procedure described in SOP-09 Equipment Decontamination.
2. Note well ID, time of day, and date in site logbook or the appropriate field form.
3. Open well and remove well cap.
4. If required in the project work plan, monitor headspace of well with a PID or plan-specified detector to assess presence of volatile organic compounds. Record results.
5. Turn on the indicator. Depress the “test button” to ensure the indicator is operating correctly. When the “test button” is depressed, the meter light should illuminate, and the audible buzzer should emit a tome. If not, assess problem.
6. Ensure the indicator’s reel is not “locked.” If it is, loosen.
7. Slowly lower the indicator probe down the monitoring well until the probe contacts the water surface or LNAPL, as indicated by the audible alarm. Do not let the probe tip and tape free-fall down the well. Always hold onto the meter’s reel handle.
8. For LNAPL:
    - Raise probe out of LNAPL until the audible alarm stops. Continue raising and lowering the probe until a precise top measurement level is determined within 0.01 foot. Record the depth.
    - Very slowly lower the probe through the LNAPL until any audio (or visual queue) is emitted from the indicator (it is important to go slowly to avoid potential mixing at the LNAPL and water interface). The audio (or visual queue) indicates the phase has passed into water. Raise and lower the probe slowly through the alternative sound depth 2 to 3 times to achieve a better lower depth for the LNAPL depth.
    - Measure the lower LNAPL depth to the nearest 0.01 foot or 5 millimeters. Record the depth.
9. For DNAPL:
    - Once the water level depth has been recorded, continue to lower the interface probe through the water column slowly. Do not let the probe tip and tape free-fall down the well.
    - Measure the upper depth of the DNAPL once an audio or visual change is emitted from the indicator. Raise and lower the probe through the alternative sound depth 2 to 3 time to achieve a better upper depth measurement for the DNAPL. Record the depth.
    - Do not continue any measurements through the DNAPL. Retrieve the probe.
10. Decontaminate the interface probe for NAPL measurement at the following well.

Note any change in the tone emitting from the interface probe when gaging for NAPL (along the length of the water column). If changes are noted at a mid-well depth, the indicator may be sensing a NAPL phase or dissolved phase present in the middle of the aquifer (i.e., neither LNAPL nor DNAPL).

1.4 Common Problems and Corrective Actions

All measuring tapes should be inspected prior to use for kinks, cracks, or tears and, if present, repaired or replaced with undamaged equipment. Bends and kinks may affect depth accuracy. The most-common problems that occur during fluid level measurement include:

No signal (audible or visible) when unit is turned on.

- Corrective Action:
  - The battery is discharged. Check or change battery.
  - The circuit is malfunctioning.

No indication of water.

Corrective Action:

- The conductive contact is dirty. Clean the contact.
- There is an open connection in the tape. Replace tape and/or probe. The circuit is malfunctioning.

The signal (audible or visible) is intermittent.
Corrective Action:

- There is an open connection in the tape. Replace tape and/or probe.
- There is a loose connection in the circuit or the probe. Repair the connection.
- Water may be cascading in from a damaged well riser or in from soil or rock layers is in an open-hole or rock well. Continue to lower the tape until the probe contacts water to emit a solid tone.

The signal (audible or visible) is continuous when not in water.
Corrective Action:

- The conductive contact is dirty (causing bridging). Clean the contact.
- There is a short in the tape and/or probe. A short in the tape usually is observed by missing plastic along the tape and exposure to the underlying wire. Replace tape and/or probe.

2 Records

Field notes will be kept in a bound field logbook or approved field documentation following the format specified in SOP-04 Field Documentation. The following information should be recorded when conducting fluid measurements:

- Well identification
- Depths to water, NAPL, and total depth
- Date and time
- Site conditions (e.g., floating oil or debris, gassing)
- Weather observations (e.g., wind speed, sunny or cloudy sky)
- Monitoring equipment used
- Any unusual well or groundwater observations.

Attachment A Fluid Level Monitoring Forms

EHS Support

FLUID LEVEL MONITORING FORM

Project: _____

Project Number: _____

Project Location: _____

Field Technician(s): _____

Weather: _____

Equipment: _____

Well ID	Top of Casing Elevation	Ground Surface Elevation	Well Info (from boring logs)			Date	Time	Product Level	Water Level	Total Depth	Comments
	(feet msl)	(feet msl)	Total Depth (feet bgs)	Screened Interval (feet bgs)	Screened Elevation (feet msl)			(feet bTOC)	(feet bTOC)	(feet bTOC)	

msl - mean sea level
bgs - below ground surface
bTOC - below top of casing

Signature: _____

EHS Field Form 021
Issue Date: August 18, 2014
Revision No: 00
Revision Date:

EHS Support

FLUID LEVEL MONITORING FORM

Project: _____

Project Number: _____

Project Location: _____

Field Technician(s): _____

Weather: _____

Equipment: _____

Well ID	Date	Time	Product Level (feet bTOC)	Water Level (feet bTOC)	Total Depth (feet bTOC)	Comments

bTOC - below top of casing

Signature: _____

SOP-43 Low Flow Groundwater Sampling

Purpose

The purpose of this SOP is to describe groundwater purging and collection procedures for groundwater samples from wells using low-flow purging and sampling techniques.

This procedure is based on the assumption that groundwater samples are able to be collected using low-flow (minimal drawdown) sampling techniques. Low-flow sampling techniques may not be practical or the best method for the collection of representative groundwater samples in all wells. In the event low-flow sampling techniques are insufficient for use, SOP 44: Groundwater Sampling Using a Volume Purge Technique will be followed to collect the groundwater sample.

Relevant EHS Support SOPs

- SOP-04 Field Documentation
- SOP-05 Sample Management and Shipping
- SOP-08 Field Equipment Operation and Calibration
- SOP-09 Equipment Decontamination
- SOP-41 Fluid Measurement
- SOP-46 Water Sampling for Chemical Analysis.

Attachments

- Attachment A EHS Support Low Flow Groundwater Sampling Form
- Attachment B Low-Flow (Minimal Drawdown) Groundwater Sampling Procedures

Required Materials

- Air monitoring instrumentation (e.g., PID) and supplies
- Water quality meters for temperature, specific conductance, pH, DO, ORP, and turbidity
- Field logbook and field documentation
- Site plan showing well or water bore locations
- Health and Safety Plan (HASP)
- Indelible ink pens and waterproof marking pen
- Pump, controller, and power source—generator or battery
- Teflon or polyethylene tubing
- Decontamination equipment and supplies
- Bucket, drums, or other large container for storing and/or transporting development water.
- Measuring equipment (tape, water level indicator)
- GPS
- Camera

- Appropriate sample containers, sampling kits, labels, coolers, ice, Chain of Custody forms, tape, plastic baggies
- Duct tape and wrapping tape.

1 Low Flow Groundwater Sampling

Low-flow sampling purges stagnant water out of the well to allow sampling of formation water; however, it is intended to purge and sample only a limited interval of the well/formation. The term "low-flow" refers to the velocity at which water enters the pump or tubing intake from the surrounding formation in the immediate vicinity of the well screen. Purging at a low flow rate within the screened interval of a well should result in minimal drawdown of the water level, minimize the mixing of stagnant water in the well with formation water, and should result in a representative sample of the formation water. The low-flow technique described in this SOP complies with the guidelines provided by Puls and Barcelona (USEPA Low-Flow (Minimal Drawdown) Groundwater Sampling Procedures, 1996).

1.1 Low Flow Groundwater Sampling Considerations

Low-flow purging has advantages and disadvantages.

Advantages	Disadvantages
• Improved sample quality by minimizing the disturbance in the well • Less mixing of the stagnant casing water with the formation water • Samples are more representative of the mobile load of contaminants present in the aquifer reducing the need for filtering the water samples • Turbidity can be lower due to the slower discharge rate • The purging and sampling time is reduced • Less operator variability, greater operator control • Better sample consistency; reduced artificial sample variability • Purge quantity is smaller resulting in less wastewater	• The necessity for more equipment such as variable speed pump with the capability to pump at low rates, a flow-through cell that includes pH, oxidation-reduction potential (ORP), dissolved oxygen (DO), temperature, specific conductance, and a turbidity probe and meter(s) • Additional cost and time can be incurred since stabilization of water parameters may require relatively longer times • Sample results may not be reproducible if the pump is placed at a different depth within the screened interval each time the well is sampled
Low-flow purging is generally most effective • with short-screened intervals (e.g., < 20 feet, < 6 m).	Low-flow purging is generally not suitable for: • aquifers with very low hydraulic conductivities where minimal drawdown cannot be maintained • long screened intervals (e.g., > 9 m) or open-hole wells where the hydraulic flow pathways are unknown • use where the aquifer is contaminated by non-aqueous phase liquids.

Selecting equipment for purging and sampling a well requires site and project specific considerations to ensure that all collected samples meet the project objectives and data quality requirements. Groundwater chemistry can be altered by changes in temperature, pressure, and exposure to air that are brought on by the sampling process. Therefore, it is important to select sample equipment and follow sampling procedures that minimize changes.

Factors to consider when selecting sample equipment include: the analytes being evaluated, the type and location of well being sampled, physical characteristics of the well (diameter and total depth), depth to water, geology adjacent to the screened interval and the groundwater chemistry.

1.2 Equipment

1.2.1 Pumps

Pumps transport water from depth to the land surface by two methods, suction lift or positive pressure. The pumping mechanism for most suction-lift pumps is at land surface. Positive-displacement pumps (e.g. submersible and bladder) are placed below the static water level.

Control of the pumping rate is an important consideration when selecting dedicated or portable pumps. Sampling rates should be high enough to fill sample containers efficiently and with minimal exposure to the atmosphere, but low enough to minimize sample alteration by agitation or aeration. This is especially important for sensitive analytes, such as volatile organic compounds (VOCs) and trace metals. Other considerations in pump selection:

- Suction pumps, (e.g., peristaltic pumps) may be inappropriate for collecting VOCs, semi-VOCs (SVOCs), volatile petroleum compounds, and some (pH-dependent) metals. Suction lift pumps are not recommended for sampling VOCs because a vacuum is created at the intake to draw the sample to the land surface and can result in the loss of volatile organics or other dissolved gases. The lift capacity of the peristaltic pump is about 25 feet (8 to 10 meters) below ground surface.
- Positive-displacement pumps are generally preferred over suction-lift pumps.
- Dedicated pumps are preferable to portable pumps because portable pumps can create a disturbance in the water column during installation and require decontamination between wells.
- If a portable pump is selected for low-flow pumping, new or dedicated tubing must be used at each sampling location, and the pump must be lowered gently into the well to minimize disturbance to the water column.
- Depth to water effects positive-displacement pump operation. The pumping rate will typically decrease with increased depth to water.
- If a gasoline- or diesel-powered generator is used to energize the sampling pump, the power source must be located at least 10- to 20-feet (5 to 10 meters) downwind of the wellhead.
- Inertial pumps (e.g., Waterra) or bailers should never be used for low- flow sampling because they generate turbulence in the well and exacerbate degasing.

1.2.2 Tubing

Teflon or Teflon-lined polyethylene tubing is preferred when sampling VOCs, SVOCs, pesticides, polychlorinated biphenyls (PCBs), and inorganics. Polyvinyl chloride (PVC), polypropylene, or polyethylene tubing are to be used when collecting samples for metal and other inorganic analyses. Tubing used in low-flow purging effort generally range have an inside diameter ranging from 1/4 inch or 3/8 inch (4 to 8 mm).

Silastic tubing is recommended for the section of tubing around the rotor head of the peristaltic pump and should be less than a foot in length.

1.2.3 Other Equipment

A multi-parameter instrument, capable of measuring pH, specific conductance, temperature, ORP, DO, and turbidity, with a flow-through cell is preferred when measuring indicator field parameters. Field instruments will be calibrated in accordance with SOP-08 Field Equipment Calibration and Operation. Details about a multi-probe water quality meter is included as Attachment B in the SOP-08.

1.3 Low-Flow Sampling Precautions

The following precautions should be considered when collecting groundwater samples using low-flow sampling procedures.

- Inaccurate sample results may be caused by using contaminated equipment, cleaning materials, or sample containers.
- Establish the order the wells will be sampled. Sample order is based on logistics or the known or suspected water quality of a sample location. For contaminated sites, wells should be sampled in order of increasing chemical concentrations (known or anticipated). This minimizes the possibility for cross contamination of the sample equipment.
- Uncontrolled ambient/surrounding air conditions (i.e., truck/vehicle exhaust) can also influence the samples.
- If groundwater is extremely turbid on initiation of purge, consider bypassing the flow-through cell until groundwater clears to a visually lower turbidity level. The length of time this may take can vary on how turbid the water is, the formation around the well screen, and the analysis required on the sample. If turbidity does not decrease, the well may need to be re-developed.
- The pump or tubing intake must be in an appropriate depth within the well screen and located at a depth specified in the work plan or QAPP. The sample depth should be consistent from sample event to sample event. Suggested intake depths might consider the following:
    - For wells with screens <10-feet (<5 m) in length, the intake should be placed approximately in the middle of the saturated portion of the screen.
    - For wells with well screens > 10 feet (>5 m), the primary flow zones and contaminant concentration intervals must be identified. Recommendations may include the middle of the saturated portion of the screen, or mid-screen.

- For wells that have measurable non-aqueous phase liquid (NAPL), a determination if the well should be sampled should be discussed with the PM. Groundwater that has NAPL may interfere with laboratory analytical equipment and has a higher potential of cross contamination if a displacement-pressure pump is used. If low-flow sampling in a well that has NAPL is determined to be appropriate, the following is recommended:
  i. Choose a purge technique such as a peristaltic pump in which the tubing can be discarded after use. A displacement-pressure pump is not recommended.
  ii. The preferred procedure is to remove the light NAPL (LNAPL) from the top of the water column prior to purging the well. Removal is generally accomplished by using a bailer, pumping/skimming the LNAPL, or absorbent pads.
  iii. If the NAPL is LNAPL and the LNAPL is not removed, lower the tubing intake a minimum of 2 feet (0.5 m) below the LNAPL/water interface. Purge at a low discharge rate and monitor the interface depth, so the drawdown of the interface does not allow LNAPL into the tubing intake.
  iv. If the NAPL is dense NAPL (DNAPL), measure the depth to the DNAPL/water interface and place the tubing intake a minimum of 2 feet (0.5 m) above the depth of the interface. Purge at a low discharge rate and monitor the water level for drawdown. Avoid purge rates that would disturb the DNAPL and allow the DNAPL to enter the tubing intake.

1.4 Low-Flow Sampling Procedures

The low-flow process can vary based on project work plan and well-specific details, and procedures may need to be adjusted to accompany variations. In general, the low-flow sampling procedures are as follows:

1. Field equipment will be calibrated in accordance with the guidelines provided in SOP-08 Field Equipment Operation and Calibration or the manufacturer's manual.
2. Field equipment will be decontaminated in accordance with SOP-09 Field Decontamination or new disposable equipment will be used as appropriate.
3. Open the well. If required, use a photoionization detector or equivalent to measure for the presence of volatile organic compounds. Record the results of the photoionization detector measurement in field logbook or approved field documentation.
4. Measure the depth to water and total depth of the well using a water level indicator. If NAPL is present, use an interface probe for fluid measurements and total depth. Fluid levels or total depths will be measured in accordance with the guidelines provided in SOP-41 Fluid Measurements. Record the measurements in the field logbook or approved field documentation.
5. Lower the pump or tubing intake slowly to the desired depth within the well screen. The determined depth should be outlined in the work plan or QAPP, or the midsection of the well screen or saturated water column of the well screen.
6. Once the pump or tubing intake is to depth, energize the pump. Set the pump controller to the desired pumping rate. Start the pump at a relatively low pumping rate--about 100 to 200 milliliters per minute (mL/min).
7. Record the purge start time.

8. Water levels, pump discharge rates, and groundwater field parameters will be measured and recorded at consistent intervals (e.g., 2, to 5-minute intervals) during purging activities.
9. Groundwater discharge rates will be measured using a graduated cylinder or equivalent to ensure purge rates are discharging between 100 to 500 milliliters per minute (ml/min). Preferably, pumping rates will be maintained between 200 to 300 mL/min.
10. Use water level measurements to help establish the optimum pump rate. Water level drawdown provides the best indication of the stress imparted by a given flow-rate for a given hydrological condition. Water level measurements during the purge will be less than 0.33 feet from the initially measured groundwater depth. If drawdown is greater than 0.33 feet, lower the pumping rate and continue to monitor the water level. If drawdown continues, lower the pumping rate until water levels are consistent or rebound. If drawdown is greater than 0.33 feet but the water level depth remains at the same water level depth or rebounds, groundwater depths will be considered stable or re-entering faster than being discharged. If water level continues to drawdown at the lowest achievable pumping rate, note on field logs.
11. During purging and sample collection the water flow should be a smooth, solid stream of water with no air or gas bubbles in the tubing or flow cell. Gradually adjust the pumping rate to eliminate bubbles, if present and able.
12. Observations of clarity, color, and odor of the purged water should be recorded at successive intervals.
13. Field indicator parameters will be recorded during purging for pH, temperature (°C or °F), specific conductance (µS/cm or mS/cm), ORP (mV), DO (mg/L), and turbidity (NTU). If other units of measurement are used, the unit of measurement will be documented in the field log book or approved field documents.
14. Turbidity will be monitored as turbidity may potentially interfere with some laboratory analyses, such as metals. Turbidity may be reduced in the sample by lowering the pumping rate.
15. Purging is considered complete when the water extraction rate and water level are consistent, and the indicators parameters have stabilized for 3 consecutive readings as outlined below:

Parameter	Stabilization Criteria
Temperature	± 3% of reading (minimum of ± 0.2 C)
pH	+/- 0.1
specific conductance	+/- 3%
ORP	+/- 10 millivolts
DO	+/- 0.3 milligrams per liter
Turbidity	No stabilization criteria, however, an NTU reading less than 10 NTU is preferred

16. If the field indicator parameters do not stabilize, a groundwater sample will be collected after removal of 1 well volume, or 1 hour, whichever occurs first. Calculation of a well volume is provided in SOP-44 Volume Purge Sampling.
17. If the well purges dry, the well should be sampled as soon as a sufficient volume of groundwater has re-entered the well.
18. Re-purging of the well will be performed if a well is inactive for more than 24 hours after full recharge.

