Rolling Knolls Landfill Settling Parties

Quality Assurance Project Plan for the Data Gaps Sampling and Analysis Plan

Rolling Knolls Landfill Superfund Site

Chatham, New Jersey

September 2014

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Superfund Site
Chatham, New Jersey

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Quality Assurance Project Plan for the Data Gaps Sampling and Analysis Plan

Rolling Knolls Landfill Superfund Site
Chatham, New Jersey

Prepared for:
Rolling Knolls Landfill Settling Parties

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B0033202

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2014 Quality Assurance Project Plan (QAPP) Worksheets

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QAPP Worksheet #1 & 2: Title and Approval Page

1. **Project Identifying Information**

    a. **Site name/project name**: Rolling Knolls Landfill Superfund Site

    b. **Site location/number**: The site is located at the southern end of Britten Road south of Green Village in Chatham Township, Morris County, New Jersey

    c. **Contract/Work assignment number**: Index No. II-CERCLA-02-2005-2034

2. **Federal Regulatory Agency**: Tanya Mitchell, Remedial Project Manager, United States Environmental Protection Agency (USEPA) Region

    _____ (Signature/Date)

3. **State Regulatory Agency**: Gwen Zervas, Case Manager, New Jersey Department of Environmental Protection (NJDEP)

    _____ (Signature/Date)

4. **Lead Organization**: ARCADIS US, Inc.

    a. **Lead Organization Project Coordinator**: John Persico, Designated Project Coordinator, ARCADIS

    _____ (Signature/Date)

    b. **Lead Organization Project Manager**: Suzanne J. Walls, Project Manager, ARCADIS

    _____ (Signature/Date)

    c. **Lead Organization Quality Manager**: Dennis K. Capria, Quality Assurance Manager, ARCADIS

    _____ (Signature/Date)

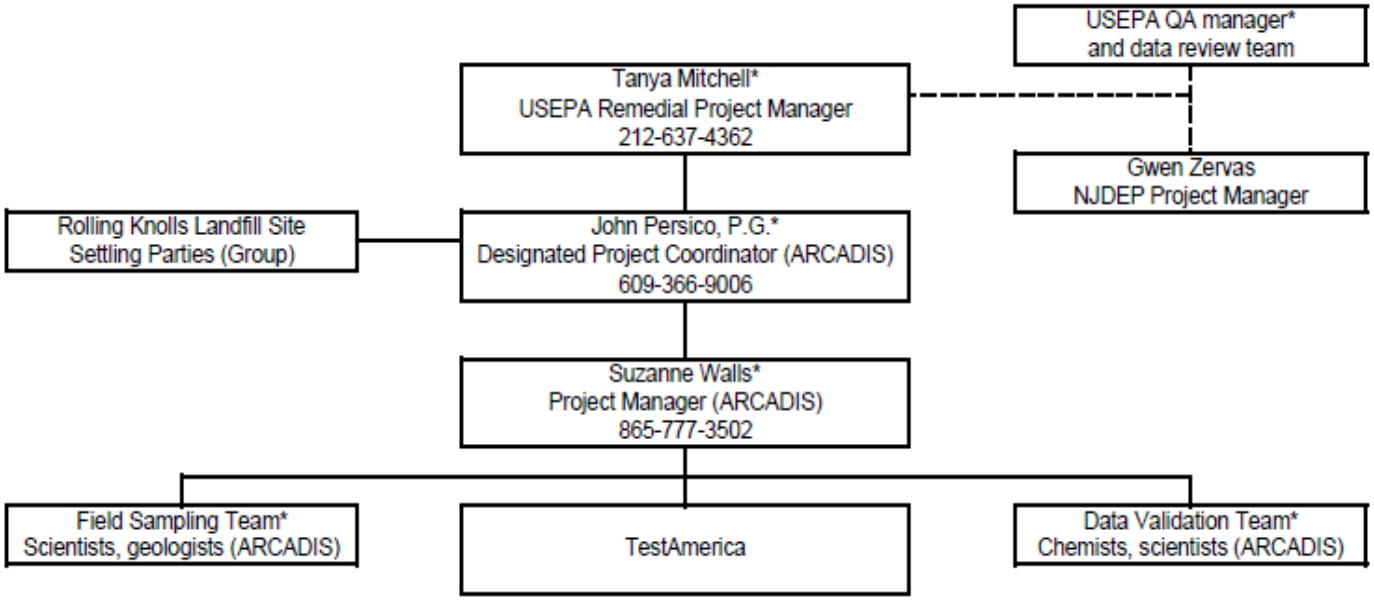
5. **Other Stakeholders**: United States Fish and Wildlife Service (USFWS), Robert J. Miele as Trustee for the Trust created by the Last Will and Testament of Angelo J. Miele and the Green Village Fire Department

6. **Plans and reports from previous investigations relevant to this project**:

    Site Characterization Summary Report (ARCADIS US Inc., February 2012) and the Baseline Human Health Risk Assessment (CDM, June 2014)

QAPP Worksheet #3 & 5: Project Organization and QAPP Distribution

*QAPP recipient Lines of authority _____ Lines of Communication ----------



* - QAPP recipient

QAPP Worksheet #4, 7 & 8: Personnel Qualifications and Sign-off Sheet

Name	Project Title/Role	Education/Experience	Specialized Training/Certifications	Signature/Date
John Persico	Designated Project Coordinator (ARCADIS)	B.A. Geology, M.S. Geology/Geochemistry, 26 years of experience RIFS	P.G.	
Suzanne Walls	Project Manager (ARCADIS)	B.S. Biology, Environmental Politics, M.S. Entomology (in progress), 9 years of ecological risk experience	Certified Ecologist	
Dennis Capria	Quality Assurance (QA) Manager (ARCADIS)	B.S. Biology, minor Chemistry; 26 years of experience		
Kathryn Kelly	Project Manager (TestAmerica)	B.A. English		
Sara Goff	Laboratory QA Manager (TestAmerica)	B.S. Health Sciences		