19. Record the volume of water discharged during the purge event from the start time to the time of sample collection.
20. The pump should not be moved or turned off between purging and sampling. The pumping rate can be decreased for sample collection but should never be increased.
21. Prior to sampling, disconnect the tubing leading to the flow-through cell.
22. Groundwater samples will be collected in laboratory-supplied jars once purging is completed. Groundwater samples will be collected directly from the tubing (i.e., the sample will not be collected from the flow-through cell port) with the pump rate consistent with stabilization purging flow rates.
23. Groundwater samples will be collected in accordance with the work plan or QAPP and will follow the sampling guidelines provided in SOP-46 Water Sampling for Chemical Analysis.
24. Collected samples will be placed in insulated coolers containing ice to maintain a temperature of 4°C. Samples will be labeled, managed, and shipped in accordance SOP-05 Sample Management and Shipping.
25. Place the discharged water into a bucket or pump directly into an appropriate container. Dispose of the discharge water or wastes in accordance with SOP-07 Investigative Derived Waste.
26. Secure the well and restore the location and area to previous site conditions.

2 Records

Field notes will be kept in a bound field logbook or approved field documentation following the format specified in SOP-04 Field Documentation. Specific documentation may include health and safety documentation, precipitation data, and photographs. Hardcopy discharge records, including all related quality control documentation, must be maintained in permanent project files. A Low-Flow Sample Sheet is contained as **Attachment A**. Documentation of the sampling event should include (at a minimum):

- Required site maps and HASP forms
- Instrument calibration
- Equipment calibration sheet from rental agency
- Well identification and location
- Type of equipment and supplies
- Well construction details
- Previous sample event or water level details
- Air monitoring readings, if required
- Low-Flow Sampling Form details
  - Physical water observation
  - Containment and volume of water removed
  - Name of the sample collectors
  - Water level depth and total depth
  - Pump or tubing intake depth in screen
  - Pumping rates, drawdown, indicator field parameters values, calculated or measured total volume pumped, and clock time of each set of measurements.
  - Times (start, finish, sample time)
  - Laboratory information (sample ID, preservative, QA/QC)
- Weather observations (e.g., temperature, wind speed and direction, cloud coverage).
- Any problems encountered or deviations from this SOP.
- Summary of daily activities and personnel onsite.

Attachment A Low-Flow Groundwater Sampling Form

EHS Support

LOW FLOW GROUNDWATER SAMPLING FORM

Project Name: _____

Project Number: _____

Time (Initial): _____

Initial Water Level: _____ ft

Depth to Product: _____ ft

Total Well Depth: _____ ft

Well Identification: _____

Sample Date: _____

Field Technician(s): _____

Inner Casing Diameter (in): _____

Pump and Tubing Type: _____

Start Purge Time: _____

Time	Flow Rate	Water Level	Temp.	pH	Conductivity	Turbidity	DO	ORP	Odor	Color	Comments
	__L/min	ft	°C / °F	S.U.	__S/cm	NTU	mg/L	mV			

Comments: _____

End Purge Time: _____

Final Water Level: _____ ft

Total Volume Purged: _____ gal

One Well Volume (prior to purging, if applicable): _____ gal

Well Purged Dry? ☐ Yes ☐ No

Tubing Inlet Depth: _____

SAMPLE ID	TIME	ANALYSES	QA/QC SAMPLE	REMARKS

Gas Concentration in Well: _____ ppm

Formula for Calculating Well Casing Volume

$$[A] = \frac{\pi D^2 L}{4} * 7.48 \frac{gal}{ft^3}$$

D = Well casing inner diameter *(converted to feet)*

L = Height of water column (ft)

Parameter	Stabilization Criteria*
Temperature	± 3% of reading (minimum of ± 0.2 C)
pH	+/- 0.1
Specific Conductance	+/- 3%
ORP	+/- 10 millivolts
Dissolved Oxygen	+/- 0.3 milligrams per liter
Turbidity	Not a stabilization criteria; however, the lower the turbidity the better

* - USEPA, 1996 (Puls and Barcelona) Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures

Signature: _____

Attachment B Low-Flow (Minimal Drawdown) Groundwater Sampling Form (Puls and Barcelona, 1996)

EHS Support

LOW FLOW GROUNDWATER SAMPLING FORM

Project Name: _____

Project Number: _____

Time (Initial): _____

Static Water Level: _____ m

Depth to Product: _____ m

Total Water Bore Depth: _____ m

Water Bore Identification: _____

Sample Date: _____

Field Technician(s): _____

Inner Casing Diameter (mm): _____

Pump and Tubing Type: _____

Start Purge Time: _____

Time	Flow Rate	Water Level	Temp.	pH	Conductivity (EC)	Turbidity	DO	Redox	Odour	Colour	Comments
	__L/min	m	°C	S.U.	__S/cm	NTU	mg/L	mV			

Comments: _____

End Purge Time: _____

Final Water Level: _____ m

Total Volume Purged: _____ litres

One Well Volume (prior to purging, if applicable): _____ litres

Water Bore Purged Dry? ☐ Yes ☐ No

Tubing Inlet Depth: _____

SAMPLE ID	TIME	ANALYSES	QA/QC SAMPLE	REMARKS

Gas Concentration in Well: _____ ppm

Formula for Calculating Well Casing Volume

$$[A] = \frac{\pi D^2 L}{4} * 1000 \ \frac{\text{Litres}}{m^3}$$

D = Water bore inner casing diameter
(converted to meters)

L = Height of water column (m)

Parameter	Stabilisation Criteria*
Temperature	± 3% of reading (minimum of ± 0.2 C)
pH	+/- 0.1
Specific Conductance	+/- 3%
ORP (Redox)	+/- 10 millivolts
Dissolved Oxygen	+/- 0.3 milligrams per liter
Turbidity	Not a stabilisation criteria; however, the lower the turbidity the better

* - USEPA, 1996 (Puls and Barcelona) Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures

Signature: _____

SOP-46 Water Sampling for Chemical Analysis

Purpose

The purpose of this SOP is to provide general procedures for the preparation of water samples for chemical analysis during field investigations. This SOP focuses on the requirements for accurate sample collection and preservation of water samples for representative quality analysis. For this SOP, water sampling refers to those samples whose main constituent is water such as samples collected from surface water, groundwater, and/or waste water. In addition, this SOP assumes bottle sets received from the laboratory will contain the required preservative (i.e., the bottles are pre-preserved by the laboratory, and preservative will not be required in the field).

Relevant EHS Support SOPs

- SOP-04: Field Documentation
- SOP-05 Sample Management and Shipping
- SOP-08 Field Equipment Operation and Calibration
- SOP-09 Equipment Decontamination

Attachments

- No attachments

Required Materials

- Field logbook and field documentation
- Site maps, site layouts, site plans
- Health and Safety Plan
- Appropriate personal protective equipment (PPE)
- Black waterproof and/or indelible ink pens
- Chain-of-custody form, sample labels, custody seals
- Material Safety Data Sheets (from the laboratory, for each preservative type)
- Filters, if applicable
- Laboratory-supplied bottle set, with preservative as needed
- Other approved sample storage containers, if applicable
- Labels, custody seals, coolers, ice, Chain of Custody forms, tape, plastic baggies
- Equipment required, if applicable, to monitor the water sample parameters

1 Water Sampling for Chemical Analysis

Water samples are collected and analyzed to evaluate the chemical quality of the water. The chemical characteristics of the water aid in understanding the groundwater or surface water system of interest, or is used as a monitoring control for wastewater treatment facilities or meeting criteria to discharge treated water.

There are two types of samples that can be collected during a sample event: grab samples or composite samples. Grab samples (or discrete samples) are discrete samples collected at a specific location and time. Composite samples (or homogenized samples) are samples composited from two or more locations at the time of sampling. Composite samples usually represent an averaged concentration for a period of time. Samples collected for VOC analysis are generally not composited or homogenized, unless specified.

Accurate sample collection and preservation is crucial in acquiring representative data. The project work plan or quality assurance project plan (QAPP) should be referenced to understand the project needs and sample requirements. The project work plan or QAPP should provide a clear understanding to sample locations, sample identification, analytical testing, number and type of quality control samples, or other project-related needs (objective, equipment, laboratory supplier, purging method-if required, etc.).

1.1 General Water Sampling Considerations

Although the procedures used to fill sample bottles may seem a minor consideration, filling them improperly can jeopardize the careful work that may have gone into properly purging a well to produce minimally-disturbed, representative sample. Improper sampling techniques can cause changes in sample composition due to agitation and exposure to air which can result in the loss of contaminants by volatilization or degassing. The following are general considerations when preparing for collection of water samples:

- The specific order of sample collection, processing and preservation for specific analytes should be adhered to consistently throughout the project. The recommended sequence for sample collection and processing is often based on logistics for maintaining sample integrity and based on the analytes' sensitivity to change. The sequence can be modified, depending on the types of samples to be collected and on data objectives.
- Volatile organic compound (VOC) samples (and other organic-sensitive analytes) are typically collected first if collecting samples for multiple analytes. The more sensitive the analytical parameters being collected (e.g., VOCs and redox-sensitive metals), the more cautious the filling procedures should be. A suggested sample order, if not specified in the project work plan or QAPP may include:
    - VOCs
    - Semi VOCs (SVOCs)
    - Herbicides/Pesticides/Polychloride Biphenyls (PCBs)
    - Total Petroleum Hydrocarbons (TPH)
    - Metals, Cyanide, or Radionuclides

  - Other water-quality parameters (microbiological, anion/cation, ammonia, sulfides/sulfates, nitrates/nitrites, etc.)
  - Nutrients (e.g., phosphorous)
  - Filtered samples (e.g., dissolved metals, ultra-trace metals, etc.,).
  - Additional sample order consideration might include a sulfate sample collected before samples preserved with sulfuric acid (e.g., nitrogen series, phenolics).
- If questions exists pertaining to sampling or laboratory concerns check with the laboratory(s) or laboratory-project manager to ensure the sample containers, required sample volume, preservation, and holding times are understood prior to the project start. Several analytes in a sample suite may be grouped together in one (or more) bottle based on the preservation method and analytical testing method.
- Laboratory quality assurance and control procedures should be referenced prior to field sampling to ensure accurate the project work plan and chain of custody procedures are followed. Sample management and shipping can be referenced in SOP-05. A laboratory example of holding times can be reference as an attachment to SOP-05.
- Ensure field equipment is properly decontaminated in accordance with the guidelines provided in SOP-09 and is calibrated with the guidelines provided in SOP-08 or the instrument's manual.
- During purging and/or sample collection the flow should be a smooth, solid stream of water with no air or gas bubbles in the tubing or flow cell. Gradually adjust the pumping rate to eliminate bubbles, if present.
- Prepare sample containers. Keep sample containers capped until it is time to fill them to avoid possible container contamination.
- If water samples are collected via bailer, it is recommended to use a bottom emptying devise to slow/control the release of the water sample into the laboratory bottles.
- Any equipment (e.g., flow through cell, multi-parameter quality meter) used to monitor water quality parameters will be disconnected to allow the sample to be collected directly from the discharge tubing.
- Groundwater samples from a purged well will be collected in a continual process following the purge cycle.
- For groundwater samples collected by using low-flow sampling techniques, the pumping/discharge rate should:
  - Be high enough to fill sample bottles efficiently and with minimal exposure to atmospheric conditions, but low enough to minimize sample alteration or aeration.
  - Allow for a smooth and uniform flow, preferably about 250 millimeters per minute.
  - Remain unchanged from the purging cycle to the sampling cycle.

1.2 Water Sample Procedures

Water samples are generally collected

- Directly from a sample port, faucet, or spigot at the sample point location.
- Directly or indirectly at a surface water location (refer to SOP-61) at the sample point location or via an intermediate container or drop-down tube.
- Directly or indirectly from a well that has been purged of groundwater (SOP-43 and SOP-44) using down-hole tubing or via an intermediate container (i.e., bailer).

Do not use a bottle containing preservative to directly collect the water sample from a surface water body, pond, or lagoon. Instead employ an intermediate container for sample collection and transfer the sample to the bottle containing preservative.

Ensure sample tubing has been disconnected from any inline equipment (e.g., flow-through cell) prior to filling sample jars.

Assuming all pre-sample activities (e.g., purging, stabilization of water quality parameters, bottle labeling) are completed

1. For water samples from a port, faucet, or spigot, disinfect the port, faucet, or spigot with an alcohol swab or approved cleaning detergent. Open the sampling port and allow the water to flow (about 250 ml/min) for 2 to 3 minutes. Collect the discharged water into a bucket.
2. If sampling for VOCs, fill the volatile organic analyte (VOA) vials first.
    a. Slowly fill each 40 ml VOA vial with water taking care not to let it over flow and lose preservative.
    b. Completely fill the VOA vial with water so a meniscus is formed at the top of the container.
    c. Place the cap with Teflon septum on the vial top and secure.
    d. Turn the VOA vial upside down and check for the presence of air bubbles. Tap the bottom of the VOA vials to dislodge any bubbles that may have formed around the cap or sides.
    e. If no bubbles are present, the sample is considered to have “No Headspace” and the sampling for that vial is complete. Move onto the next VOA vial or sample container.
    f. If bubbles are present, remove the cap and fill the VOA vial with additional sample water to completely fill the vial and form a meniscus. Replace the cap and reconfirm there are no bubbles in vial. If air bubbles are still present after three attempts, discard the sample jar and obtain a new VOA vial for sample collection.
    g. If the purge water has observable entrained gas bubbles in the effluent, or if the sample effervesces or fizzes during collection of the water sampling into the (HCl) pre-preserved VOA, the collected sample and/or vial will be discarded. Instead, use a new VOA vial containing no preservative, or rinse the VOA vial with the representative purge water to completely remove the HCl preservative, to collect the sample. The sample will be contained in the VOA vial with the “No Headspace” procedures d) to f) and the chain of custody will note the sample is unpreserved. It is recommended to inform the laboratory of the unpreserved sample and holding time change.
    Notes:
    - A sample that is off-gassing in a sealed container may cause a potential eruption hazard.
    - The hold time of an unpreserved sample is reduced from 14 days to 7 days.
3. Fill remaining sample containers for other analytes, and seal sample containers. Ensure sufficient volume is available to fill the bottle set or testing method criteria (“No Headspace” for other analytes) is achieved. Consult with the project manager, project work plan, QAPP, or laboratory representative if potential concerns arise to assess possible corrective actions.
4. If water samples require filtration (further discussed in the next section):
    - Attach the in-line disposable filter to the sample tubing or hose. Using the water pressure from the pump, press the water through the filter. Allow (and discard) a minimum of 100 milliliters of water to pass through the filter cartridge before filling the appropriate sample

containers with the sufficient container volume. Discard any filters that become clogged and attach a new filter as appropriate. Discard filter between sample locations.

- Set up the filtration assembly, positive vacuum system, or syringe. Transfer the representative water into the appropriate holding chamber. Push or press the sample across the filter. The filtered sample will be placed directly into the appropriate sample jar, or transferred from the filtered-water chamber and into the appropriate sample jar. Discard any filters that become clogged and attach a new filter as appropriate. Discard filter between sample locations.

5. Complete the chain of custody noting sample identification, time, date, analytical testing required, quality control samples, and any other notes that would be useful to a laboratory. (For instance, if a sheen is observed in the sample, note on the chain of custody. This may assist the laboratory in preventing potential instrument issues.)
6. Place, package, and ship the appropriately labeled sample containers to the subcontracted laboratory following the guidelines provided in SOP-04 Field Documentation and SOP-05 Sample Management and Shipping.
7. Discard purged water in accordance with the project work plan and in accordance with SOP-07 Investigative Derived Waste.

1.3 Field Filtration Guidelines

Filtration is the physical process used to separate the particulate and aqueous fractions of a water sample. Samples are filtered for several purposes; for example, to remove microorganisms in order to help preserve ambient analyte concentrations, to remove suspended materials that interfere with specified analytical procedures, and to determine chemical speciation and fractionation of trace elements for geochemical studies.

Field filtration may be required for dissolved metals, alkalinity, hexavalent chromium, ultra-trace metals, total organic content (TOC), dissolved organic content (DOC), and speciated analytes such as ferrous iron, arsenic and selenium. In some of these analytes, zero headspace is required in the bottle. Be sure to check with the project work plan, QAPP, and laboratory for sample collection and containment requirements.

Accomplish in-line filtration through the use of disposable, high capacity filter cartridges (barrel-type) or membrane filters in an in-line filter apparatus. The high capacity, barrel-type filter is preferred due to the higher surface area associated with this configuration. If a membrane filter is utilized, a minimum diameter of 142 mm is suggested. The filter size and material should be appropriate for the expected quality of the water sample, the volume of water to be filtered, the analyte(s) to be measured, and the method of filtration. The filtration technique should minimize the sample exposure to air.

A generally accepted filter size is 0.45 microns, however, 0.2-micron filters can be used if the removal of bacteria or metal colloids is required. The most commonly used field filtration techniques are:

- In-line disposable filters (filter during sample collection)

Examples of a field filters including barrel-type filter cartridge or membrane filter.

- Hand-held and operated positive vacuum pump or syringe filters (filter after collection)

Examples of a hand-help positive vacuum pump and syringe-type filter.

2 Records

Field notes will be kept in a bound field logbook or approved field documentation following the format specified in SOP-04 Field Documentation. Field notebooks and field documentation should be used to record:

- Sample Identification
- Sample time and date
- Media collected
- Sample location
- Sample testing method
- Location and identification of quality control samples and types
- Chain of Custody forms

Appendix D EHS Support NSZD Methodology SOPs

SOP For Use of Passive CO2 Traps

1 Summary

Natural Source Zone Depletion (NSZD) estimation is an important component of assessment of natural attenuation process on petroleum hydrocarbon impacted sites. The passive trap method measures carbon dioxide (CO_2) flux to the ground surface over time to estimate hydrocarbon mass depletion rates in the unsaturated zone.

This standard operating procedure (SOP) is designed to:

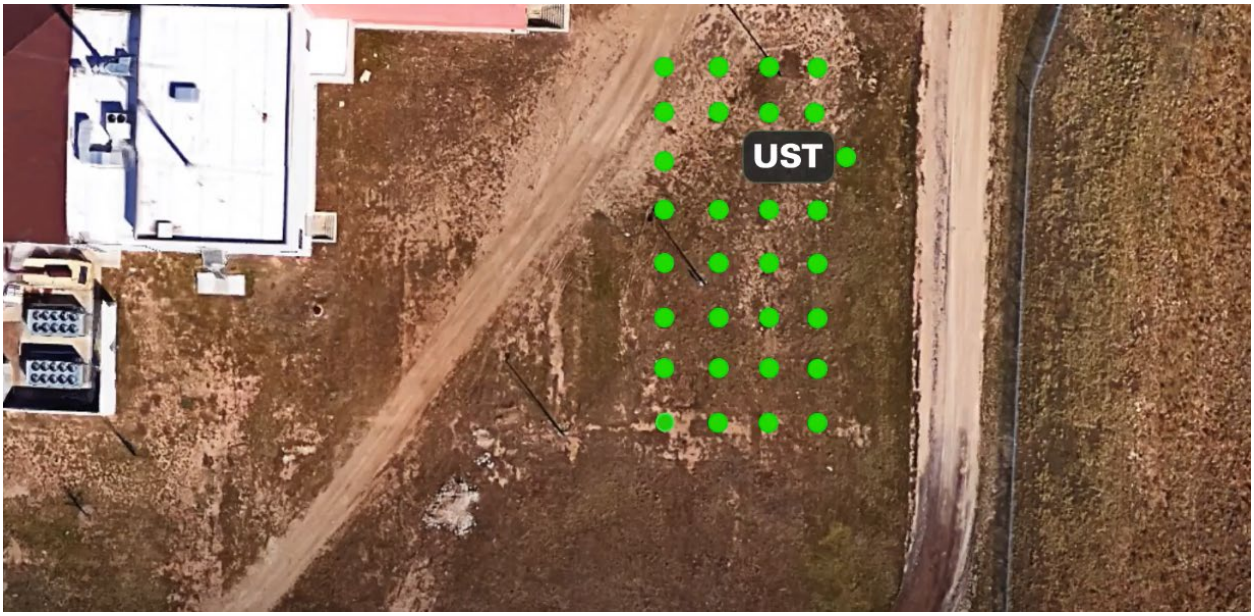
- Cover field installation and data logging of the E-Flux Fossil Fuel trap, or equivalent carbon dioxide (CO_2) efflux trap.
- Introduce the laboratory analytical procedures.
- Provide the data analysis methodology.
- Describe Quality Assurance/Quality Control (QA/QC) procedures

This SOP is intended as a practical guide to implementing and assessing results of a passive trap study. It is assumed the reader is familiar with the underlying scientific principles[1].

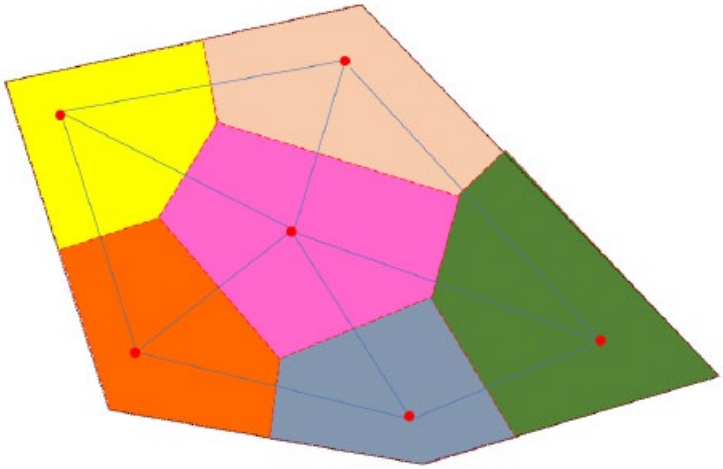
1.1 Sample Grid Design

The method relies on the collection of data on a sampling grid across the light non-aqueous phase liquid (LNAPL)/hydrocarbon affected areas to determine the magnitude of natural mass losses from an affected area. An understanding of the lateral and vertical distribution of hydrocarbon impacts, and variability on the subsurface geology, is critical before undertaking this type of sampling to ensure that representative sample locations (and an associated grid is established across the area).

[1] McCoy, K., Zimbron, J., Sale, T. and Lyverse, M., 2015. Measurement of natural losses of LNAPL using CO_2 traps. Groundwater, 53(4), pp.658-667.



- Best practice is to establish a standardized grid should over the plume area to provide multiple data points for assessing gas flux. Typically, grid sizes extend up to and may exceed 20 meters (m) x 20 m.



- Due to financial and logistical constraints, Theissen Polygons may be created to assign areas to each trap, and the flux measured within the cross-sectional area of the CO_2 trap can be extrapolated to its Theissen Polygon.
- In this case, the traps should be arranged near groundwater monitoring locations or soil borings, where knowledge of the subsurface conditions is available to help interpret measurement results.
- At minimum, assign an individual CO_2 trap to all distinct areas of LNAPL consistency, geologic, and hydraulic characteristics.

- It is recommended that areas of elevated wind are avoided if and when possible.

1.2 Training

The following training and procedures will be performed to maximize data quality:

- Training will be conducted to ensure that staff are aware of handling and operation of the cannisters prior to deployment in the field.
- Field staff will be trained so that they understand the scope of SOP and note-taking requirements.
- The field supervisor will check notes in the field daily and correct inconsistencies in the field.
- The field supervisor will sign off on field forms daily to verify quality and consistency.
- The project manager will also periodically check forms and data to verify quality and consistency.

1.3 Equipment and installation

- Rubber mallet or slide hammer
- Safety gloves
- Flathead screwdriver

Provided in each E-Flux kit (one kit per soil gas sampling location):

- 3 6-inch Eye bolts
- 3 U-nuts (roughly 0.5” square)
- 8-inch diameter Receiver pipe
- 3 Stabilization spikes
- Rubber connector
- 2 Hose clamps
- CO_2 Trap
- Rain cover
- Identification label

1.3.1 Procedure – Receiver Pipe Installation

- Clear designated area of all vegetation
- Locate receiver pipe – white hard plastic pipe, with one beveled end
- Ensure hose clamp around receiver pipe is tight and secure, rotating bolt on hose clamp clockwise to tighten with screwdriver if needed
- Ensure three u-nuts are secure on hose clamp around receiver pipe
- Place an eye bolt into each u-nut and tighten by hand, making sure hole on eye bolt is rotated to be parallel to hole in receiver pipe
- Place beveled side of receiver pipe on the ground

Receiver pipe with U-nuts and eye-bolts attached. Stakes laying aside pipe

- Hammer receiver pipe into ground using rubber mallet or slide hammer, rotating hits evenly across top to remain level, until reaching 2” burial depth, as noted on side of receiver pipe
- Place a stabilization stake through each eye bolt, hammering the stake down to ground level to secure the receiver pipe
- Ensure the reliever pipe is vertical
- Compact soil both inside and outside of the receiver pipe to original condition with hand or hammer

1.3.2 Procedure – CO_2 Trap Installation

- Loosen hose clamps on the rubber connector with screwdriver
- Slide rubber connector over installed receiver pipe, leaving the bottom two inches of the receiver pipe showing
- Tighten bottom hose clamp with screwdriver until connection is airtight
- Label the trap (using a permanent marker) with the sample location ID, deployment date and time.
- Remove bottom metal cap from CO_2 trap, twisting the cap counterclockwise with hand
- Remove top metal cap from CO_2 trap, twisting the cap counterclockwise with hand
- Place the metal caps in a plastic bag for use when retrieving the traps after deployment (see below)
- Screw rain cover onto top of trap by hand
- Slide trap into rubber connector until contact with receiver pipe. Around 2 inches of the CO_2 trap should be showing over the top of the rubber connector
- Tighten the top hose clamp around the rubber connector until connection is airtight
- Place identification label on rubber connector, between hose clamps

1.3.3 Procedure – Data Logging and Retrieval

- Leave the trap connected to the receiver pipe for a two-week period
- Removed the trap from the pipe by loosening the hose claim and removing the rain cover.
- Reinstall the screw lids onto the traps and place the traps in a sealed heavy duty zip lock bag (1 gallon).
- Complete a chain of custody form and place the zip lock bag in a cooler for transportation to E-flux laboratory in Colorado for analysis

- Place laboratory provided trip blank in cooler

1.4 QA/QC Samples and Procedures

QA/QC samples and procedures consist of:

a. Radiogenic carbon (^{14}C) analysis to quantify contributions to CO2 flux from non-hydrocarbon sources.
b. Analysis of a trip blank for CO_2
c. Analysis of a duplicate sample (recommended if high spatial variability is suspected).
d. Deployment of a background trap in a location upgradient and where LNAPL is known to be absent (recommended where high background CO_2 values are suspected).

Each set of field samples included a trip blank (TB) to correct for a small amount of CO_2 originally present in the media and potential CO_2 sorption other than during deployment. The trip blank is provided by the vendor and is shipped to the site with the primary sample cannisters. The trip blank is maintained in a cooler for the duration of the project and shipped back to the lab with the primary samples.

The duplicate sample (typically one per 10 samples) is installed approximately 3 feet from the associated primary sample, exposed to conditions for the same duration as the associated primary sample, and treated and analyzed identically to a primary sample. The purpose of the duplicate sample is to identify spatial variability.

1.5 Laboratory Analysis

^{14}C is measured according to the laboratory methods and QA/QC procedures outlined in the American Society for Testing Materials (ASTM) Method D6866-21: 'Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis[2]'.

The CO_2 content of the passive trap is analyzed gravimetrically following the procedure of Bauer (1972)[3] as outlined in ASTM McCoy et al. (2015)[4]. Carbonate analysis of each trap/sample is based on method ASTM 4373-14, which does do not provide acceptable variability (CV) standards. Similar methods (e.g., ASTM D513-16) allow typical errors of ≤ 20%. Analysis is therefore conducted in duplicate if the coefficient of variation (CV) of the duplicates is < 5%. If CV ≥ 5%, duplicate analyses are repeated until CV < 5%

1.6 Data Analysis

A standard data report from the vendor E-FLUX is shown below:

[2] ASTM, 2021. D6866-21. Standard test methods for determining the biobased content of solid, liquid, and gaseous samples using radiocarbon analysis, 1–19.
[3] Bauer, H.P., P.H.T. Beckett, and S.W. Bie. 1972. A rapid gravimetric method for estimating calcium carbonate in soils. Plant and Soil 37, no. 3: 689–690.
[4] McCoy, K., Zimbron, J., Sale, T. and Lyverse, M., 2015. Measurement of natural losses of LNAPL using CO_2 traps. Groundwater, 53(4), pp.658-667.

EOFLUX
Easy set-up. Expert results.

This report contains Confidential Information and is to be delivered only to the indicated Customer.

Project: [redacted]
Customer: EHS Support LLC
Customer Contact: [redacted]
Report Date: 5-Feb-2021

Sample ID	Sampling Information			Raw Results[a]				Final CO_2 Results[b]			^{14}C Results[a]			NSZD Results[b]				
	Deployed	Retrieved	Days in Field	Moisture content (%)	Dry Sorbent Mass (g)	Avg. % CO_2[c]	CV[d] CO_2 (%)	CO_2 content (%)	CO_2 mass (g)	CO_2 Flux ($\mu mol\ m^{-2} s^{-1}$)	Fm_{sample} As Reported[e]	bb_{sample} As of Today[f]	ff_{sample} As of Today[f]	Bio-based CO_2 Flux ($\mu mol\ m^{-2} s^{-1}$)	ff_{sample} As of Today (TB-corrected)	Fossil Fuel CO_2 (g)	Fossil Fuel CO_2 Flux ($\mu mol\ m^{-2} s^{-1}$)	Equivalent NSZD Rate (gal. $acre^{-1} yr^{-1}$)
10197-R1-CO2-TB	N/A	N/A	N/A	18.8%	41.72	0.92%	0.37%	-	-	-	68.20	66.87%	33.13%	-	-	-	-	-
10197-R1-CO2-01	12/7/20 10:00	12/24/20 10:00	17.0	22.7%	43.06	2.28%	2.57%	1.36%	0.59	1.12	83.00	81.38%	18.62%	1.02	8.77%	0.05	0.10	61
10197-R1-CO2-02	12/7/20 10:30	12/24/20 10:05	17.0	24.0%	42.67	3.30%	2.50%	2.38%	1.01	1.94	90.16	88.39%	11.61%	1.87	3.24%	0.03	0.06	39
10197-R1-CO2-03	12/7/20 10:45	12/24/20 10:10	17.0	23.8%	42.96	2.86%	2.21%	1.93%	0.83	1.59	88.66	86.92%	13.08%	1.53	3.50%	0.03	0.06	35
10197-R1-CO2-04	12/7/20 10:15	12/24/20 10:15	17.0	22.1%	42.60	2.23%	1.16%	1.31%	0.56	1.06	86.64	84.94%	15.06%	1.04	ND	ND	ND	ND
10197-R1-CO2-05	12/7/20 11:00	12/24/20 10:20	17.0	24.5%	42.25	2.75%	1.90%	1.83%	0.77	1.47	89.19	87.44%	12.56%	1.44	ND	ND	ND	ND

1.6.1 ^{14}C Data Treatment

Measurement of ^{14}C enables quantitation of the fraction of modern CO_2 carbon (decaying organic matter in soil, plant root respiration) in each sample that may bias NSZD rate estimates high. The LNAPL degradation percentage of the sample (ff_{sample}) and the modern CO_2 carbon percentage ($1\text{-}ff_{sample}$) are related by the following two-component mass balance equation:

$$Fm_{sample} = (ff_{sample})(Fm_{ff}) + (1\text{-}ff_{sample})(Fm_{atm}) \qquad \text{Equation 1.}$$

Fm_{sample} is the total measured fraction modern of the sample. Fm_{ff} is the fraction modern of only the fossil fuel portion of the sample. This number is 0, as there is no 14C in fossil fuel-derived CO2. Fm_{atm} is the fraction modern of the part of the sample derived from natural soil respiration processes. This value, currently equal to 1.02. Equation 1 is rearranged and solved for ff_{sample}:

$$ff_{sample} = 1\text{-}(Fm_{sample})/1.02 \qquad \text{Equation 2}$$

The ff_{sample} value is used to in the CO_2 correction as described below.

1.6.2 CO_2 Data Treatment

The mass of fossil fuel-derived CO_2 in each trap is calculated by subtracting the total fossil fuel CO_2 in the TB from the total fossil fuel CO_2 in the trap. Only data that are not TB-corrected (i.e., ff_{sample} and raw % CO_2) are used in this calculation:

$$(g\ CO_{2(ff)})_{sample} = g_{sorbent} * [((\%CO_2)_{sample} * (ff_{sample})) - ((\%CO_2)_{TB}(ff_{TB}))]$$

Here, $g_{sorbent}$ is the mass of sorbent used in the bottom layer of the trap, $(\%CO_2)_{sample}$ is the average weight percentage of CO_2 in the sample, ff_{sample} is the percentage of carbon in the sample derived from fossil fuels, $(\%CO_2)_{TB}$ is the average weight percentage of CO_2 in the travel blank, and ff_{TB} is the percentage of carbon in the travel blank that is derived from fossil fuels.

1.6.3 Flux Calculation

Carbon flux is converted equivalent LNAPL loss rate as follows. Raw CO_2 results are corrected by subtracting CO_2 detected in the trip blank from the primary sample.

The corrected CO_2 mass is converted to a total CO_2 efflux (J_{total} in $\frac{\mu mol}{m^2 s}$) using the following equation:

$$J_{Total} = \frac{M_{CO_2\ (TB\ corrected)} \times \left(\frac{1\ mol\ CO_2}{44\ g\ CO_2}\right) \times \left(\frac{1000000 \mu mol\ CO_2}{mol\ CO_2}\right)}{days\ deployed\ \times 24 \frac{hr}{day} \times 3600 \frac{s}{hr} \times 8.11 \times 10^{-3} m^2}$$

In this example, the cross-sectional area of the receiver pipe is $8.11 \times 10^{-3} m^2$. The background CO_2 efflux is corrected for by multiplying J_{total} by the fraction of fossil fuel CO_2 (ff_{CO_2}):

$$J_{NSZD} = J_{Total} \times ff_{CO_2}$$

Lastly, the NSZD rate (R_{NSZD}) for the Thiessen polygon is calculated as follows:

$$R_{NSZD} = \left(\frac{J_{NSZD} \times m_r \times MW}{10^6}\right) \times \frac{86400s}{d}$$

Where R_{NSZD} is in units of g/m^2/d, m_r is the stoichiometric molar ratio of hydrocarbon degraded (see **Section 4.3.3**), and MW is the molar weight of the representative hydrocarbon. The value of R_{NSZD} may be presented in alternate units, calculated using standard conversion factors.

1.7 Disclosures and Limitations with Methods

Factor	Effect	Mitigation
Impervious ground cover or highly compacted, confining soil layers	Soil gas can migrate laterally in the vadose zone and is affected by various manmade and geologic materials.	Avoid impervious areas or areas with highly compacted, low-permeability surface soil. Consider use of a new trap design that utilities a gas tight top cap with pressure equilibration to minimize short-circuit effects.
Wind effects	Wind can cause the passive flux trap method to over-estimate the actual efflux (Tracy 2015).	Use latest trap design, adjusted to provide most accurate results. At sites with excessive winds, monitor wind speeds and consider correcting for wind effects (Tracy 2015; E-Flux 2015)
Precipitation during deployment	The rain cover on the trap assembly may prevent wetting of immediately underlying soil, causing a rain shadow in which preferential flow can develop. Research is ongoing to determine effects of precipitation on trap measurements.	Minimize deployment duration and schedule time of year to avoid heavy rainfall events. Turn off irrigation systems during deployment. Schedule monitoring during dry weather, preferably a week or more after heavy rainfall.
Low lying locations	Traps placed in low laying locations can more easily become flooded after precipitation	Place traps away from low lying areas or depressions

SOP for Gas Gradient NSZD Rate Estimate

1 Summary

Natural Source Zone Depletion (NSZD) estimation is an important component of assessment of natural attenuation process on petroleum hydrocarbon impacted sites. The gas gradient method uses soil gas measurements (CO_2, O_2) taken at discrete depths to estimate the magnitude of hydrocarbon degradation in the unsaturated zone.