*Signatures indicate personnel have read and agree to implement this QAPP as written

QAPP Worksheet #6: Communication Pathways

Communication Driver	Organization	Name	Contact Information	Procedure (timing, pathway, documentation, etc.)
Regulatory agency interface	USEPA	Tanya Mitchell	212.637.4362	To be contacted as needed.
Field progress reports	ARCADIS	Suzanne Walls, Project Manager	865.777.3502	To be provided daily field progress reports (through email or phone calls). Will provide complete sets of daily field progress reports, sampling logs, chains-of-custody forms, and other information to the Remedial Investigation (RI) Field Program Coordinator.
Coordinate Field Program	ARCADIS	Suzanne Walls, Project Manager	865.777.3502	To be notified of field related questions or problems by phone or email.
Stop work due to safety issues	ARCADIS	Any employee		Any employees who feel the workplace is unsafe can stop work until the safety issue is resolved.
QAPP changes prior to field work and during project executions	ARCADIS	Dennis Capria, QA Manager	315.671.9299	Any major changes to the QAPP must be approved by Dennis Capria and the Project Coordinator and USEPA before the changes can be implemented.
Unfulfilled or changes to bottle orders	TestAmerica	Kathryn Kelly, Project Manager	802.923.1021	To be notified of any problems or changes related to bottle orders.
Field equipment	Pine Environmental Services	Pine Environmental Services Staff	800.301.9663	To be notified of any problems or changes to field equipment rentals.
Sample receipt or chain of custody variances	ARCADIS	Suzanne Walls, Project Manager	865.777.3502	To be notified of any sample receipt or chain of custody variances.

Communication Driver	Organization	Name	Contact Information	Procedure (timing, pathway, documentation, etc.)
Laboratory quality control variances	ARCADIS	Dennis Capria, QA Manager	315.671.9299	To be notified of any laboratory control variances.
Analytical corrective actions	ARCADIS	Dennis Capria, QA Manager	315.671.9299	The need for corrective action for analytical issues will be determined by Dennis Capria in conjunction with the Project Coordinator, the Field Program Coordinator or the Laboratory QA Manager, as appropriate.
Field corrective actions	ARCADIS	Suzanne Walls, Project Manager	865.777.3502	The need for corrective action for field issues will be determined by Suzanne Walls with the Project Coordinator, the Field Program Coordinator or the Laboratory QA Manager, as appropriate.
Reporting Lab Data Quality Issues	TestAmerica	Kathryn Kelly, Project Manager	802.923.1021	All QA/QC issues with project field samples will be reported by contact person from TestAmerica to Suzanne Walls and Dennis Capria within 2 business days.
Data validation issues, e.g., non-compliance with procedures	TestAmerica	Kathryn Kelly, Project Manager	802.923.1021	All data validation concerns will be reported to Dennis Capria and TestAmerica.
Data review corrective actions	ARCADIS	Dennis Capria, QA Manager	315.671.9299	The need for corrective action during data review will be determined by John Persico in conjunction with Suzanne Walls.

QAPP Worksheet #9: Project Planning Session Summary

Date of planning session: August 13, 2014
Location: Fair Lawn, NJ and conference call
Purpose: Discuss progress on the Data Gaps Sampling and Analysis Plan and QAPP
Participants:

Name	Organization	Title/Role	Email/Phone
John Persico	ARCADIS	Designated Project Coordinator	John.Persico@arcadis-us.com
Suzanne Walls	ARCADIS	Project Manager	Suzy.Walls@arcadis-us.com
Dana Drew	ARCADIS	Geologist	Dana.Drew@arcadis-us.com

Notes/Comments:

- Discussion of the USEPA comments on the Baseline Ecological Risk Assessment (BERA) Work Plan and Data Gaps Memo.
- Discussion of the revised sampling locations and analyses in the Data Gaps Memo and BERA Work Plan.
- Discussion of the Baseline Human Health Risk Assessment (BHHRA) results from CDM Smith (CDM).

Date of planning session: August 14, 2014
Location: Conference call
Purpose: Discuss USEPA comments on the Data Gaps Memo
Participants:

Name	Organization	Title/Role	Email/Phone
John Persico	ARCADIS	Designated Project Coordinator	John.Persico@arcadis-us.com
Suzanne Walls	ARCADIS	Project Manager	Suzy.Walls@arcadis-us.com
Andrew Gutherz	ARCADIS	Task Manager	Andrew.Gutherz@arcadis-us.com
Dana Drew	ARCADIS	Geologist	Dana.Drew@arcadis-us.com

Notes/Comments:

- Discussion of the Data Gaps Sampling and Analysis Plan.
- Review of additional sampling locations and analyses requested by the USEPA.
- Discussion of well X-7, which was previously not sampled due to the lack of water and recharge during sampling.
- Discussion of the pattern of the previously proposed temporary well locations.

Date of planning session: August 14, 2014
Location: Conference call
Purpose: Discuss USEPA comments on the Data Gaps Memo
Participants:

Name	Organization	Title/Role	Email/Phone
John Persico	ARCADIS	Designated Project Coordinator	John.Persico@arcadis-us.com
Suzanne Walls	ARCADIS	Project Manager	Suzy.Walls@arcadis-us.com
Andrew Gutherz	ARCADIS	Task Manager	Andrew.Gutherz@arcadis-us.com
Dana Drew	ARCADIS	Geologist	Dana.Drew@arcadis-us.com
Gary Fisher	Alcatel-Lucent	Remedial Project Manager	gary.fisher@alcatel-lucent.com
Michael Draikiwicz	Novartis	Remediation Project Manager	michael.draikiwicz@novartis.com
Richard Hughes	Jackson Walker LLP	Counsel to Chevron	rhughes@jw.com
Rich Ricci	Lowenstein Sandler LLP	Counsel to Group	rricci@lowenstein.com
Mark Stella	Chevron	Remediation Project Manager	MarkStella@Chevron.com
Mickey Faigen	Issues Management LLC	Consultant to Group	Mfaigen@issuesllc.com

Notes/Comments:

- Discussion of the USEPA comments on the Data Gaps Memo and proposed responses.

Date of planning session: August 19, 2014
Location: 290 Broadway New York, NY and conference call
Purpose: Discuss comments on the Data Gaps Memo with USEPA
Participants:

Name	Organization	Title/Role	Email/Phone
John Persico	ARCADIS	Designated Project Coordinator	John.Persico@arcadis-us.com
Andrew Gutherz	ARCADIS	Task Manager	Andrew.Gutherz@arcadis-us.com
Tanya Mitchell	USEPA	Remedial Project	Mitchell.Tanya@epa.gov

Name	Organization	Title/Role	Email/Phone
		Manager	
Michael Sivak	USEPA	Chief, Mega Projects Section	Sivak.Michael@epa.gov
Michael Clemetson	USEPA	Ecological Risk Assessor	Clemetson.Michael@epa.gov
Katherine Mishkin	USEPA	Geologist	Mishkin.Katherine@epa.gov
Juan Fajardo	USEPA	Counsel at USEPA	Fajardo.Juan@epa.gov
George Molnar	CDM Smith	Consultant to USEPA	MolnarGC@cdmsmith.com
John Dougherty	CDM Smith	Consultant to USEPA	DoughertyJ@cdmsmith.com
Mark Stella	Chevron	Remediation Project Manager	MarkStella@Chevron.com
Gary Fisher	Alcatel-Lucent	Remediation Project Manager	gary.fisher@alcatel-lucent.com
Michael Draikiwicz	Novartis	Remediation Project Manager	michael.draikiwicz@novartis.com
Mickey Faigen	Issues Management LLC	Consultant	mfaigen@issuesllc.com
Rich Ricci	Lowenstein Sandler LLP	Counsel to Group	rricci@lowenstein.com

Notes/Comments:

- Discussion of the EPA comments on the Data Gaps Memo.
- Consensus decisions made on sampling locations and analyses for the Data Gaps Sampling and Analysis Plan.
- Action Items:

Action	Responsible Party	Due Date
ARCADIS will prepare the Data Gaps Sampling and Analysis Plan and Quality Assurance Project Plan and send to USEPA for approval.	ARCADIS	Week of September 15, 2014
USEPA will review Data Gaps Sampling and Analysis Plan within 3 weeks and 2 days after receipt, and the Quality Assurance Project Plan within 3 weeks after receipt.	USEPA	October 2014

QAPP Worksheet #10: Conceptual Site Model

Background Information

1. Site Description

The Rolling Knolls Landfill Superfund Site consists of a former privately operated municipal waste landfill located at the southern end of Britten Road, south of Green Village in Chatham Township, Morris County, New Jersey (Figure 1). The landfill covers 141 acres and consists of a relatively thin (18 feet or less) layer of waste material directly overlying native soil and/or wetlands. An area of surface debris was identified on 29 acres west of the landfill. The central and western portions of the landfill are owned by Robert J. Miele as Trustee of the Trust created by the Last Will and Testament of Angelo J. Miele, the former landfill operator. Eastern and southern portions are located within the Great Swamp National Wildlife Refuge (GSNWR) and owned by the United States Fish & Wildlife Service (USFWS). A northeastern portion of the landfill occurs on a parcel owned by the Green Village Fire Department.

2. Site History

The former privately operated municipal waste landfill located at the southern end of Britten Road reportedly operated from the 1930s to 1968. During this period, materials disposed at the landfill consisted primarily of municipal solid waste, but also included other waste such as industrial waste.

During the RI, an extensive characterization was implemented to evaluate the extent and composition of the landfill and potential landfill-related impacts to environmental media (Site Characterization Summary Report, February 2012). The RI efforts consisted of test pits, drum investigations, surface and subsurface soil collection, soil borings, monitoring well installations, sub slab vapor intrusion sampling, and surface water and sediment sampling.

Nature and Extent of Constituents

1. Constituent Sources

Sources of constituents detected in environmental media during RI activities can be considered as point sources and non-point sources. The largest potential source is the landfill itself. It is broad (141 acres) and relatively thin (18 feet or less) and directly overlies native soil. Because it consists almost entirely of municipal solid waste, the landfill is a diffuse source of organic and inorganic constituents. Limited areas of various waste materials that likely serve as individual point sources have been observed, but are a minor component of the total waste volume. Other potential sources of constituents are precipitation (e.g., mercury), natural background concentrations in soil and groundwater (i.e., inorganics), and/or current human activities such as hunting, skeet shooting, activities at the landscaping areas (e.g., vehicle/equipment storage and maintenance, storage of mulch, rocks and other landscaping supplies, storage of fertilizers and/or pesticides), activities during landfill operations, or uncontrolled disposal by trespassers. Based on the conditions within the landfill boundary, historical information regarding landfill disposal and maintenance activities, and the nature and extent of constituents in environmental media, it is probable that only a small amount of industrial waste has been disposed of at the landfill.