Measurements may be made in permanent, soil gas monitoring points installed at a range of depths in each location, or in temporary gas probe points that may be installed using a drill rig or a slide hammer. The scope of this SOP does not cover installation procedures for soil gas monitoring points. Monitoring points may also include monitoring wells screened across the water table[1]

This standard operating procedure (SOP) is designed to:

- Cover field implementation of a temperature monitoring program.
- Discuss instrument calibration.
- Describe Quality Assurance/Quality Control (QA/QC) procedures.
- Introduce data analysis methodology.

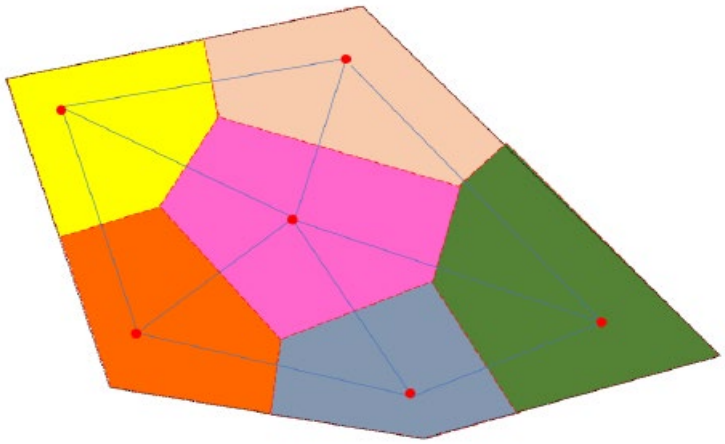
This SOP is intended as a practical guide to implementing and assessing results of a temperature gradient study. It is assumed the reader is familiar with the underlying scientific principles[2].

[1] Sweeney, R.E. and Todd Ririe, G., 2017. Small purge method to sample vapor from groundwater monitoring wells screened across the water table. Groundwater Monitoring & Remediation, 37(4), pp.51-59.
[2] Johnson, P., Lundegard, P. and Liu, Z., 2006. Source zone natural attenuation at petroleum hydrocarbon spill sites—I: Site-specific assessment approach. Groundwater Monitoring & Remediation, 26(4), pp.82-92.

2 Sample Grid Design

The method relies on the collection of data across the light non-aqueous phase liquid (LNAPL)/hydrocarbon affected areas to determine the magnitude of natural mass losses from an affected area. Monitoring points are typically nested soil gas points, however, monitoring wells screened across the water table may also be used.

It is critical that a background location is included; several background locations may be required where subsurface heterogeneity is suspected. Therefore, an understanding of the lateral and vertical distribution of hydrocarbon impacts, and variability on the subsurface geology, is critical before undertaking this type of sampling to ensure that representative sample locations are selected.



- Theissen Polygons (see above) are calculated over the survey network and the NSZD rate at each monitoring location is extrapolated over the associated Theissen Polygon.
- At minimum, a monitoring point should be assigned to all distinct areas of LNAPL consistency, geologic, and hydraulic characteristics.
- Depending upon the local climate and depth to the hydrocarbon oxidation zone, seasonal and climatic effects may be dramatic[3] and multiple field deployments may be warranted.

[3] Sihota, N.J., Trost, J.J., Bekins, B.A., Berg, A., Delin, G.N., Mason, B., Warren, E. and Mayer, K.U., 2016. Seasonal variability in vadose zone biodegradation at a crude oil pipeline rupture site. Vadose Zone Journal, 15(5).

3 Procedures

Use of the gradient method to estimate the rate of NSZD involves the following steps:

- Install new multi-level vapor sampling probes or establish alternative means for vapor sampling (e.g., monitoring wells screened across the water table, temporary soil gas monitoring points) (specific details are beyond the scope of this SOP).
- Sample the monitoring points:
    - Soil vapor sampling from the monitoring probes to measure O_2, CO_2, CH_4, and volatile organic compounds (VOCs) concentrations.
    - In-situ tracer tests to estimate a representative range of soil vapor diffusion coefficients
- Plot the data and estimate the concentration gradient.
- Assess the background O_2 consumption and CO_2 production and compensate for background flux.
- Calculate the NSZD rate.

3.1 Training

The following training and procedures will be performed to maximize data quality:

- Training will be conducted to ensure that staff are aware of calibration and operation of the unit prior to deployment in the field.
- Field staff will be trained to ensure PID and multigas meters give plausible ambient value readings prior to each measurement. Acceptable readings are:
    - zero (methane, carbon dioxide, hydrogen sulfide, volatile organic compounds [VOCs])
    - 19.5-22% by volume for oxygen
    - 76.5-79.5% by volume for nitrogen
- Field staff will trained so that they understand the scope of SOP and note-taking requirements.
- The field supervisor will check notes in the field daily and correct inconsistencies in the field.
- The field supervisor will sign off on field forms daily to verify quality and consistency.
- The project manager will also periodically check forms and data to verify quality and consistency.

3.2 Equipment

<u>Soil gas diffusion coefficient estimate</u>

Site-specific soil vapor diffusion coefficient estimate are recommended. However, estimates from literature values will suffice if site conditions preclude collection of site-specific data. Equipment needs for the soil vapor diffusion coefficient estimate are as follows:

- Sulfur hexafluoride (SF_6) or helium tracer gas cannister
- 1-L Tedlar bag (may be reused between locations)
- 10 ml disposable syringes with marked gradations (ml) and luerlok fittings (e.g., BD™ Syringe, Male Luer Lock C3307)
- Large volume (500 ml or 1 liter) syringe
- Teflon Luer lock syring valve(s)

- Portable gas chromatograph equipped with an electron capture detector (GC-ECD) capable of quantifying SF_6 (or a meter suitable for the selected tracer gas)
- Field notebook and pen
- Stopwatch

Soil gas concentration measurement

The following instruments are commonly used:

- Landtec GEM™5000 hand-held multi gas meter capable of measuring O_2, CO_2, CH_4. Ensure the pumping rate (volume/time) is programmable or known.
- A granular activated carbon or charcoal filter on the inlet to the multi gas meter to ensure that VOCs are excluded from the CH_4 measurement.
- Foxboro TVA1000 (or similar) flame ionization detector (FID) and photo-ionization detector to analyze VOCs
- A granular activated carbon or charcoal filter on the inlet to the FID to measure CH_4-related response. Subtraction of the filtered from the unfiltered measurements provides the VOC concentration.
- Use of a nitrogen (N_2) analyzer (recommended but not essential) to serve as a check-sum on the other gas results, because the sum of O_2, CO_2, CH_4, N_2 and VOCs should approach 100%.
- Tubing of sufficient length to extend from the monitoring well head to 1 to 2 feet above the water table. Tubing of sufficiently small diameter to minimize purge time, but not unduly stress the equipment motor is recommended. Check manufacturer specifications.
- A means to create an air-tight plug at the well head (if using the monitoring well method).
- Fittings to connect handheld gas meter to tubing (monitoring well method or temporary gas probe) or valves (permanent gas monitoring point).

3.3 Measurement procedures

3.3.1 Phase 1 soil gas screening

An initial screening of soil gas concentrations in existing monitoring wells is recommended to:

- Qualitatively verify active biodegradation is occurring.
- Identify potential heterogeneity of mass depletion processes and the required density of the soil gas monitoring network.
- Identify highly active and less active areas to inform siting of temporary or permanent soil gas monitoring network.

Soil gas readings should be taken using both the multi-gas meter and combination FID/PID (or equivalent) in existing wells by lowering tubing to into the screen interval of the well. Typically, instantaneous reading should be collected at 2 feet above the water table (ensuring water does not get into the tubing). The annulus of the well should be kept covered as much as practical to prevent the releases of gases from the subsurface.

This data is only used qualitatively to identify areas of higher and lower soil gas concentrations and also to aid in the interpretation of downhole thermal profile data (if collected).

3.3.2 Soil gas diffusion coefficient estimate[4]

1. Prepare a gas mixture containing approximately 10 parts per million by volume (ppmv) SF_6 (or other conservative tracer gas such as helium at a measurable concentration).
2. Inject 5 mL of 1 ppmv SF_6 into a 1-L Tedlar bag containing 1-L of SF_6-free air.
3. Measure the resulting concentration in the 1-L Tedlar bag (should be approximately 5 ppbv); record and denote this value as Cmax.
4. Inject 5 mL of 1 ppmv SF_6 into the desired location in the vadose zone through small diameter tubing (1/8" stainless steel [SS] tubing is preferred). Follow this injection with sufficient SF_6-free air to ensure that the 5 mL of SF6 has just been flushed from the tubing into the vadose zone (it is desired that the total injected volume be minimized; approximately 1 mL/ft for 304 SS 1/8" tubing with 2.1 mm i.d.).
5. Immediately withdraw enough soil gas to fill a 1-L Tedlar bag. Analyze and record the SF_6 concentration in the 1-L Tedlar bag.
6. Inject 5-10 L of clean air into the vadose zone at this sampling point before conducting a longer test.
7. Repeat Steps 4, 5, and 6 except wait for periods of 15, 60, and 120 min before withdrawing the soil gas sample for analysis.
8. Reduce the data by dividing the measured concentrations by Cmax (this is equivalent to determining η, the fraction of mass recovered).

3.3.3 Soil gas concentration measurement

The following considerations are for soil gas concentration measurement:

- For the monitoring well method, measure the length of tubing and tubing inner diameter (ID). Use the equation for a cylinder to calculate volume (V=πr2h; r is 0.5*ID, h is length). Calculate the time needed to remove dead air volume from tubing by using the known pumping rate of the hand-held gas meter (divide pumping rate by tubing volume, ensure all units in calculations are equivalent). Ensure the meter runs at minimum for the calculated time. Record gas concentrations after this time in a field log book.
- For temporary and permanent gas monitoring points, utilize the procedure above for the known tubing length. Ensure that one tubing volume at minimum is recorded prior to recording gas concentrations.
- Record O_2, CO_2, and CH_4 concentrations in a field log book. Ensure concentration units are included in ppmv or % by volume).
- Implement precautions to ensure that VOCs are excluded from the CH_4 measurement through use of a granular activated carbon or charcoal filter on the inlet to the meter.
- Measure VOCs ensuring measurements are made with and without a charcoal filter on the inlet to the FID.
- Record the nitrogen (N_2) concentration (if implemented in field program).
- Typically, the soil vapor concentration profiles at a single sample probe cluster location can be measured in approximately one hour. A network of up to 10 locations can typically be measured in a one day field effort.

[4] Based on the method of Johnson, P.C., Bruce, C., Johnson, R.L. and Kemblowski, M.W., 1998. In situ measurement of effective vapor-phase porous media diffusion coefficients. Environmental science & technology, 32(21), pp.3405-3409.

- An example field record log for the multigas meter is provided in **Appendix A**.

4 QA/QC

QA/QC measures are used to ensure the accuracy and precision of the data collected. Manufacturer-recommended calibration procedures will be followed for all field instruments. Directions on the use, calibration, and tracking for standard field equipment is provided in EHS Support SOP-08: Field Equipment Operation and Calibration

4.1 Instrument Specifications

Several instruments are available on the market, and should be selected based on accuracy, precision, and stability. The following instrument specifications are provided for reference. Instruments selected should have comparable metrics to those given below:

Landtec GEM5000 multi gas monitor:

- CH_4 range 0-100 %, accuracy 0.5 % by volume (vol) in the 0-70% vol. range.
- CO_2 range 0-100 %, accuracy 0.5 % by volume (vol) in the 0-60% vol. range.
- O_2 range 0-25 %, accuracy 1.0 % by volume (vol) in the 0-25% vol. range.
- H_2S range 0-50 parts per million (ppm), accuracy 2.0 %.
- Pump flow rate 550 ml/min
- Flow fail point -200 millibar vacuum
- The GEM5000 gas analyzer is carefully calibrated at manufacture and when returned for service.

For portable gas chromatograph instruments intended for SF_6 measurement, documentation is available at this link.

FOXBORO Toxic Vapor Analyzer 1000:

- Minimum detectable level 100parts per billion (ppb) benzene, 200ppb hexane
- Pump flow rate 1000ml/min
- Precision ±1%
- Range 0 2000 ppm (benzene) 0 to 50,000 ppm (hexane).

4.2 Instrument Calibration

Instruments are factory calibrated, and typically calibration is verified by the instrument manufacturer or vendor. All factory calibration and vendor verification certificates and documentation should be retained in the project files. For long-duration field initiatives (greater than 2 to 3 days or one week) single-point field verification of gas meters may be performed utilizing calibration gases of known concentrations, where Federal and international shipping laws allow transport of pressurized gas cannisters, if appropriate for site conditions and as specified in the site sampling and analysis plan.

For sulfur hexafluoride portable gas chromatograph instruments, the vendor will perform the following before field work begins[5]:

[5] https://www.cdc.gov/niosh/docs/2003-154/pdfs/6602.pdf

- Establish a laboratory calibration graph by at least three replicate determinations of at least five analyte volumes. Plot peak height (or area) vs. volume of sulfur hexafluoride.
- Determine detector drift, averaged over the time period expected to be used in the field.
- Determine the ability of the GC column to separate the sulfur hexafluoride from other substances known or predicted to be present in the field samples.

Daily field calibration graph of peak height (or area) vs. volume of sulfur hexafluoride by triplicate determinations of working standards if possible, in the field.

The PID/FID (TVA-1000 or equivalent) should be field calibrated. The FID is calibrated against methane (typically 1%) and the PID should be calibrated by isobutylene (100 ppmv). Higher and lower concentrations of calibration gases can be utilized based on anticipated field concentrations. No field calibration is typically conducted on the multi-gas meter, however, extended field efforts may utilize a mixed multigas calibration standard or a set of single gas calibration standards to calibrate the instrument in the field and/or verify instrument stability and drift. Instructions on field calibration are included in the user manual for the meter, and provided on EHS Support **SOP 008 'Field Equipment Calibration'**. An example calibration sheet is provided in Appendix A.

5 Calculations

5.1 Estimate the vapor diffusion coefficient (D_v^{eff}).

The vapor diffusion coefficient (D_v^{eff}) can be estimated using either field testing or literature sources. This section describes estimation using field measurement. The η value is determined from field test data as described in **Section 3.22** of this SOP. The η value is then used to read a β value using **Figure 1** below.

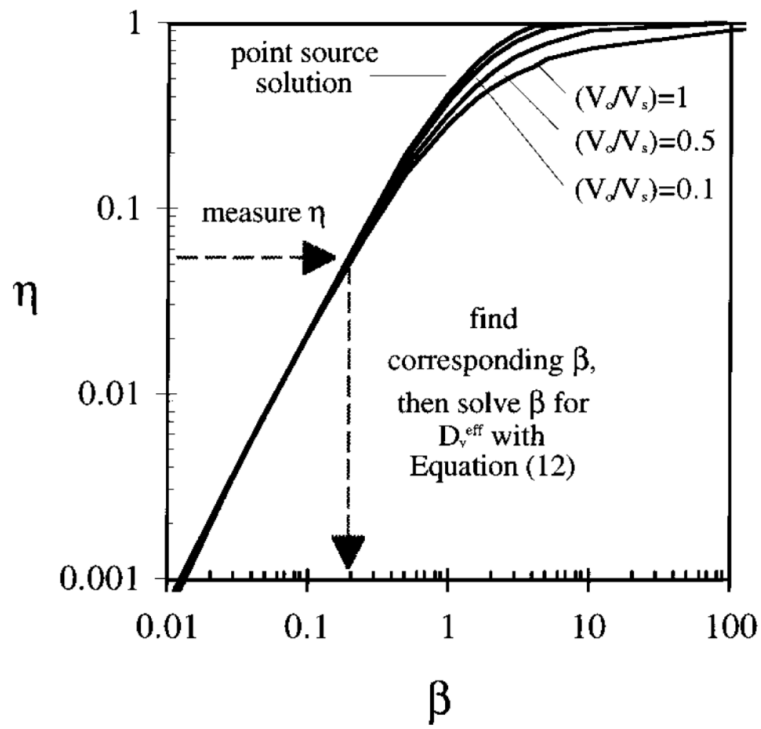


Figure 1. Estimation of vapor diffusion coefficient (D_v^{eff}). η is determined by field tracer gas measurement, and the corresponding β value is determined using this chart.

The estimated β value is then input into Equation 1 below to calculate D_v^{eff}.

$$D_{tracer}^{eff} = \left[\frac{\theta_V^{\frac{1}{3}}}{\beta}\right]\left[\frac{1}{4t_S}\right]\left[\frac{3V_S}{4\pi}\right]^{\frac{2}{3}}$$ Equation 1.

where Θ_V is the air-filled porosity (cubic meter (m^3)-vapor/m^3-soil), t_S is the sampling time (s), and V_S is the volume of vapor extracted at the end of the test (m^3). The value of Θ_V can be estimated from literature values or measured. If the soil type is known, this value can be estimated sufficiently accurately that laboratory testing is not generally warranted[6].

[6] Johnson, P.C., Bruce, C., Johnson, R.L. and Kemblowski, M.W., 1998. In situ measurement of effective vapor-phase porous media diffusion coefficients. Environmental science & technology, 32(21), pp.3405-3409.

5.2 Calculate the gas flux.

The calculation utilizes Fick's first law of diffusion applied to both background and source area monitoring points:

$$J = D_v^{eff}\left(\frac{dC}{dZ}\right)$$

Where:

J = the steady-state diffusive flux (g/m^2-soil/second)
D_v^{eff} = the effective soil vapor diffusion coefficient (m^2/second)
v = gas specific (i.e., O_2, CO_2, or CH_4)
$\frac{dC}{dZ}$ = the soil gas concentration gradient (gram per meters cubed per meter [g/m^{3}m])

1. Estimate the concentration gradient: $\frac{dC}{dZ} = \frac{C_2 - C_1}{Z_2 - Z_1}$; where C_1 and C_2 are the concentrations and Z_1 and Z_2 are the depths of samples 1 (shallow) and 2 (deep), respectively.
2. Compensate for background fluxes. This will be accomplished by subtracting average background concentrations of gases from source area and downgradient locations using the following equation:

$$J_{NSZD} = J_{Total} - J_{Background}$$

Where J_{NSZD} is the gas flux associated with NSZD processes, J_{Total} is the total gas flux in source are well Theisen polygons, and $J_{Background}$ is the gas flux in background locations.

5.3 Calculate the NSZD rate.

The NSZD rate (R_{NSZD}) is then calculated by dividing the calculated gas flux (negative for oxygen utilization, positive for carbon dioxide production) by the stoichiometrically produced (for CO_2) or consumed (for O_2) of the site-specific hydrocarbon degradation reaction. NSZD rates should not be the sum of calculated values using oxygen depletion and carbon dioxide production, but one or the other.

Attachment A Example Field Measurement Log

Multi-gas Meter Field Record Log

Project Name	Equipment Type
Project Location	Make/Model/Serial No.
Project Number	Page _____ of _____
Technician Name:	

Date/Time	CO_2		O_2		CH_4		H_2S		Other		Comment
	Value	*Units*	*Value*	*Units*	*Value*	*Units*	*Value*	*Units*	*Value*	*Units*	

Attachment B Example Calibration Verification Logs

Multi-gas Meter Calibration Log

Project Name	Equipment Type
Project Location	Make/Model/Serial No.
Project Number	Page _____ of _____

Calibration Reference Solution

Parameter	*Concentration*	*Units*	*Gas Expiration Date*
CO_2			
CH_4			
O_2			
H_2S			
Other:			

Date/Time	**Calibrated By**	**CO_2**		**O_2**		**CH_4**		**H_2S**		**Other**		**Comment**
		Air	***Cal. Gas***	***Air***	***Cal. Gas***	***Air***	***Cal. Gas***	***Air***	***Cal. Gas***	***Air***	***Cal. Gas***	

SOP For Use Of Dynamic Closed Chamber (LICOR meter)

1 Summary

Natural Source Zone Depletion (NSZD) estimation is an important component of assessment of natural attenuation process on petroleum hydrocarbon impacted sites. The dynamic closed chamber (DCC) system measures carbon dioxide (CO_2) (model LI-870) or CO_2 and methane (CH_4) flux to the ground surface over time to estimate hydrocarbon mass depletion rates in the unsaturated zone.

This standard operating procedure (SOP) is designed to:

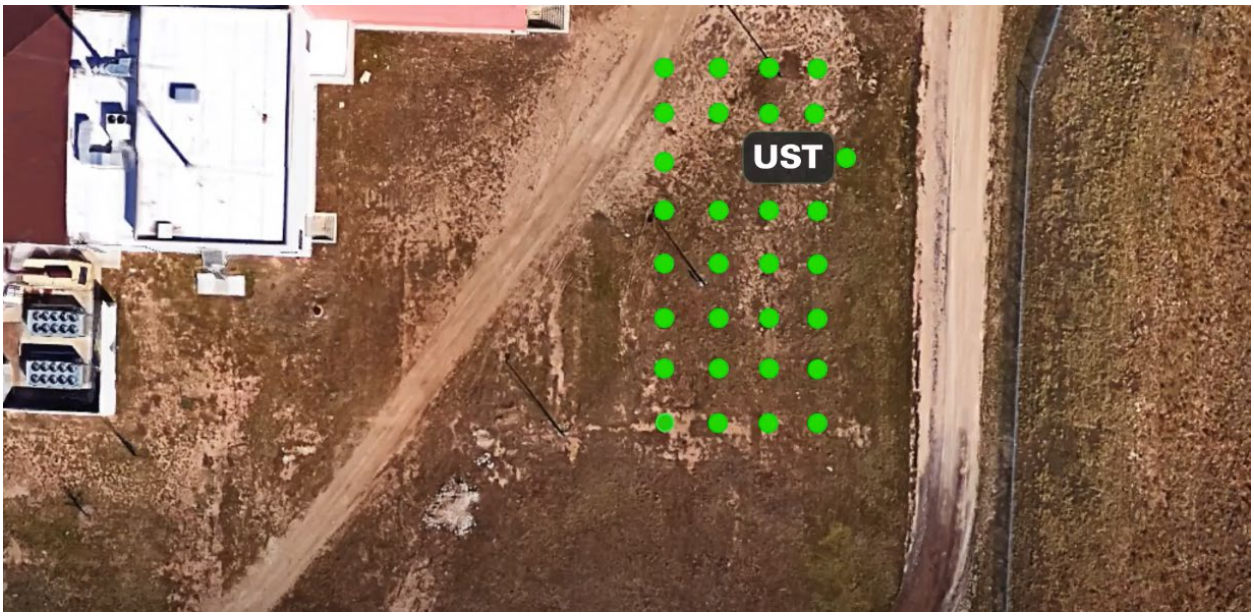
- Cover field installation and data logging using a LI-COR meter.
- Discuss instrument calibration.
- Describe Quality Assurance/Quality Control (QA/QC) procedures.
- Introduce data analysis methodology.

This SOP is intended as a practical guide to implementing and assessing results of a DCC study. It is assumed the reader is familiar with the underlying scientific principles[1].

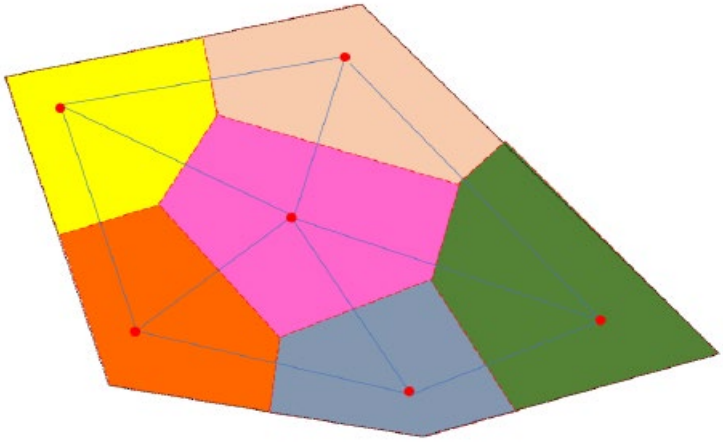
[1] Sihota, N.J., Singurindy, O. and Mayer, K.U., 2011. CO_2-efflux measurements for evaluating source zone natural attenuation rates in a petroleum hydrocarbon contaminated aquifer. Environmental Science & Technology, 45(2), pp.482-488.

2 Sample Grid Design

The method relies on the collection of data on a sampling grid across the light non-aqueous phase liquid (LNAPL)/hydrocarbon affected areas to determine the magnitude of natural mass losses from an affected area. An understanding of the lateral and vertical distribution of hydrocarbon impacts, and variability on the subsurface geology, is critical before undertaking this type of sampling to ensure that representative sample locations (and an associated grid is established across the area).



- Best practice is to establish a standardized grid over the plume area to provide multiple data points to assess the nature of the soil-vapor flux. Typically grid sizes extend up to and may exceed 20 meters (m) x 20 m.



- Due to financial and logistical constraints, Theissen Polygons (see above) may be created to assign areas to each monitoring point, and the flux measured within the cross-sectional area of the monitoring point can be extrapolated to its Theissen Polygon.
- In this case, monitoring points should be arranged near groundwater monitoring locations or soil borings, thus knowing subsurface conditions which can be used to help interpret measurement results.
- At minimum, assign an individual CO_2 trap to all distinct areas of LNAPL consistency, geologic, and hydraulic characteristics.

3 Procedures

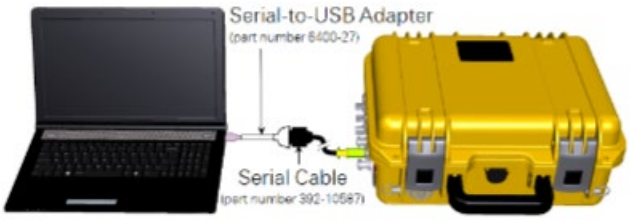
3.1 Training

The following training and procedures will be performed to maximize data quality:

- Training will be conducted to ensure that staff are aware of calibration and operation of the unit prior to deployment in the field.
- Field staff will trained so that they understand the scope of SOP and note-taking requirements. An example field record form is provided as **Attachment A**.
- The field supervisor will check notes in the field daily and correct inconsistencies in the field.
- The field supervisor will sign off on field forms daily to verify quality and consistency.
- The project manager will also periodically check forms and data to verify quality and consistency.

3.2 Equipment

- DCC soil flux system
  - Chamber
  - Circulation pump
  - CO_2 gas analyzer
  - Methane gas analyzer
  - Software/controller
  - Serial cable
  - Serial to USB adapter



- 20 centimeter (cm) diameter collars
- hand trowel
- rubber mallet or slide hammer
- Personal Protective Equipment (PPE) including safety glasses, hard hat
- Field logbook
- Camera

3.2.1 Procedure – Receiver Pipe (Collar) Installation

- Clear designated area of all vegetation
- Locate receiver pipe – white hard plastic pipe, with one beveled end
- Ensure hose clamp around receiver pipe is tight and secure, rotating bolt on hose clamp clockwise to tighten with screwdriver if needed
- Ensure three u-nuts are secure on hose clamp around receiver pipe

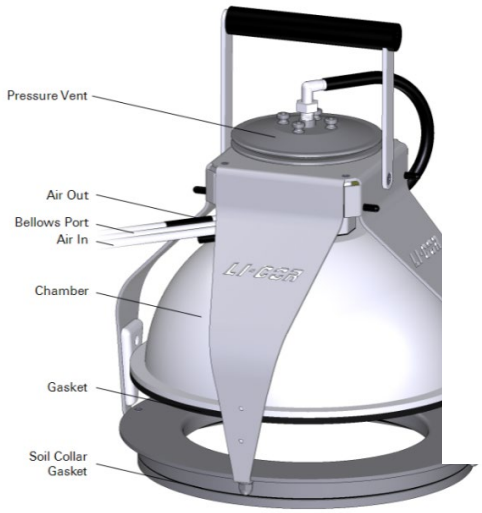
- Place an eye bolt into each u-nut and tighten by hand, making sure hole on eye bolt is rotated to be parallel to hole in receiver pipe
- Place beveled side of receiver pipe on the ground

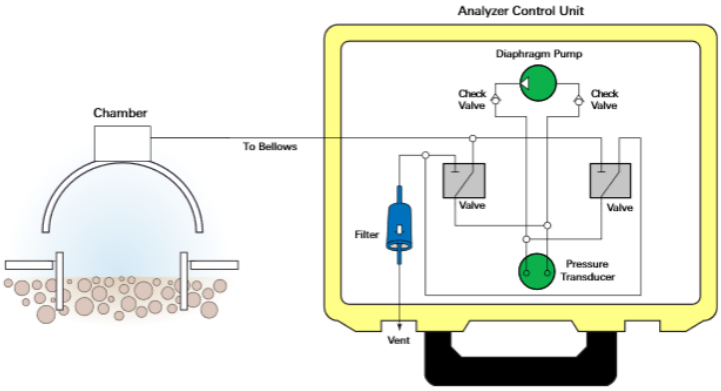
Receiver pipe with U-nuts and eye-bolts attached. Stakes laying aside pipe

- Hammer receiver pipe into ground using rubber mallet or slide hammer, rotating hits evenly across top to remain level, until reaching 2” burial depth, as noted on side of receiver pipe
- Place a stabilization stake through each eye bolt, hammering the stake down to ground level to secure the receiver pipe
- Ensure the reliever pipe is vertical
- Compact soil both inside and outside of the receiver pipe to original condition with hand or hammer
- Collar must be installed at least 16 hours prior to measurement of soil-vapor to return to equilibrium
- The height of the collar above ground surface time, and location of the collar should be recorded in the field log book

3.2.2 Procedure – CO_2 Gas Analyzer Installation

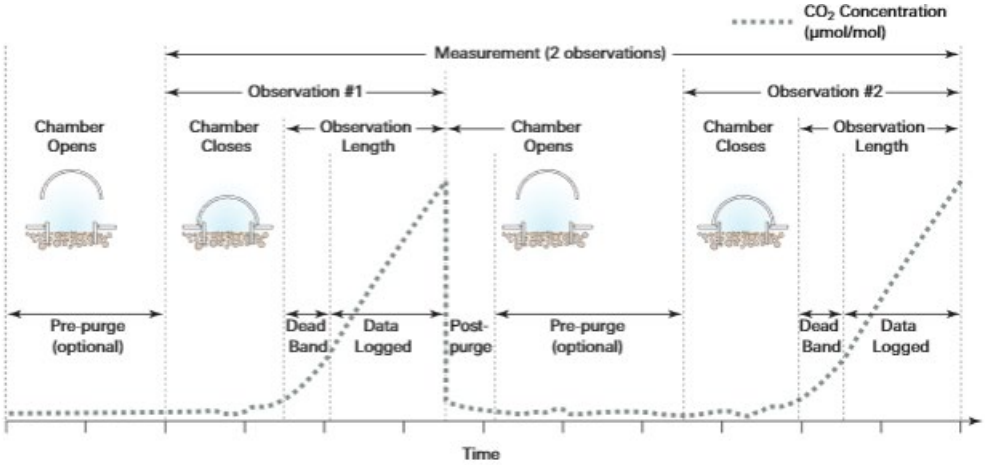
Efflux measurements are made by placing the chamber onto the soil collar and using the DCC soil flux system control software to initiate the measurement cycle. The pneumatically actuated bellows closes the chamber and starts the IRGA measurements of CO_2 concentration, temperature, and relative humidity. Following the end of the measurement period (e.g. 90 seconds), the bellows opens the chamber, and a purge cycle ensues to clear the system. After the purge, the system continues to close the chamber and perform routine measurements until the user-set number of measurements are taken. The unit then opens and goes idle until the unit is picked up and moved to the next measurement location.





- The latest version of SoilFluxPro should be downloaded from the LICOR website (www.LICOR.com/env/support).
- The DCC system measures changes in CO_2 concentration, temperature, pressure, initial water vapor mole fraction and water corrected CO_2 mole fraction. The height of the collar above ground must be entered so the system can calculate chamber volume.
- A laptop or smartphone with the installed SoilFluxPro should be connected to the DCC system via ethernet cable.
- The labelled AIR OUT, AIR IN and bellows hoses should be connected to the control unit and the chamber.
- The DCC system chamber is set directly on the collar, receiver side down.
- The measurement sequence should be started from the app which includes:
    - A predefined purge timer, of roughly 10 seconds
    - The chamber closing onto the collar and bellows inflating to form a seal
    - An initial “deadband” measurement time, of roughly 10 seconds where data is collected, but not used in efflux calculations
    - A predefined measurement period, around 90 seconds
    - Bellows deflating to release seal
    - A predefined post sampling purge timer, of roughly 10 seconds.

- A minimum of 3 sequential CO_2 efflux measurements are needed at each location, due to the short period of measurement. After the completion of the preset number of measurements, the user evaluates the data to assess whether additional measurements are needed at the same location or whether measurements are complete at that location.



- Variability in sequential measurements may be observed greater than 10% of each other. If this situation arises, it is recommended to perform a second round of measurements at the same location. If efflux measurements are to be repeated at the same collar within an individual day, delay the subsequent measurement by 20 minutes to allow re-equilibration of vapours in the soil.
- Records are maintained on the instrument record log or in a field notebook. An example field record form is provided in **Attachment A**.

3.3 Instrument Precision and Calibration

A two-point field calibration to a 0 parts per million by volume (ppmv) CO_2 standard (zero gas) and a span gas cylinder with a 500-ppmv CO_2 concentration is recommended. Calibration procedures are outlined in the instrument manual. Accuracy is tested following calibration by analyzing the span gas as a sample. Calibration results should be record daily. An example calibration log is provided in **Attachment B**.

The following instrument precision metrics are supplied by the manufacturer (as of 2021).

CH_4 Measurements:

- Measurement Range: 0.1 to 100 ppm
- Precision (1σ):
  - 0.60 ppb at 2 ppm with 1 second averaging
  - 0.25 ppb at 2 ppm with 5 second averaging
- Maximum Drift: < 1 ppb per 24-hour period

CO_2 Measurements:

- Measurement Range: 1 to 10,000 ppm

- Precision (1σ):
    - 3.5 ppm at 400 ppm with 1 second averaging
    - 1.5 ppm at 400 ppm with 5 second averaging

Factory calibration is an integral step in the manufacture and repair of all LI-COR measuring instruments. The characteristics of optical and other components change with time, and may be affected by environmental conditions.

Recommended Recalibration Frequency: No regular factory recalibration required. Calibration is recommended based on QA/QC results and drift in replicate analyses over time.