2. Constituent Detections in Soil and Groundwater

a. Soil

Surface soil samples were collected from known human use areas, both on and adjacent to the landfill, (baseball field, shooting range, landscape areas and near the Hunt Club building) as well as throughout the landfill. These samples exhibited detections of volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), polychlorinated biphenyls (PCBs), pesticides, dioxins, furans, and/or inorganic constituents. The most commonly detected constituents in surface soil were polycyclic aromatic hydrocarbons (PAHs), phthalates, PCBs, pesticides and inorganic constituents. Concentrations of some of these constituents exceed New Jersey Residential and/or Nonresidential Soil Remediation Standards (SRSs) and ecologically based screening levels (EBSLs).

Fewer exceedances of the Residential and Nonresidential SRSs are noted in the human use areas, in particular the baseball field, shooting range, and Landscape Area 2 and Hunt Club building. The baseball field and shooting range are located north of the landfill. Test pits excavated in this area did not identify waste at the ground surface or at depth and analytical results do not suggest that soil in this area has been impacted by the landfill. Landscape Area 2 and the Hunt Club building occur within the surface debris area located in the western portion of the landfill. Exceedances of SRSs from surface soil in these three areas were limited to certain PAHs and vanadium (at one location in the shooting range). Landscape Area 1 occurs near the center of the landfill and directly abuts landfilled materials. Higher exceedances of Residential and Nonresidential SRSs in these samples, relative to the other human use areas, identify potential impacts from the landfill and/or the ongoing activities at the landscaping area (e.g., maintenance and storage of equipment and vehicles).

Surface soil samples collected across the entire landfill (inclusive of the landscaping and Hunt Club areas) exhibit exceedances of Residential and/or Nonresidential SRSs for PAHs, phthalates, PCBs, certain pesticides and inorganic constituents. Few VOCs were detected at concentrations greater than SRSs, and exceedances were limited to isolated locations. Few exceedances are noted in the surface debris area in the western portion of the landfill and along the western and southwestern perimeter of the landfill.

Subsurface soil samples collected within the potentially developable portion of the landfill exhibited detections of VOCs, SVOCs, PCBs, pesticides and/or inorganic constituents. The most commonly detected constituents in subsurface soil were PAHs, phthalates, PCBs, pesticides and inorganic constituents. Concentrations of some of these constituents exceed Residential and/or Nonresidential SRSs, including certain PAHs, bis(2-ethylhexyl) phthalate, PCBs, pesticides and inorganic constituents.

b. Groundwater

Sources of contamination to groundwater, within the landfill, include groundwater infiltration through the impacted waste materials and soil, as well as some potential sources upgradient of the landfill, particularly inorganic constituents.

Groundwater sampling results indicate that a variety of constituents were detected in groundwater. In general, detections of organic constituents in samples collected from groundwater monitoring wells during both the December 2007 and February 2008 sampling events were limited to a subset of VOCs, SVOCs and pesticides. Inorganic constituents were ubiquitously detected in groundwater samples. PCBs were not detected in groundwater samples collected during either sampling event. Detected VOCs included chlorinated solvents (e.g., cis-1,2-dichloroethene [cis-1,2-DCE], trichloroethylene [TCE] and tetrachloroethylene [PCE]), benzene, toluene, ethylbenzene, and xylene (BTEX) compounds and chlorofluorocarbons (CFCs), among others. Exceedances of New Jersey (NJ) Groundwater Quality Criteria (GWQC) were limited to a small subset of these organic and inorganic constituents and occurred most frequently in three monitoring wells: MW-3, MW-7 and MW-10.

Exceedances of NJ GWQC at MW-7 were limited to iron and manganese in December 2008 and aluminum, iron, lead, manganese, thallium and indeno(1,2,3-cd) pyrene in February 2008. The monitoring well installation log for MW-7 indicates that minor amounts of brick and glass were observed in the upper 5 feet of the boring. Approximately one-half of the screen interval was not logged due to a lack of sample recovery, with the other half noted as screened in a silty/organic material. The nearest test pit to MW-7 is TP-33 (approximately 350 feet to the north); waste materials noted at this location included concrete, rubber, bricks and plastic scraps. No potential industrial waste was observed during the excavation of TP-33 and PID readings recorded during excavation were all less than 10 ppm. The nearest soil sampling location to MW-7 is SS-66, located approximately 50 feet south of MW-7. The surface soil sample collected at SS-66 exhibited exceedances of Nonresidential SRSs for benzo(a)pyrene, arsenic, lead and PCBs. The nearest upgradient soil sampling location to MW-7 is SS-58. The surface soil sample collected at SS-58 exhibited exceedances of Nonresidential SRSs for aldrin, lead and PCBs. Based on these results, the source of indeno(1,2,3-cd)pyrene to groundwater at MW-7 is localized in groundwater at this location.

Exceedances of NJ GWQC at MW-10 were limited to one VOC (dichlorodifluoromethane), aluminum, arsenic, iron and manganese. The monitoring well installation log for MW-10 does not identify waste materials in the boring log and indicates that most of the material in the screened interval was clay. Dichlorodifluoromethane is a component of Freon and its presence in groundwater at monitoring well MW-10 appears to be related to old refrigerators, which are present on the ground nearby at POI-10. Low concentrations of CFCs were also observed in a surface soil sample collected at POI-10, but these concentrations did not exceed Residential or Nonresidential SRSs. Impacted groundwater at this well is considered localized.

The highest concentrations of constituents exceeding NJ GWQC were generally observed in groundwater collected from MW-3. Organic constituents detected at concentrations greater than NJ GWQC in MW-3 include benzene (both sampling events), bis(2-chloroethyl)ether (both sampling events) and three BHC pesticides (December 2007 sampling event). Inorganic constituents detected at concentrations greater than NJ GWQC in MW-3 include aluminum, arsenic, manganese and sodium during both sampling events. The monitoring well installation log for MW-3 indicates that waste materials were not observed in the boring and that the screened interval is completed in clay, silt and sand. Test pit TP-09 was excavated immediately adjacent to MW-3 and was identified as wet at the ground surface, which is consistent with the observations of water levels observed above the ground surface elevation at MW-3. Rusted drums and an oil boom were observed in TP-09 and a sheen and high PID reading were

observed at the interval from 4 to 6 feet below ground surface (bgs). One sample of potential industrial waste collected from TP-09 identified the presence of benzene at 20 mg/kg. The source of organic impacts in groundwater at MW-3 is likely the materials observed at TP-09.

Groundwater from MW-3 has the most constituents in excess of NJ GWQC. Exceedances of the NJ GWQC down gradient from MW-3 (at monitoring well MW-4) were limited to aluminum, iron and manganese. Only aluminum was detected at concentrations greater than the NJ GWQC during both sampling events at MW-4. This indicates that the extent of organic impacts in groundwater at MW-3 is localized. The impacts at MW-3 are related to the presence of potential industrial waste in nearby test pit TP-09. Based on the results of groundwater sampling at other monitoring well locations, the organic impacts in groundwater at MW-7 and MW-10 are also localized.

While shallow groundwater that flows through the landfill has the potential to flow into low-lying areas and/or surface-water bodies, water quality results from the ponds and the downstream portions of the Loantaka Brook and Black Brook indicate that the concentrations of VOCs, SVOCs and inorganic constituents are consistent with concentrations measured in surface-water samples upstream of the potential influence of the landfill. PCBs and pesticides were either not detected or were detected at concentrations lower than those observed in upstream portions of the surface-water bodies. This indicates that water from the landfill has not degraded the water quality in the surface-water bodies adjacent to the landfill.

Impacted groundwater in the materials overlying the clay likely flows laterally (the dominant direction of flow) at very low rates until reaching areas of discharge (low-lying areas or surface-water bodies). Vertical transport through the materials beneath the landfill is anticipated to be limited due to the presence of the glaciolacustrine clay that underlies the entire landfill. The presence of the clay means that lateral transport is the more significant transport direction instead of vertical.

c. Fate and Transport of Constituents

Fate and transport processes that describe the migration and attenuation of dissolved constituents in groundwater include advection, diffusion, sorption and degradation. Additionally, the fate and transport of inorganic constituents is a function of geochemical conditions that can create environments that limit or enhance their mobility. Likewise, different degradation reactions will occur under different geochemical conditions.

Advection refers to the bulk movement of constituents with groundwater. Diffusion is a mass transfer mechanism that refers to the movement of mass from the advective, flow-focusing features such as sands and gravels into less permeable clays and silts that act as storage reservoirs. This mass transfer occurs as a function of concentration gradients between the two types of materials, as well as physical characteristics of the units.

Sorption refers to the processes of absorption and adsorption, in which the organic matter provides specific binding sites that immobilize (adsorb) the dissolved molecules. Absorbed solute molecules partition between the aqueous and organic matter phase under assumed equilibrium conditions, and this serves to slow the velocity of a solute relative to the groundwater flow velocity. Adsorbed solute

molecules are effectively pinned in place and do not move freely through the binding matrix (Payne et al. 2008) and therefore represent a reduction in the mobile mass of solutes in groundwater.

At the landfill, estimates of groundwater velocity in the shallow water-bearing zone are fairly low with a range of 0.001 to 0.3 foot/day. It is important to note that the groundwater velocity is taken from the equivalent hydraulic conductivity, meaning that it represents the average behavior. As indicated above, groundwater and solute migration will occur in the more permeable sands and gravels and the silt and clay materials will not transmit significant volumes of water or solutes to any significant degree. Most of the VOCs detected in groundwater at the landfill will tend to sorb and be slowed via that mechanism, or will be diffused into and out of the low-permeability storage reservoirs as a function of concentration gradients. It is likely that constituents are not significantly migrating away from the landfill via advection.

The geochemical conditions can be either aerobic (oxidizing) or anaerobic (reducing) and each condition could be present within the landfill. Depending on which geochemical condition(s) are present within the groundwater, the mobility of certain dissolved-phase inorganics will be inhibited or enhanced. Likewise, degradation pathways (biological or chemical transformation of solutes) will be enhanced or inhibited based on geochemical conditions. For example, low concentrations of TCE detected in the December 2007 sampling event but not in the February 2008 sampling event, along with the presence of TCE degradation products (primarily cis-1,2-DCE and vinyl chloride) in both sampling events, is one line of evidence that the geochemical conditions within groundwater beneath the landfill are anaerobic or reducing because the transformation of TCE to these degradation products is favored under reducing conditions.

Due to the importance and relevance of geochemical conditions within landfills as related to the fate and transport of COCs, the following summary is provided to enhance the understanding of the mobility of inorganic constituents that exceed the NJ GWQC.

d. Groundwater Geochemical Conditions and Mobility of Inorganic Constituents

Inorganic constituents detected at concentrations greater than NJ GWQC during the most recent sampling event (i.e., February 2008) include the following:

- Aluminum (MW-3, MW-4, MW-5, MW-7, MW-8, X-2, X-3, X-4)
- Arsenic (MW-3, MW-10)
- Iron (MW-1, MW-2, MW-3, MW-4, MW-5, MW-6, MW-7, MW-8, MW-10, X-1, X-2, X-3, X-4, X-6)
- Lead (MW-7)
- Manganese (MW-1, MW-2, MW-3, MW-4, MW-5, MW-6, MW-7, MW-8, MW-9, MW-10, X-1, X-2)
- Sodium (MW-3, X-1)

- Thallium (MW-7).