A factory recalibration includes the following:

- Calibration
    - Zero, span, and verification
    - Pressure sensor calibration
- Tests and Maintenance
    - Plumbing inspection and leak test
    - Replace dry-down chemical
    - Change user-replaceable inlet filters
    - Inspect O-Rings, filter housing support on inlet/outlet connection
    - Lithium coin cell battery changed (as needed)
    - Upgrade software to the most recent version (please download a copy of your files before sending to LI-COR)
    - Check pump and flow rates
    - Other repairs and maintenance as needed; customers are notified if additional fees are required for repairs
    -

3.4 QA/QC Procedures and Data Validation

- A field blank measurement is collected during each field event. A collar with a sealed bottom cap is used for the field blank. The chamber is set upon the sealed collar in the field and allowed to run a total of 60 measurements. The results of the field blank are then averaged, three times the standard deviation is added, and the resulting value is assigned the limit of detection for the particular measurement event.
- After tabulation of the raw field data, data validation occurs. The process of validating the DCC field measurement data is as follows:
    - Tabulate the data from the CO_2 efflux field survey
    - Assign non-detect values by comparison of raw results to the field blanks
    - Optimize the CO_2 concentration curve fits. Adjust the deadband and observation time in order to optimize the curve fit parameter (R2) and evaluate the validity of the individual efflux measurements
    - Eliminate data that are outliers, poor curve fit correlations, results from poor field procedures, or outside the manufacturer's recommended operating

- After data is collected, the dead band and observation times may be adjusted to optimize R^2 values in the dataset
- One of every 10 locations should be duplicated, with a second collar set up immediately adjacent to the original, with measurements taken as close as possible to each other
- Background correction is a subtraction of natural soil CO2 (modern CO2) efflux from the measured total CO2 efflux. At a minimum one background location outside and preferrably upgradient of the LNAPL footprint is needed. Additional background locations are required if vegetated/non-vegetated ground cover exists, and major differences in the type of vegation cover exists (e.g. lawn pararie, forest, cropland).
- Duplicate collar (recommended). A duplicate collar be installed and efflux measurement be made at a frequency of one for every 10 locations. Collect the duplicate location measurement during the same time of day as the normal (parent) sample location. Locate the normal and the duplicate locations less than 0.3 m apart and within the same ground cover. General statistics such as RPD between normal and duplicate sample locations are performed to assess data quality and identify potential differences in soil collar installation, ensure a good seal with the subsurface was attained, and evaluate any heterogeneities in the subsurface. Generally, an RPD greater than 30% indicates that the practitioner should evaluate installation procedures and influences of soil heterogeneities. The 30% RPD is a target only and may not be achievable at many sites due to soil heterogeneities.

3.5 Records

A record will be maintained of the field blank tests, duplicate sampling results, and background measurements and correction procedures. The records will include the following information, where applicable:

- Date and time of calibration activity
- Project name and number
- Personnel conducting the test
- Serial number and/or meter numbers
- Instrument name and model number
- Instrument readings of field blank verification data.

Additional documentation that will be retained include:

- Equipment rental shipping and calibration documents (provided by the Rental Company)
- Service and repair records
- Certificates of traceability for reference standards.

The above data will be recorded in the field logbook. Data will be recorded in the Instrument Log and/or the field logbook. An example of a field record log is included in **EHS Support SOP 008 – Field Equipment Operation and Calbration.**

3.6 Calculating NSZD Rate

- The total flux, as measured by CO_2 traps on the site includes background flux due to other decaying organic matter in the subsurface, and should be accounted for by a flux trap clearly out of range of the LNAPL body or horizontal diffusion from the LNAPL body
- To calculate background flux, a collar will have to be set up in a location with a similar subsurface composition and level of vegetation, but not located over any existing LNAPL/hydrocarbon spill
- If multiple soil types or vegetation levels are present, multiple background traps should be set up and measured at the same rate as the active traps
- If seasonal changes are suspected, due to a shallow smear zone, collection throughout the year may be beneficial to accurate readings
- Input data into EHS Support , LLC calculator to determine estimated total mass losses. Data provided by the system is in units that can be directly input into the calculator.
- The flux should be integrated over time at each location and across the site, to determine total mass loss from the LNAPL body in the vadose zone and hot spots within the site that may require additional attention

3.7 Calculations

Flux: $J = \frac{M}{A*t}$

Where:

J = Flux

M = Mass, (grams)

A = trap cross sectional area (m)

T = deployment time (days)

Carbon Dioxide Loss On-Site

$$A_{Theissen} * \frac{J_{Trap}}{A_{Trap}} = J_{Theissen}$$

$$\frac{M_{Theissen}}{M_{Trap}} = \frac{J_{Trap}}{J_{Theissen}}$$

$$A_{Site} * \frac{M_{Theissen}}{A_{Site}} = M_{Site}$$

Carbon Conversion

$$1\ C_8H_{18} + 12.5O_2 = 8\ CO_2 + 9\ H_2O$$

3.8 Contact Information

Leon Castro
Technical Sales Representative
LI-COR Biosciences
4647 Superior Street
Lincoln, Nebraska 68504
+1.402.467.0722

Attachment A Example Field Record Form

EHS Support

Field Record Log Site Name and Location:_____ Field Technician:_____

Location	Date (mm/dd/yyyy)	Surface Cover	Type of Product	Pressure ☐ kPa ☐ Bar ☐ in/Hg	Temperature ☐ °C ☐ °F	Total CO_2 efflux (µmol/m²/s)	Standard Deviation	Notes
EXAMPLE	4/15/2021	Silty sand/gravel	Petroleum	80.58 kPa	24 °C	0.38	0.05	Rained previous day/high wind

Attachment B Example Calibration Log

LI-COR Calibration Log

Project Name	Equipment Type
Project Location	Make/Model/Serial No.
Project Number	Page _____ of _____
Calibration	
Calibration Gas Type	Calibration Standard Concentration

Date/Time	Calibrated By	Calibration Results	Comments

SOP for Temperature Gradient NSZD Rate Estimate

1 Summary

Natural Source Zone Depletion (NSZD) estimation is an important component of assessment of natural attenuation process on petroleum hydrocarbon impacted sites. The temperature gradient method uses soil temperature measurements taken at discrete depths to estimate heat flux in the vadose zone.

Typically, monitoring wells, deep soil gas vapor probes, and/or dedicated soil borings are used. The data is then used to calculate hydrocarbon mass depletion rates in the unsaturated zone. The method may be modified to provide an estimate of mass depletion rates in the saturated zone with additional data (e.g. heat capacity of water, groundwater advection).

Key assumptions that must be considered are that there is: homogenous and isotropic soil, a steady-state biogenic heat source, conductive heat transfer, and instantaneous and complete reaction. Complications with this method as applied to the Site may require 'parceling' areas for distinct calculations based on areas of distinct lithology.

This standard operating procedure (SOP) is designed to:

- Cover field implementation of a temperature monitoring program.
- Discuss instrument calibration.
- Describe Quality Assurance/Quality Control (QA/QC) procedures.
- Introduce data analysis methodology.

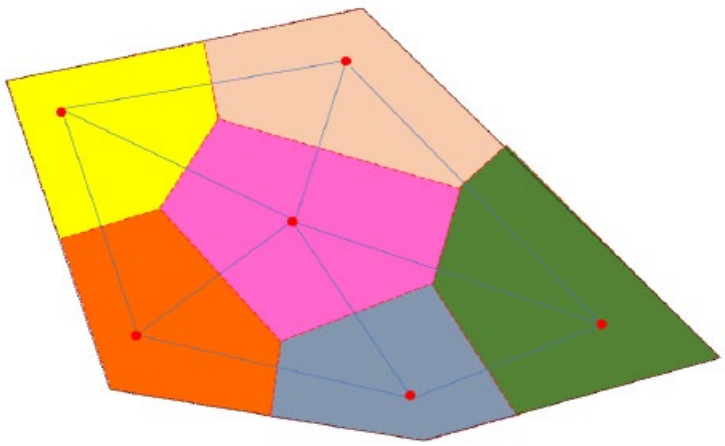
This SOP is intended as a practical guide to implementing and assessing results of a temperature gradient study. It is assumed the reader is familiar with the underlying scientific principles[1].

[1] Sweeney, R.E. and Ririe, G.T., 2014. Temperature as a tool to evaluate aerobic biodegradation in hydrocarbon contaminated soil. Groundwater Monitoring & Remediation, 34(3), pp.41-50.

2 Sample Grid Design

The method relies on the collection of data across the light non-aqueous phase liquid (LNAPL)/hydrocarbon affected areas to determine the magnitude of natural mass losses from an affected area. Monitoring wells are typically used for temperature gradient surveys, although deep soil vapor probes may also be utilized.

It is critical that a background location is included; several background locations may be required where subsurface heterogeneity is suspected. Therefore, an understanding of the lateral and vertical distribution of hydrocarbon impacts, and variability on the subsurface geology, is critical before undertaking this type of sampling to ensure that representative sample locations are selected.



- Theissen Polygons (see above) are calculated over the survey network and the NSZD rate at each monitoring point is extrapolated over the associated Theissen Polygon.
- At minimum, a monitoring point should be assigned to all distinct areas of LNAPL consistency, geologic, and hydraulic characteristics.
- Depending upon the local climate and depth to the hydrocarbon oxidation zone, seasonal and climatic effects may be dramatic and multiple field deployments may be warranted.

3 Procedures

3.1 Training

The following training and procedures will be performed to maximize data quality:

- Training will be conducted to ensure that staff are aware of calibration and operation of the unit prior to deployment in the field.
- Field staff will be trained to ensure thermocouples give plausible ambient value readings prior to each measurement. Acceptable readings will be based on the local weather report.
- Field staff will trained so that they understand the scope of SOP and note-taking requirements.
- The field supervisor will check notes in the field daily and correct inconsistencies in the field.
- The field supervisor will sign off on field forms daily to verify quality and consistency.
- The project manager will also periodically check forms and data to verify quality and consistency.

3.2 Equipment

There are several options to monitor soil temperature profiles:

- Dedicated nested string of thermistor or thermocouples installed in a backfilled soil borehole
- Existing monitoring wells – thermocouple and reel, and
- Existing monitoring well – dedicated string of button-type temperature loggers.

Example of a thermocouple and reel (Thermoprobe TP7-D)

Example of a thermistor string (GEOKON Model 3810)

Example of button temperature logger (Thermochron Model DS1922L)

3.3 Installation and measurement procedures

Measurement depths:

- At a minimum, measurements are needed within and above the hydrocarbon oxidation zone so that an accurate estimate of the upward thermal gradient can be made.
- Measurements below the oxidation zone and into the groundwater table may also be valuable to assess the downward heat flux and impacts to the shallow groundwater.
- A resolution of 2 to 3-foot intervals may be used to avoid missing thermal maximums, particularly in areas with large seasonal variations where the position of the thermal maximum may fluctuate.

Measurement devices:

- Numerous devices are available from different vendors. The ideal capability is 0.1 ^{o}C precision (often called resolution by manufacturers) and better than ± 0.5 ^{o}C accuracy.

Measurement procedures:

- For the thermocouple and reel method, thermocouples are lowered to the specified monitoring depth within the vadose zone for a minimum of 3 minutes and groundwater for a minimum of 1 minute to allow for equilibration before recording the temperature and lowering to the subsequent monitoring depth. Readings are recorded in a field notebook.
- For the thermistor string method, the thermistor string is installed in a dedicated borehole that is backfilled with dry to medium-fine sand to ensure efficient thermal connectivity with the surrounding formation. Procedures for drilling boreholes are beyond the scope of this SOP. Thermistors are wired to an at-grade datalogger that is set to record temperatures at least twice daily, once at a time of maximum temperature (e.g. 2 PM) and once at the lowest (e.g. 2 AM).
- For the button method, it is recommended that buttons are fitted with a water proof case (available from vendor) and fixed to an inert (preferably stainless steel) string. The string is typically placed in a monitoring well or deep soil gas probe for approximately one year, after which the string is removed and data from the loggers is downloaded.

Thermal conductivity measurements:

- It is recommended that site-specific thermal conductivity readings be collected if dedicated boreholes are used for the installation of thermistor strings. If not possible, literature values may be used.
- If monitoring wells or deep soil gas probes are utilized, consideration should be given for advancing a borehole (or boreholes) for the purpose of collecting site-specific thermal conductivity data that accounts for site soil moisture conditions.
- Several hand-held devices are available for measuring soil thermal conductivity. A device with a factory or vendor calibration certificate should be used. A reliable device is the THERMTEST TLS-100, which follows ASTM D5334-14[2]

Procedures for drilling boreholes and installing monitoring wells are provided elsewhere.

[2] ASTM, 2014. D5334-14 Standard Test Method for Determination of Thermal Conductivity of Soil and Soft Rock by Thermal Needle Probe Procedure

4 QA/QC

QA/QC measures are used to ensure the accuracy and precision of the data collected. Manufacturer-recommended calibration procedures will be followed for all field instruments. Thermocouples are typically calibrated by the manufacturer prior to shipping, and calibration may be checked in the field by immersing the thermocouples in an ice bath filled with distilled water (0°C). Directions on the use, calibration, and tracking for standard field equipment is provided in EHS Support SOP-08: Field Equipment Operation and Calibration

4.1 Instrument Specifications

Several instruments are available on the market, and should be selected based on accuracy, precision, and stability. Preferred instruments are factory calibrated. The following instrument specifications are provided for reference. Instruments selected should have comparable metrics to those given below:

ThermoProbe TP7-D thermocouple/reel instrument:

- Factory calibrated.
- Precision: 0.01 ^{o}C.
- Calibrated Accuracy: ± 0.1 ^{o}C (from 0 to 100 ^{o}C).
- Long term drift: does not exceed 0.05% per year.

GEOKON Model 3810 thermistor string:

- Factory calibrated.
- Precision: 0.1 ^{o}C.
- Calibrated Accuracy: ± 0.2 to 0.5 ^{o}C (from -20 to 80 ^{o}C), depends upon the specific model.
- Design for long-term deployment (years)

Thermochron Model DS1922L button logger:

- Factory calibrated
- Precision: 0.0625 ^{o}C (11 bit model).
- Calibrated Accuracy: ± 0.5 ^{o}C (from 20 to 75 ^{o}C).
- Designed for ~5-year deployment.

4.2 Instrument Calibration

Instruments are factory calibrated, and typically calibration is verified by the instrument vendor. All factory calibration and vendor verification certificates and documentation should be retained in the project files. The following field tests may be used to verify instrument performance:

- Calibration verification to test accuracy and instrument drift may be checked in the field by stirring the thermocouple/thermistor string in an ice water bath and verifying the instrument reads 0 ^{o}C within the calibrated accuracy stated for the specific instrument.

- Calibration verification frequency should be performed daily (non-dedicated instruments) or prior to deployment and following recovery of instruments.
- A second verification test is to allow the thermocouple to equilibrate with ambient air for a minimum of three minutes, and with the thermocouple tip not in contact with any surface (i.e., suspended in air). The thermocouple reading may be compared to a daily local temperature record or on-site thermometer to ensure a plausible temperature reading is obtained.
- Calibration verification test records should be maintained in the project file. An example calibration verification form is provided in **Attachment A**.

5 Calculations

5.1 Calculate ΔT

Net temperature change (ΔT) will be calculated to qualitatively assess the presence of metabolic heat flux signatures by comparing the difference in groundwater temperature between source and background wells (ΔT = Ti – Tb, where Ti is the temperature of well I, and Tb is the temperature of background well). This calculation will be performed for the maximum, average, and minimum upgradient groundwater temperature for all three monitoring zones. Example tables that will summarize calculations are provided in **Table 1** and **Table 2.**

Table 1 Example Background and Downgradient Well Statistics (Tb)

Well	T Minimum (°C)	T Average (°C)	T Maximum (°C)
Background wells			
Depth 1			
Depth 2			
Depth 3			
Downgradient wells			
Depth 1			
Depth 2			
Depth 3			

°C = degrees Celsius
T = Temperature
Tb = Temperature of background well

Table 2 Example Source Area Well Statistics Well Calculations (Tb)

Well	T. (°C) [Measured = Ti]	ΔT (Minimum) [Relative to Background]	ΔT (Av.) [Relative to Background]	ΔT (Max.) [Relative to Background]	ΔT (Minimum) [Relative to Downgradient]	ΔT (Av.) [Relative to Downgradient]	ΔT (Max.) [Relative to Downgradient]
Source Area Well MW-1							
Depth 1							
Depth 2							
Depth 3							
Source Area Well MW-2							
Depth 1							
Depth 2							
Depth 3							
etc.							

°C = degrees Celsius
ΔT = temperature difference

Av. = average
Max. = maximum
T = temperature
Tb = temperature in background well
Ti = temperature of well "i"

5.2 Estimate the soil thermal conductivity

Thermal conductivity (K_T) can be estimated using either lab/field testing or literature sources. A volume-weighted average value (or geometric mean) should be used that is representative of all different lithologies within the oxidation zone.

Literature values may be used, and range from between 0.1 to 4 J/m/s/°K for most materials. Some typical values are included in Table 3 below (note, W m^{-1} C^{-1} is equivalent to J m^{-1} s^{-1} K^{-1}):

Table 3 Thermal conductivity of some geologic materials[3]

Rock Type	Pore Volume* (mm^3/g)	Thermal conductivity (W m^{-1} C^{-1})	
		Dry (air-saturated)	Water-sorbed
Iceland Spar Calcite	0	3.2**	-
Translucent calcite spar	0.4	3.1**	--
Limestone	4	3.0	3.1
Limestone	17	2.9	2.9
Limestone	38	2.5	2.9
Limestone	53	2.4	2.9
Limestone (chalk)	216	1.2	1.7
Dolomite	7	5.1	5.5
Dolomite	31	3.1	4.2
Magnesite	14	5.0	5.1
Sand	--	0.15-0.25	2-4
Water	--	--	0.60
Air	--	0.03	--

* = Determined by mercury porosimetry
** = Determined perpendicular to the {1014} planes
Source: Thomas Jr. et al. 1973.
°C = degrees Celsius
mm^3/g = cubic millimeters per gram

[3] Data from Thomas Jr, J., Frost, R.R. and Harvey, R.D., 1973. Thermal conductivity of carbonate rocks. Engineering Geology, 7(1), pp.3-12; and Sweeney, R.E. and Ririe, G.T. (2014). Temperature as a Tool to Evaluate Aerobic Biodegradation in Hydrocarbon Contaminated Soil. Groundwater Monitoring & Remediation 34(3), 2014.