Groundwater samples were unfiltered and represent total recoverable inorganic concentrations. The lowest concentrations of iron and manganese and generally higher concentrations of dissolved oxygen were identified at wells along the periphery of the landfill area (e.g., MW-4, MW-5, MW-8, X-2 through X-6). Higher concentrations of manganese and/or iron and generally lower concentrations of dissolved oxygen at wells were identified in the interior of the landfill area (e.g., MW-1, MW-2, MW-3, MW-6, MW-7). This may indicate suboxic groundwater conditions in the periphery of the landfill area and more reducing conditions in the interior of the landfill area. Because the samples were unfiltered, the results can also correlate to turbidity, with inorganic concentrations due to particles in the groundwater samples. For example, groundwater from monitoring well MW-3 exhibited the highest turbidity and relatively higher concentrations of iron, manganese and arsenic. Conversely, groundwater from monitoring well X-5 exhibited the lowest turbidity, low concentrations of iron and manganese and no detections of other inorganic constituents.

The mobility of inorganic constituents in groundwater may be controlled by many processes, including precipitation, sorption, complexation and redox reactions, and can be affected by pH, organic carbon and microbial processes (Violante et al. 2010). Reducing groundwater conditions may be created through microbial activity that results in the consumption of dissolved oxygen and nitrate, and the dissolution of iron and manganese minerals present in soil. Organic carbon serves as a source of electrons in these environments, and a series of electron acceptors (oxygen, nitrate, manganese, iron, sulfate) is used for microbial growth. Soil data indicate the presence of organic carbon at >10 to 20 percent TOC in the solid phase in many locations. Soil pH measured at the site ranged between 3.75 and 8.29 standard units, and groundwater pH ranged from 5.04 to 7.08 standard units.

Iron, Manganese and Aluminum

The concentrations of iron, manganese and aluminum exceeded NJ GWQC in groundwater samples collected during the February 2008 sampling event. Iron and manganese are abundant, naturally occurring elements in soil, with aluminum a major component of clay minerals and sand, and the groundwater samples were unfiltered. Geochemical conditions that can lead to the dissolution of iron and manganese minerals include a decrease in redox potential, as well as a change in ionic strength in groundwater. Natural organic carbon stimulates anaerobic microbial processes that result in reductive iron and manganese dissolution (Donahoe and Liu 1998). The iron and manganese are used as electron acceptors by naturally occurring microorganisms that metabolize the organic carbon. This natural process transforms insoluble ferric iron [Fe(III)] and Mn(IV) in solid phases to soluble ferrous iron Fe(II) and Mn(II). Organic carbon may be provided by hydrocarbons or VOCs, or natural organic matter present in the aquifer. High ionic strength in groundwater can lead to the dissolution of iron minerals, and some hydroxide minerals (aluminum, iron, manganese) and clay minerals are soluble under acidic conditions.

Arsenic

The concentration of arsenic exceeded the NJ GWQC in groundwater samples collected from monitoring wells MW-3 and MW-10 during the February 2008 sampling event. These locations are also associated with relatively high concentrations of manganese and iron and relatively high turbidity at MW-3. Arsenic

occurs naturally in soil as a trace element and is usually incorporated into iron minerals or sorbed to iron mineral surfaces. In this form, it is generally insoluble in groundwater at neutral pH, at moderate ionic strengths (e.g., sodium concentrations from 10 to 100 milligrams per liter) and under oxidizing conditions.

Certain geochemical conditions in groundwater can result in the mobilization of naturally occurring arsenic. These conditions include a decrease in redox potential (i.e., reducing conditions) generally associated with biogeochemical processes, and an increase in ionic strength (Smedley and Kinniburgh 2002). Microbial activity, stimulated by the presence of natural organic matter in groundwater, results in the dissolution of iron and release of arsenic incorporated into iron minerals or sorbed onto iron mineral surfaces. Reductive iron dissolution, with the transformation of insoluble Fe(III) to soluble Fe(II), is caused by the use of iron minerals by microorganisms for the metabolism of organic carbon. Electrons provided by the organic carbon are transferred to the iron minerals, resulting in reductive iron dissolution (Lovley and Phillips 1988). This promotes a decrease in the redox potential in the aquifer, and arsenic that is released from the iron is stabilized in a dissolved form. High groundwater ionic strength can also result in the release of naturally occurring arsenic that may be sorbed to iron minerals.

Lead

The concentration of lead exceeded the NJ GWQC in the groundwater sample collected from monitoring well MW-7, a location that exhibited potentially more reducing conditions, during the February 2008 sampling event. In general, the mobility of lead is not directly related to redox conditions; however, because lead may form stable precipitates with redox-sensitive elements such as sulfur, lead mobility may be indirectly related to redox conditions. In sulfate-reducing systems, lead is expected to form insoluble lead sulfide precipitates. In moderately reducing systems, reductive dissolution of iron oxides that contain adsorbed lead could result in lead mobilization. Under oxidizing conditions, lead solubility in aqueous solutions is highly pH dependent. In general, lead mineral solubility is low at near neutral to moderately alkaline pH, and higher at low pH or very high pH. Lead mobility is controlled primarily by adsorption, precipitation and complexation with organic matter. Lead is strongly adsorbed onto ferric oxides, hydrous oxides, aluminum oxides, oxyhydroxides and clay minerals in soil. Exceptions to this behavior are low-pH systems or environments with high concentrations of dissolved organic carbon, which may form stable, highly soluble complexes with lead.

Thallium

The concentration of thallium exceeded the NJ GWQC in the groundwater sample collected from monitoring well MW-7 during the February 2008 sampling event. Thallium sorbs to clay, organic matter, and iron and manganese oxides in soil, and is more mobile at low pH (WHO 1996). In highly reducing environments, thallium may precipitate as a sulfide.

3. Overview of the Landfill, Constituent Transport Processes and Constituent Distribution

As discussed above, the landfill consists of municipal solid waste. Some potential industrial wastes have been identified, but they are small in area and do not comprise a significant portion of the volume of the waste. This is expected based on the historical use of the landfill for disposal of municipal waste from

Chatham Township and nearby municipalities. The surface of the landfill in some areas is covered by a thin soil layer and/or vegetation; in other areas, municipal waste is visible at the ground surface.

VOCs, SVOCs, PCBs, pesticides and inorganic constituents are found in surface and subsurface soil collected from the landfill. Many of these constituents are likely components of the municipal waste. Some of the current uses of the landfill (hunting and the maintenance activities at the landscape areas) and the areas north of the landfill (shooting range) may also contribute to the constituents observed in environmental media. The pesticides at the landfill likely come from historical pesticide use to combat mosquitoes and rodents. Inorganic constituents, such as arsenic, lead, vanadium and others, are naturally occurring and their presence in the soil samples is at least partially due to their natural occurrence.

Precipitation that falls on the landfill transpires back to the atmosphere, recharges groundwater or runs off to the neighboring wetlands or surface-water bodies (i.e., the ponds, Loantaka Brook and Black Brook). The shallow groundwater beneath the site occurs in a thin, sandy and silty material that extends to 20 to 25 feet bgs. New Jersey regulation (N.J.A.C. 7:9D-2.3[a]) prohibits installation of potable wells with casings less than 50 feet in depth; therefore, no potable wells would be expected in the shallow water-bearing zone.

Two areas of impacted groundwater are observed in the shallow water-bearing zone (monitoring wells MW-3 and MW-10). Constituents observed at monitoring well MW-3 include VOCs such as benzene and may be related to VOC-impacted soil and drums located at nearby test pit TP-09. The VOC dichlorodifluoromethane, a component of Freon, was present in groundwater at monitoring well MW-10 and its presence appears to be related to old refrigerators, which are present on the ground nearby. Based on the absence of these constituents in nearby wells, the constituents found in groundwater at wells MW-3 and MW-10 are localized and not widespread.

The landfill and shallow water-bearing zone are underlain by a thick, continuous, plastic clay unit. RI soil borings indicate that this unit is at least 25 feet thick and literature values indicate that it is more than 100 feet thick and locally as much as 128 feet thick at the east end of the GSNWR (Minard 1967). This clay unit is a barrier to vertical groundwater flow and constituent migration, protecting the underlying water-bearing material. Given the relatively low levels of constituents in the shallow water-bearing zone beneath the landfill, the nearby availability of surface discharge areas, and the thickness and lack of permeability of the clay, impacts to groundwater beneath the clay unit are not expected.

Surface water and sediment in the ponds and streams (Loantaka Brook and Black Brook) on or adjacent to the landfill exhibit some constituents that are found at the landfill. Many of these constituents are also found in surface water and sediment upstream of the landfill. Therefore, their presence in the streams is at least in part due to sources upgradient of the landfill. The results of the semiquantitative comparison of upstream and downstream data and the distribution of exceedances of ARARs or EBSLs downstream of the landfill indicate that the downstream extent of constituents related to the landfill, if any, has been defined.

Key Physical Aspects of the Site

Summary of Hydrogeologic Conditions

The hydrostratigraphy underlying the landfill consists of a shallow water table saturated zone, comprising silt and sand deposits underlain by a layer of glaciolacustrine clay that serves as a confining unit to the geologic formations below. Ten new monitoring wells were installed in 2007 to characterize the hydrogeologic conditions in this shallow water-bearing zone. Monitoring well screens cross silt, sand and clay deposits, and in some cases, the landfilled materials.

The depth and extent of saturation of waste material varied widely across the landfill, based on observations during test pit excavation, soil boring advancement and monitoring well installation activities. In most of the soil borings and monitoring wells, the waste material was dry and the native material beneath the waste was saturated. Test pit excavation logs indicated that the depth to saturation ranged from the ground surface to beneath the waste material (if present) and in some instances saturation was not observed for the entire test pit depth. In areas where the waste material was observed to be saturated at the surface, saturation was likely from precipitation and/or overland flow.

Water likely flows vertically through the unsaturated waste materials with some small horizontal component, and upon reaching the saturated material, flows laterally with the natural groundwater flow patterns. Groundwater flow is expected to occur laterally through the sand and/or silty sand units. The groundwater flow in the shallow water-bearing zone above the clay is expected to be horizontal until reaching areas of discharge.

The presence of clay at the base of the soil borings and monitoring wells is evidence of the remnant glacial lake. The clay is grey in color with some brown or reddish brown intervals, cohesive, and plastic, with only a small proportion of silt or fine sand. At the deepest boring (SB-8), the top of the clay was 25 feet bgs and the clay continued to the bottom of the boring at 50 feet bgs with little to no change in its properties. This clay is continuous beneath the landfill, reported to be more than 100 feet thick and locally as much as 128 feet thick at the east end of the GSNWR (Minard 1967), and will restrict vertical flow and constituent migration into the aquifer below, and confines the underlying groundwater.

Identification of Data Gaps and Uncertainty

Data gaps in the understanding of site conditions are summarized below:

- The extent of certain constituents at concentrations above the New Jersey SRSs in soil in portions of the site is not fully delineated.