5.3 Calculate the heat flux.

Heat flux is estimated using Fournier's first law of conduction, that is modified to estimate heat flux (q_H [J/m^2-soil/s]:

$$q_H = K_T \left(\frac{\Delta T}{\Delta Z}\right)$$

Where:

q_H = Heat flux
$\frac{\Delta T}{\Delta Z}$ = the temperature gradient (^{o}K/m)
K_T = the thermal conductivity of the soil (J/m/s/^{o}K) in the hydrocarbon oxidation zone

5.4 Calculate the NSZD rate.

The NSZD rate (R_{NSZD}) is then calculated by dividing the calculated heat flux by the enthalpy (ΔH^o) of octadecane ($C_{18}H_{38}$) oxidation. The enthalpy of octadecane oxidation is calculated following the method described in Sweeney et al (2014), which utilizes the stoichiometry of octadecane oxidation

$$C_{18}H_{38} + 27.5O_2 = 18CO_2 + 19H_2O$$

and the following enthalpies of formation at standard state of the reaction components (in kilojoules per mole [kJ/mol] at 298.15 Kelvin [K]): $\Delta H_f{}^o{}_{C18H38}$ = -414.6; $\Delta H_f{}^o{}_{O2}$ = 0; $\Delta H_f{}^o{}_{CO2}$ = -393.5; $\Delta H_f{}^o{}_{H2O}$ = -285.8. By solving for the standard enthalpy of the reaction, (i.e. $\Delta_r H^\circ = \Sigma v\ \Delta_f H^\circ$(products)–– $\Sigma v\ \Delta_f H^\circ$(reactants), $\Delta H_r{}^o$ of the above reaction is -12092.9 kJ/mol, which when divided by the molar weight of octadecane (254.5 g/mol) gives 47.5 kJ/g of heat released. Therefore, the NSZD degradation rate (in grams/m^2/day) is:

$$R_{NSZD} = \frac{q_H}{47500\ kJ/g} \times \frac{86{,}400\ s}{1\ d}$$

6 Contact Information

ThermoProbe Inc.
112-A Jetport Drive
Pearl, MS 39208 USA
(601) 939-1831
www.thermoprobe.net

Attachment A Example Calibration Verification Log

Thermocouple Calibration Verification Log

Project Name	Equipment Type
Project Location	Make/Model/Serial No.
Project Number	Page _____ of _____
Calibration	
Calibration Gas Type	Calibration Standard Concentration

Date/Time	Calibrated By	Calibration Method	Calibration Results	Ambient Air Temperature (Weather Report)
Example: 4/15/2020	A. Technician	Ice Bath	0.1 ^{o}C	25 ^{o}C – local airport.
Example: 4/15/2020	A. Technician	Ambient Air	23.6 ^{o}C	25 ^{o}C – local airport.

Appendix E Health and Safety Plan

Site Safety Plan
For
Groundwater Monitoring and O&M at

ST. CROIX ALUMINA:

1 Estate Anguilla,
Kingshill, St. Croix

Updated on
October 28, 2020

GMS
GeoMonitoring Services
Environmental Remediation & Consulting

St. Croix Alumina
1 Estate Anguilla,
Kingshill, St. Croix

EMERGENCY PHONE NUMBERS

Local Police **911**

Local Fire **911**

Local Rescue **911**

Local Hospital Name, Number & Address:

Juan F. Luis Hospital & Medical Center
4007 Estate Diamond Ruby
Christiansted, St. Croix U.S.V.I. 00821
(340) 778-6311

Directions from St. Croix Alumina to Hospital:

1.	Head north on VI-75 / Queen St toward VI-70 / Queen Mary Hwy	187 ft
2.	Turn right onto VI-70 / Centerline Rd	0.8 mi
3.	Turn right onto VI-70 / VI-709 / Queen Mary Hwy	0.3 mi
4.	Turn left onto VI-70 / Queen Mary Hwy	0.7 mi
5.	Turn left onto VI-79 / Claude A Bennie Benjamin Memorial Dr	0.1 mi
6.	Turn right onto Diamond Estate *Unpaved Road*	0.4 mi
7.	Arrive at Diamond Estate on the left	

National Response Center 1-800-424-8802

Poison Control Center 1-800-682-9211

GeoMonitoring Services Main Number: (281) 375-5101

Brian Epperson
Project Supervisor
Office: (713) 496-7296
Cell Phone: (701) 389-0547

Brad Freeman
Project Manager
Office: (281) 375-5101 ext. 3
Cell Phone: (713) 417-6141

DO NOT TRANSPORT SERIOUSLY INJURED
CALL LOCAL RESCUE

In the event of an incident, the Project Manager will immediately notify the Portfolio Manager and Hess Project Supervisor.

ATTACHMENT A

ROUTE TO LOCAL HOSPITAL MAP

bing maps

A 1 Clifton Hill Estate, Kingshill, Virgin Islands 00850, United States Virgin Islands

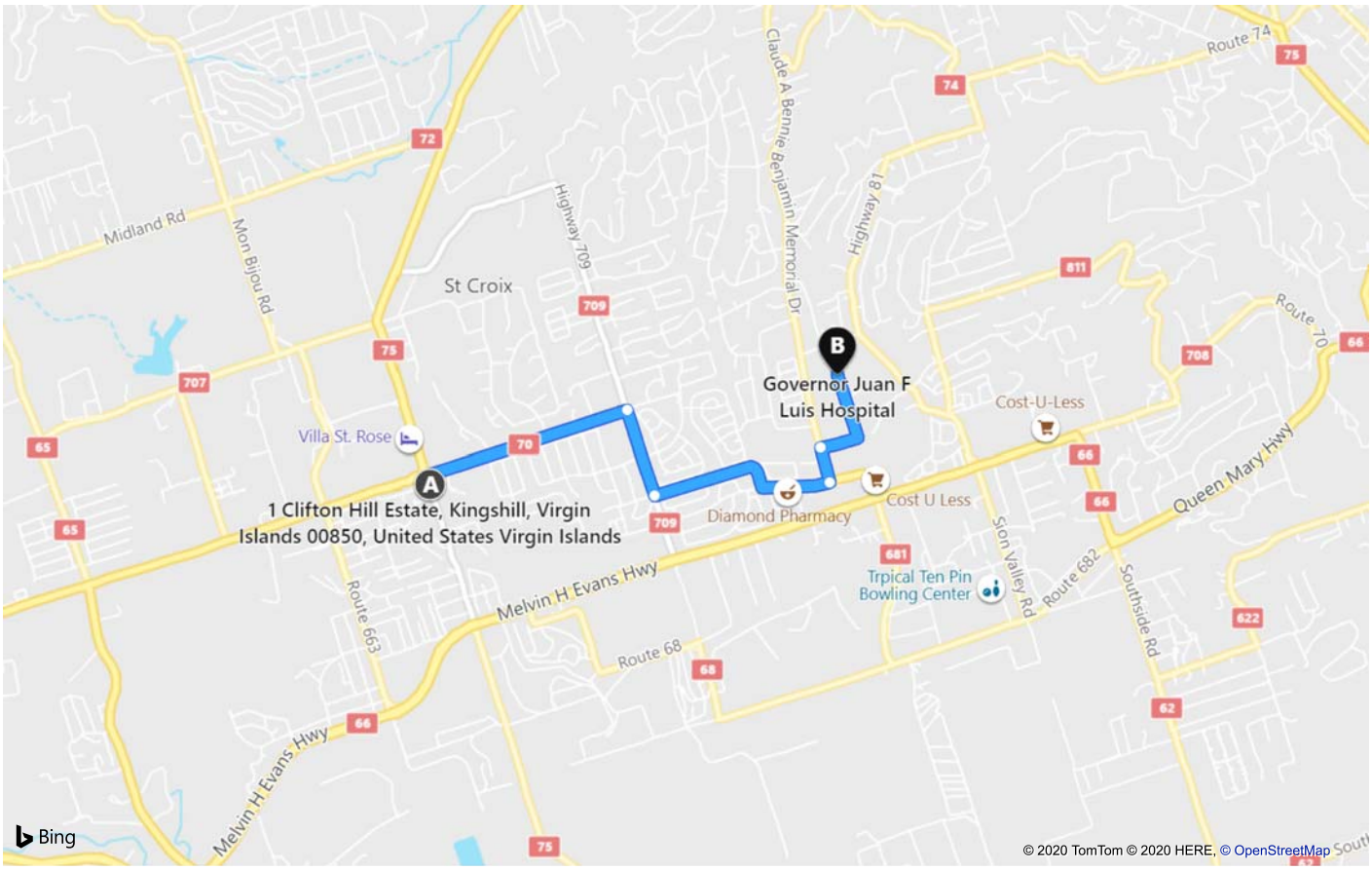
B Governor Juan F Luis Hospital

7 min , 2.4 miles
Light traffic
Via VI-70, Diamond Estate
· Unpaved roads

A 1 Clifton Hill Estate, Kingshill, Virgin Islands 00850, United States Virgin Islands

↑	1.	Head **north** on **VI-75 / Queen St** toward VI-70 / Queen Mary Hwy	187 ft
↱	2.	Turn **right** onto **VI-70 / Centerline Rd**	0.8 mi
↱	3.	Turn **right** onto **VI-70 / VI-709 / Queen Mary Hwy**	0.3 mi
↰	4.	Turn **left** onto **VI-70 / Queen Mary Hwy**	0.7 mi
↰	5.	Turn **left** onto **VI-79 / Claude A Bennie Benjamin Memorial Dr**	0.1 mi
↱	6.	Turn **right** onto **Diamond Estate** • *Unpaved Road*	0.4 mi
	7.	Arrive at **Diamond Estate** on the left The last intersection is Zion Hill Rd	

B Governor Juan F Luis Hospital



A 1 Clifton Hill Estate, Kingshill, Virgin Islan...

B Governor Juan F Luis Hospital

These directions are subject to the Microsoft® Service Agreement and are for informational purposes only. No guarantee is made regarding their completeness or accuracy. Construction projects, traffic, or other events may cause actual conditions to differ from these results. Map and traffic data © 2020 TomTom.

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1.0 INTRODUCTION

1.1 APPROVALS

Prepared By: Brad Freeman

Date: August 14, 2018

Updated By: Rick Dolan

Date: October 28, 2020

Approved By: Brad Freeman Date: 10/28/20

1.2 SITE BACKGROUND

Project Name: St. Croix Alumina

Site Address: 1 Estate Anguilla, Kingshill, St. Croix

Nearest Intersection: Melvin Evans Highway

Township/Municipality: St. Croix, USVI

County: N/A

Additional Site Information:

The site is a former aluminum plant that is adjacent to the HOVENSA refinery. HOVIC notified the USEPA of potential off-site contamination in 1993 based on a report from VIALCO to HOVIC. USEPA directed HOVIC to conduct a groundwater investigation at SCA in May 1994. A hydrocarbon characterization study was submitted to the USEPA in April 1997. USEPA determined that all current and former owners of both properties were the responsible parties. An Administrative Order between Lockheed Martin, VIALCO/Century, ALCOA, HOVIC and HOVENSA was executed in May 2001 and required all parties to work together to remediate contaminated groundwater at SCA. Site-wide hydrocarbon recovery is ongoing.

The system is operated solely off of solar power. Hydrocarbon recovery will cease once PSH thickness is less than the practical limits of mobility value of 0.2 feet and/or below the site-wide stability threshold of PSH velocity of 0.1 feet per day and assessment of containment indicates there is no potential for PSH migration.

1.3 SCOPE OF WORK

- Well Gauging
- Groundwater Monitoring
- Hydrocarbon Recovery System Maintenance

2.0 PROJECT ORGANIZATION AND RESPONSIBILITIES

Responsibility	Name	Task Description
Project Manager	Brad Freeman	Oversee and coordinate all budget and technical aspects for the project
Site Safety Officer	Brad Freeman	Oversee and coordinate all health and safety operations for the project site
Field & Safety Technician	Brad Freeman	Oversee and coordinate all health and safety aspects from the project site

3.0 OSHA TRAINING REQUIREMENTS

3.1 GENERAL TRAINING REQUIREMENTS

All GeoMonitoring Services (GMS) personnel performing activities covered by this plan must be trained in accordance with the requirements of 29 CFR 1910.120(e)(3)(ii), which reads: "Workers on site only occasionally for a specific limited task (such as, but not limited to, ground water monitoring, land surveying, or geophysical surveying) and who are unlikely to be exposed over permissible exposure limits and published exposure limits shall receive a minimum of 24 hours of instruction off the site, and the minimum of one day actual field experience under the direct supervision of a trained, experienced supervisor."

GMS employees serving in a supervisor capacity will receive OSHA-40 Hour Supervisor Training, as required by 29 CFR 1910.120(e)(4). In addition, all GMS employees will receive annual OSHA eight-hour refresher training. The GMS Safety Director, Rick Dolan, will verify and document that all GMS personnel meet the applicable training requirements prior to the start of site work.

In accordance with Section 6.6 of the GMS Contractor and Subcontractor Management Program, "Contractors and Subcontractors are held to the same safety standards and violation reporting that all GMS employees are required to follow. Unsafe work practices will be immediately reported to the appointed Site Safety Officer, as noted in the Site Safety Plan. Any issues will lead to work being stopped until the situation can be resolved. The contractor, subcontractor, and GMS will perform daily job safety inspections during site work. Site personnel will be advised if a Job Safety Analysis (JSA) needs to be revised and the revisions will be discussed during the next tailgate safety meeting." At the completion of site work, GMS employees will complete a Post-Job Safety Analysis. All of the GMS policies are available on the company server under the Safety Folder.

3.2 PRE-ENTRY MEETING

A pre-entry meeting reviewing the Site Safety Plan for all personnel shall be held and documented in this Site Safety Plan and in the site log. This meeting shall be prior to the commencement of any on-site work activities.

3.3 FIRST AID/CPR TRAINING

GMS staff assigned to the project will have American Red Cross (or equivalent) first aid and cardiopulmonary resuscitation (CPR) training. At least one trained individual will be present on-site at all times. The GMS Safety Officer will maintain all training documentation.

3.4 POST-JOB SAFETY ANALYSIS

At the completion of work involving multiple GMS employees, a Post-Job Safety Analysis will be completed and reviewed. Any near misses that occurred will be identified and recorded for the Project Manager to review.

4.0 MEDICAL SURVEILLANCE REQUIREMENTS

4.1 GENERAL MEDICAL SURVEILLANCE REQUIREMENTS

In accordance with 29 CFR 1910.120(f), all personnel will be enrolled in a medical surveillance program if performing the following activities: "All employees who are or may be exposed to hazardous substances or health hazards at or above the established permissible exposure limit, above the published exposure levels for these substances, without regard to the use of respirators, for 30 days or more a year; All employees who wear a respirator for 30 days or more a year or as required by 1910.134."

A medical surveillance program is not necessary at this site, as site activities do not consist of the above requirements.

4.2 DRUG AND ALCOHOL COMPLIANCE

All GMS personnel performing activities covered by this plan must have had a negative drug and alcohol screen performed within the last 12 months; unless otherwise requested by Hess or the facility owner.

4.3 ACCIDENT / INCIDENT MEDICAL SURVEILLANCE

As a follow-up to a work-related injury, all employees are entitled and encouraged to seek medical attention. All accidents and potential exposures must be reported **immediately** to the Site Safety Officer, who will coordinate with the GMS Safety Officer to arrange for appropriate medical attention. Depending on the type of incident, it may be critical to perform tests within 24 to 48 hours. *Failure to report an injury or incident immediately will result in disciplinary action*. Events surrounding near-miss accidents/injuries will be documented in and reviewed in an incident report.

5.0 HAZARD ASSESSMENT

As stated in the GMS Behavior Based Safety (BBS) Program, "the objective of the BBS Program is to foster continuous improvement wherein employees, in addition to conforming to company safety policies and procedures, accept the responsibility to proactively identify risks and take corrective action before such risks cause incidents. This responsibility stems from an understanding that such proactive behavior is in the best interest of all employees, their families, GeoMonitoring Services (GMS), their community, and the environment." Job specific hazards have been identified for each activity that takes place at the site by completing Job Safety Analysis (JSA) forms, and are found in **Attachment F**.

5.1 CHEMICAL HAZARDS

5.1.1 Contaminant Characterization and Potential Routes of Exposure

The main routes of exposure for field personnel include:

- Inhalation of contaminant vapors
- Inhalation of contaminated particulate matter

- Ingestion of contaminated material
- Dermal absorption of contaminated material
- Injection of contaminated material

Site personnel can reduce their exposure potential by:

- Using the proper personal protective equipment (PPE)
- Practicing contamination avoidance
- Following proper decontamination procedures
- Observing good personnel hygiene

5.1.2 General Chemical Data

As stated in the GMS Hazard Communication Program, "GMS will ensure that the hazards of all chemicals used at work sites are evaluated and that information concerning the associated hazards is transmitted to all employees. This standard practice instruction is intended to comprehensively address the issues of evaluating the potential hazards of chemicals, communicating information concerning these hazards, and establishing appropriate protective measures for employees."

An Exposure Monitoring Program will be implemented to control potential chemical exposures. **Attachment C** contains this program along with data tables on the contaminants of concern. These tables provide information on each contaminant's characteristics, such as routes of exposure, health hazards, ionization potentials, exposure limits, etc. All hazardous chemicals brought on-site by GMS personnel or its subcontractors will be managed in accordance with 29 CFR 1910.1200, which will include: proper labeling, an inventory list of all hazardous materials brought onsite, and a copy of each chemical's Safety Data Sheet (SDS) will be maintained on-site. **Attachment D** contains SDSs of chemicals used onsite by GMS personnel. If the potential arises for GMS personnel to come into contact with additional chemicals used by St. Croix Renaissance Group, those SDSs will be obtained at that time.

5.2 PHYSICAL HAZARDS

A variety of physical hazards may be present, but these hazards are similar to those associated with any field project.

5.2.1 Slip/Trip/Fall/Cuts

* Utilize proper housekeeping practices, such as removal of debris and tools from the work area to keep the area clear of trip hazards.
* Use caution tape or barricade fencing where warranted to keep unauthorized personnel from entering the work area.
* Replace manhole covers securely to prevent tripping and vehicle accidents.
* Use hose cutters when cutting piping.
* Walkways and work spaces will be kept clear of cords, hoses, pipes, etc. that cause trip hazards.
* If trip hazards cannot be removed from the work area, they shall be taped down and cones shall be placed to identify the hazard.

5.2.2 Excessive Noise

* Use hearing protection during loud mechanical operations such as drilling, Geoprobing, and excavating operations.
* Use hearing protection inside a remedial shed when equipment is operating loudly.

5.2.3 Airborne Particulate (ears, eyes, nose, mouth, inhalation)

* Eye protection is to be worn at all times on site.
* Respiratory protection is to be worn when site activities cause excessive particulates, such as performing carbon change outs.

5.2.4 On-site Traffic

* If traffic is present, cones should be placed around the work site.

* Use caution tape or barricade fencing where warranted to prevent unauthorized personnel from entering the work area.

5.2.5 Ladder Safety

In accordance with the GMS Ladder Safety Program, "Only individuals properly trained in the procedures of ladder usage will be permitted to use ladders in the workplace. GMS will take measures to ensure subcontractors dealing with ladders have a plan in place to ensure their employees are trained and know the techniques and guidelines for proper ladder use." GMS employees are trained on the information regarding ladders found below; however, they are advised to avoid performing work that requires ladders. Optimally, Subcontractors with ladder experience will perform this work.

Setup

* If electrical work is to be done while using the ladder, a wooden or fiberglass ladder must be used.
* All ladders used shall conform to OSHA requirements and an OSHA approved label must be present.
* Make sure the ladder is capable of supporting the weight of both the person and equipment to be used.
* Ladders should be set on a flat, level surface and tied to supporting building whenever possible.
* Straight ladders must lean against objects so that the distance from the base of the object to the feet of the ladder is equal to ¼ the total height of the object to be climbed. E.g., if the object to be climbed is 10 feet tall, the base of the ladder must be 2.5 feet from the base of the object.
* Ladders must be positioned so that work can be done without leaning the ladder to either side.
* Do not place the ladder in front of doors that could accidentally be opened and knock the ladder over.

* No ladder should be used to gain access to a roof unless the top of the ladder shall extend at least 3 feet above the point of support, at eave, gutter, or roofline.
* Two short ladders shall not be spliced or bound together to form a longer section.
* All ladders should be shored (tied on) at the top of the ladder when possible.

Use

* All ladders must be inspected before each use. If a ladder is found to be defective, it must be taken out of use until repaired or replaced.
* Always face the ladder when climbing up or down
* Three points of contact shall be maintained at all times when climbing up or down a ladder. Two hands and one foot or two feet and one hand.
* Spreaders on step ladder shall be fully opened and locked in place. Do not lean a step ladder against an object and try to use it as a straight ladder.
* Never exceed the maximum safe working load of the ladder.

Storage, Care, and Maintenance

* Always store ladders where they will be protected from the elements.
* Do not paint ladders, this may cover OSHA labels or labels which indicate the maximum safe working load of the ladder.
* Do not use defective ladders or ladders that have cracks or other signs of deterioration. These ladders should be removed from service until repaired or replaced.

5.2.6 Air Compressor

* Eye protection is to be worn at all times on site.
* Use proper pressure relief valves before performing O&M on an air compressor.

5.2.7 Electrical

As stated in the GMS Electrical Safety Program, "No GMS employee is qualified to work on electrical equipment." If electrical work is required, a qualified subcontractor will be brought in to perform the work. The qualified subcontractor will adhere to the following requirements:

* Inspect all electrical equipment and extension cords prior to use.
* All electrical circuits and equipment must be grounded in accordance with the NEC regulations.
* Equipment producing sparks are not to be used in operating remedial system sheds.
* Lockout/Tagout procedures will be in effect if equipment is to be repaired.
* Use three-pronged plugs and heavy-duty extension cords.
* Plugs and receptacles will be kept out of water (unless they are approved for submersion).
* A Ground Fault Circuit Interrupter (GFCI) is required when using an extension cord.
* Workers must not have wet hands or be standing in water while plugging/unplugging energized equipment.

5.2.8 Power Tools

* Equipment will be inspected for defects prior to use.
* Eye protection is to be worn at all times on site.
* Employees using tools that may subject their hands to an injury, such as cuts, abrasions, punctures, or burns will wear protective gloves.
* Loose or frayed clothing, dangling jewelry, or loose long hair will not be worn when working with power tools.
* A GFCI will be used with all power tool operations.
* Shielding or guarding will be in effect if applicable.

5.2.9 Back Strain

* Utilize proper lifting procedures when loading and unloading heavy equipment.
* Bend down at the knees rather than bending the back.
* Use a mechanical lifting device or a lifting aid such as hand carts, drum dolly's or lift gates when lifting heavy objects.

5.2.10 Site Security

* Do not permit anyone who is not properly trained and outfitted with the appropriate PPE to enter the Exclusion or Contamination Reduction Zones (this includes GMS personnel, clients, etc.)
* Use caution tape or barricade fencing where warranted to keep unauthorized personnel from entering the work area.

5.2.11 Biological Hazards (insects, snakes, poisonous plants and animals)

* Do not touch or contact poisonous plants, such as poison ivy and poison oak.
* If available, apply an over-the-counter barrier cream, such as Ivy Block® to prevent contact with plant oils.
* Wash hands and arms immediately with soap and water if skin contacts the plants.
* Wear long pants with socks pulled over legs to prevent skin contact with plants and insects.
* Inspect yourself carefully for insects or ticks after being outdoors.
* Spray any wasp/hornet nests with an insect repellant from a safe distance recommended by the product's manufacturer.
* Do not antagonize snakes or wild animals.

5.2.12 Heat Stress

* Know and recognize the signs and symptoms of heat-related illnesses, as follows:

- Heat cramps
- Heat exhaustion:
    - Cool, moist, pale, or flushed skin
    - Headache
    - Nausea
    - Dizziness, weakness and exhaustion
- Heat stroke:
    - Red, hot, dry, skin
    - Changes in consciousness
    - Rapid, weak pulse
    - Rapid, shallow breathing

* Adjust work schedules to provide time intervals for intake of water in an area free from contamination.

5.2.13 Cold Stress

* Know and recognize the signs and symptoms of cold-related illnesses, as follows:
    - Frostbite:
        - Lack of feeling in the affected area
        - Skin that appears waxy, is cold to the touch or is discolored (flushed, white, yellow or blue)
    - Hypothermia:
        - Shivering
        - Numbness
        - Glassy stare
        - Apathy
        - Loss of consciousness
* Have appropriate clothing available and dress in layers to protect against cold weather.

* Adjust work schedules to provide sufficient rest periods in a heated area for warming up during operations conducted in cold weather.

5.2.14 Confined Space (CS) Entry

As stated in the GMS Confined Space Program, "GMS will not allow employees to enter a confined space. GMS employees will report any known or potential confined spaces to their appointed Site Safety Officer or customer representative. Under no circumstances will a GMS employee enter any confined space. Only qualified, trained employees that are properly trained to protect themselves will be able to work in confined spaces. GMS will rely on trained contractors to perform all confined space work."

5.2.15 Fall Hazards

* No activities at the work site require fall hazard protection.
* GMS employees are not permitted to perform work requiring fall protection
* In the event fall hazards become present, safety controls will be implemented, and properly trained subcontractors will be hired to perform the work.

5.2.16 Hot Work

* No hot work activities occur at the site.
* In the event hot work activities occur, safety controls will be implemented, and properly trained subcontractors will be hired to perform the work.

5.3 RADIOLOGICAL HAZARDS

Based on available site historical information, there are no radiological contaminants of concern at this site. If site-specific potential radiological information becomes available, the hazards will be addressed in an addendum to this Site Safety Plan.

6.0 SITE CONTROL MEASURES

6.1 SITE ZONES

A controlled work area should be established in the immediate vicinity of the site activities covered by this plan. Only those persons who can comply with the requirements of this plan should be allowed into this area during any work activities, which may result in exposure to the hazards associated with the specific task being performed.

When activities involve invasive activities on sites in which the Project Manager or Site Safety Officer have determined the area to be highly-contaminated, a three-zone system will be used to control the potential spread of contamination. For the purpose of this plan, the following definition of terms is provided:

Exclusion Zone - The immediate area of the work activity to be performed or an area fully enclosing the hazards present.

Contamination Reduction Zone - The transition area between the contaminated area and the uncontaminated area. Decontamination procedures take place within this zone.

Support Zone - The uncontaminated area where exposure to hazardous conditions is not anticipated.

6.2 COMMUNICATIONS

Emergency numbers are listed on the first page of this Site Safety Plan. Work will not be conducted onsite without access to a mobile phone.

7.0 PERSONAL PROTECTIVE EQUIPMENT

7.1 GENERAL

The level of protection worn by site personnel will be enforced by the Site Safety Officer. The required level of protection at this site is Level D. Levels of protection may be upgraded or downgraded at the discretion of the Site Safety Officer based on prior site experience and current conditions at the site. Any changes in the level of protection will be documented. Levels of protection less than those designated in this Site Safety Plan must first be approved by the GMS Safety Officer.

7.2 LEVEL D PROTECTION

Level D PPE provides minimal protection against chemical hazards. A respirator is not required. Level D PPE includes:

- Cotton coveralls or long pants and a shirt with sleeves
- Reflective safety vest (as required by task)
- Safety glasses
- Steel-toe/steel-shank work boots
- Work gloves
- Hearing protection (as required by task)
- Hard Hat (as required by task)
- Chemical resistant gloves (as required by task)

7.3 MODIFIED LEVEL C PROTECTION

Modified Level C PPE includes the items listed in Section 7.2 above, and the following items:

- Full-face APR or Half-face APR respirator equipped with the appropriate chemical cartridges

7.4 LEVEL C PROTECTION

Level C PPE provides a higher level of respiratory and skin protection against chemical hazards than Level D. Level C PPE includes the items listed in Section 7.2 above, and the following items:

- Poly-coated tyvek (yellow) or Saranax® (shiny white)
- Steel-toe/steel-shank work boots and chemical resistant over-boots, or chemical resistant steel-toe/steel shank boots
- Inner chemical resistant gloves
- Chemical resistant outer gloves
- Seal arm, leg, and zipper joints with tape, as required
- Half-face or full-face, air-purifying respirator equipped with appropriate cartridges

7.5 LEVEL A AND B PROTECTION

Level A PPE should be worn when the highest level of respiratory and skin protection is needed, or if the contaminants of concern are unknown. Level B PPE should be worn when the highest level of respiratory protection is required, but a lesser level of skin protection is needed. The tasks covered under this HASP do not require the use of Level A or B PPE.

Separate Health and Safety Plans will be developed for Level A/Level B investigations and for Emergency Responses, which may involve the use of Level A and/or Level B health and safety measures.

8.0 DECONTAMINATION

8.1 GENERAL

At a minimum, the procedures outlined below shall be followed for decontamination:

- Remove gross contamination from tools, respirator, monitoring equipment, boots, etc., prior to leaving the “exclusion zone”, using paper towels, handi-wipes, etc.

- Completely decontaminate soiled equipment in the Contamination Reduction Zone using detergent and water and dispose of all cleaning materials as follows.
    1. Due to the small quantity of waste generated during decontamination, it is allowable in most states to dispose of lightly contaminated materials in the site dumpster. It is important, however, to ensure that there is no chance of vapor generation or fluid leaking from the dumpster. At no time are materials containing free product to be disposed of in this manner. In this case, arrangements must be made for use of labeled drums and proper disposal.
    2. All decontamination materials including protective sheeting, rags, sorbents, disposable personal protective equipment, and decontamination fluids should be carefully screened with an OVA/OVM prior to disposal to determine relative levels of contamination.
    3. Lightly contaminated decontamination fluids should either be treated via the site treatment system prior to discharge or disposed of via the sanitary sewer system. Highly contaminated decontamination fluids must be stored in labeled drums and proper disposal arrangements must be made.
- Dispose of contaminated gloves, Tyvek suits, used cartridges, paper towels, etc., by placing in a plastic bag and discarding in accordance with applicable standards.
- Wash hands and face thoroughly with soap and water before lunch or coffee breaks, and as soon as possible after finishing work for the day.
- Particular care should be taken to protect any skin injuries. If open wounds exist on hands or forearms, handling chemicals should be restricted or eliminated.
- Shower as soon as possible.

9.0 EMERGENCY ACTION PLAN

9.1 PERSONAL INJURY WITHIN THE EXCLUSION ZONE

Site operations shall be temporarily halted and all site personnel shall assemble in the Contamination Reduction Zone. The Site Safety Officer shall evaluate the nature of the injury and, if indicated by the hazards present onsite, the injured person shall be decontaminated to the extent possible prior to movement to the Support Zone.

Contact shall be made for an ambulance and with the designated medical facility (if required). An individual certified in Standard First Aid and Adult CPR may choose to initiate the appropriate first aid. No persons shall reenter the Exclusion Zone until:

a. The conditions resulting in the emergency have been corrected;
a. The hazards have been reassessed;
b. The Site Safety Plan has been reviewed; and
d. Site personnel have been briefed on any changes in the Site Safety Plan.

9.2 PERSONAL INJURY WITHIN THE DECONTAMINATION ZONE

The Site Safety Officer shall evaluate the nature of the injury and, if indicated by the hazards present on site, the injured person shall be decontaminated to the extent possible prior to movement to the Support Zone.

Contact shall be made for an ambulance and with the designated medical facility (if required). An individual certified in Standard First Aid and Adult CPR may choose to initiate the appropriate first aid.

If the injury increases risk to other site workers, all site personnel shall move to the Contamination Reduction Zone and site activities will stop until the risks can be assessed and either removed or minimized.

9.3 PERSONAL INJURY WITHIN THE SUPPORT ZONE

The Site Safety Officer will assess the nature of the injury and determine if the cause of injury or loss of the injured person will affect continuation of site operations. If the injury will not affect the safety or performance of other site workers, operations may

continue, with the person certified in first aid initiating the appropriate first aid and necessary follow up as stated above.

If the injury increases risk to other site workers, all site personnel shall move to the Contamination Reduction Zone and site activities will stop until the risks can be assessed and either removed or minimized.

9.4 FIRE/EXPLOSION

As stated in the GMS Fire Protection and Extinguisher Program, "GMS provides employees with information and training on general fire awareness in and around their work site at the time of their initial assignment, annually, and whenever there is a potential hazard that may be introduced into their work site that could present a potential hazard. Employees will be generally trained on information of the health hazards associated with fires, respirator usage, medical surveillance program, contact information for public health organizations which provide information and materials, and posted warning signs at customer workplaces."

If a fire is observed in the incipient phase (i.e., when it begins) and if the site personnel witnessing the fire feel secure in attempting to control the fire, the individual can attempt to extinguish the fire by using the onsite fire extinguisher. The fire extinguisher should be a 10 or 20 pound (lb) dry chemical, Class A, B, and C extinguisher and is adequate for paper and wood based products (A), flammable and combustible liquids (B), and electrical (C) type fires.

If there is no fire extinguisher available or if site personnel do not feel secure in attempting to extinguish the fire, site personnel shall perform the following:

- Secure the site, if possible.
- Evacuate the area using the nearest safe pathway from the area.
- Proceed to the nearest phone and call 911 and provide the emergency operator all required information. This will activate the emergency response system.

If more than one individual is on the site, the individual activating the evacuation plan shall verbally communicate to the other site personnel that there is an emergency condition, and that they should evacuate from the work area. If contact cannot be made verbally with the other site personnel, any of the following systems can be used as long as the system is audible above background noise. The system can be the site vehicle horn, a whistle, an air horn, or other acceptable device. The system used for initiating an evacuation from the site shall be discussed during the tailgate meeting with the other site personnel prior to beginning the workday. The system that is decided upon shall be documented in the site logbook.

If an explosion or other unsafe condition occurs that the site supervisor had determined will place the other site personnel at risk, then the evacuation system described above should be activated immediately.

9.5 PERSONAL PROTECTIVE EQUIPMENT FAILURE

If any site worker experiences a failure or alteration of PPE that affects the protection factor, that person and his/her buddy, if applicable, shall immediately leave the Exclusion Zone. Reentry shall not be permitted until the equipment has been repaired or replaced.

9.6 EQUIPMENT FAILURE

If any other equipment on site fails to operate properly, the Site Supervisor shall be notified and then determine the effect of this failure on continuing operations. If the failure will affect the safety of personnel, all personnel shall leave the Exclusion Zone until the situation is evaluated and appropriate actions are taken.

10.0 STANDARD OPERATING SAFETY PROCEDURES, ENGINEERING CONTROLS, AND WORK PRACTICES

10.1 WORK PERMITS

Work permits are not required for this site. Upon arrival, GMS personnel will sign in at the guard shack and sign out prior to leaving each day.

10.2 GENERAL SITE RULES

The following general site rules apply to all personnel while on the site:

- Before daily site operation begins, a pre-entry briefing will be held to review the Site Safety Plan and emergency procedures. This meeting will be registered in this Site Safety Plan, and attendance will be documented. All personal on location will complete the COVID-19 forms and the SSO will take and record the temperature of all personal daily.

- In the event of an incident, the Project Manager will immediately notify the Portfolio Manager and Hess Project Supervisor. GMS will defer to the Hess Project Supervisor to determine if communication with the property owner is necessary.

- The Site Safety Officer will be assigned to keep the daily log for all health- and safety-specific site activities, unless otherwise specified.

- All personnel will wear steel-toe safety boots and long pants. Hard hats will be worn when working in areas where the potential for falling rocks exists, near heavy equipment (drill rigs, excavating equipment, etc.), or when individuals are working overhead.

- Eye protection will be worn at all times while on site.

- Possession of alcohol or illegal substances on the job site or consumption during hours of site operation is strictly prohibited.

- Food and/or beverages are not permitted in the site's Exclusion or Contamination Reduction Zones. Food and/or beverages will be permitted in the Support Zone, if proper decontamination procedures are being followed.

- Smoking is not permitted on site.

- Field personnel should not stand with their head directly over a well when it is being opened.

- First aid kit(s) and a fire extinguisher(s) will be available in all company vehicles.

Any revisions to the final Site Safety Plan must be reviewed by the Project Manager and approved by the Site Safety Manager.