- The extent of certain constituents in groundwater at monitoring wells MW-3 and MW-10 is not fully delineated.

- Surface water and sediment in ponds on the landfill that were not previously sampled has not been characterized.

- The potential presence of certain VOCs in sediment pore water downgradient of monitoring well MW-10 has not been evaluated.
- Current constituent concentrations in groundwater are not known.
- The connection between groundwater and surface water in the small ponds at the northern boundary of the landfill has not been evaluated.
- Conditions at the existing Hunt Club well HC-1 have not been fully assessed.

QAPP Worksheet #11: Project/Data Quality Objectives

1. *State the Problem*

a. **Conceptual Site Model**: The Rolling Knolls Landfill Superfund Site is located in Chatham, New Jersey and was formerly a privately operated municipal waste landfill. The landfill was in use from the 1930s to 1966 and contains municipal and industrial waste. A more complete conceptual site model is provided in Worksheet #10.

b. **Description of the Problem**: Data gaps sampling has been proposed to complete the delineation of contamination across the site. The main goals of this sampling are 1) to delineate the extent of certain constituents (VOCs, SVOCs, pesticides, PCB Aroclors, PCB congeners, dioxins and furans, and metals and cyanide) in soil, groundwater, pore water, and surface water, 2) to measure the current concentrations of constituents in groundwater, 3) to investigate the connection between surface water and groundwater, and 4) to assess conditions at the Hunt Club well. These data gaps were identified by the USEPA following the completion of the Site Characterization Summary Report (SCSR). Additional data collected during this sampling will be used to further characterize the site and will be included in the evaluation of potential risk to ecological receptors that will be investigated in the BERA.

Planning Team Members and Decision Makers

Planning team members and decision makers include the following:

- existing project team members who are familiar with the site and the results of previous investigations;
- geologists, environmental scientists, and engineers;
- representatives of the Settling Parties who have agreed to conduct the Remedial Investigation and Feasibility Study at the site; and
- representatives of the USEPA.

Available Resources and Relevant Deadlines

The Settling Parties will ensure that adequate resources are available for sample collection, sample analysis, data evaluation, and report preparation. Relevant deadlines are:

- Samples will be collected in two phases. The first phase, including surface water, sediment, pore water, and temporary groundwater well data, will be completed in November 2014. The second phase, including permanent groundwater well data, will be completed in May 2015.

- The Scope of Work in the Administrative Settlement Agreement and Order on Consent between the Settling Parties and USEPA (September 30, 2005) allows 60 days for report preparation and submittal of the Data Gaps SAP report after receipt of the validated data.

2. *Identify the Goals of the Study*

The goal of this study is to address all remaining data gaps identified by the USEPA following the approval of the SCSR and to constrain the fate and transport of chemical constituents (see Worksheet #10 for greater detail on chemical constituents). This will allow for evaluation of potential risks to ecological receptors.

- Further delineate the extent of constituents that were present at concentrations above the New Jersey SRSs in soil in portions of the site.

- Delineate the extent (downgradient) of VOCs observed in the shallow water-bearing zone in the western and southwestern portions of the site (monitoring wells MW-3 and MW-10), which is likely related to VOC-impacted soil and drums.

- Characterize surface water and sediment in ponds on the landfill that were not previously sampled.

- Investigate the potential presence of VOCs in pore water downgradient of well MW-10.

- Obtain a full round of groundwater samples from all monitoring wells to characterize the current constituent concentrations in groundwater.

- Investigate the connection between groundwater and surface water in the small ponds at the northern landfill boundary.

- Assess conditions at the existing Hunt Club well HC-1.

Principle study question: What is the extent of chemical constituents in the Rolling Knolls Landfill and how are groundwater, surface water and soil communicating in different areas of the site to produce the observed contamination?

Alternative Actions

Results of Comparison to the Site Characterization Summary Report	Alternative Action
Contaminants are consistent with concentrations reported in the Site Characterization Summary Report and those used in the Human Health Risk Assessment.	Complete the Data Gaps report, and implement the BERA. Reevaluate the results of the Human Health Risk Assessment.
Contaminants exceed concentrations of the SRS, Site Characterization Summary Report and those used in the Human Health Risk Assessment.	Complete the Data Gaps report, and implement the BERA. Reevaluate the results of the Human Health Risk Assessment. Consider additional sampling to be incorporated with any necessary BERA sampling or in a pre-design investigation.
Contaminant concentrations are inconsistent with previous sampling and conceptual site model.	Recommend additional sampling.

Decision Statement

Determine whether concentrations in soil, sediment, surface water, groundwater, and pore water indicate concentrations above regulatory limits and/or acceptable risk levels for human and ecological exposures.

If soil, groundwater, pore water, surface water and/or sediment constituents exceed concentrations determined for the SCSR and changes to the Human Health Risk Assessment (CDM, June 2014) are suspected, then the Human Health Risk Assessment may be re-evaluated. These data will also be used to update the Screening-Level Ecological Risk Assessment refinements that will be evaluated prior to conducting the BERA.

3. *Identify Information Inputs*

Type of information needed:

Analytical results for environmental samples

- Soil samples: will be used to delineate the extent of constituents associated with the landfill that are present at levels above their SRS.
- Groundwater samples from temporary monitoring wells: will be used to identify potential sources of VOCs around permanent monitoring wells MW-10 and MW-3.
- Groundwater samples from permanent wells: will be used to characterize current constituent concentrations.

- Pore-water samples: delineate constituents in groundwater that are migrating to surface water downgradient of well MW-10.

- Groundwater level measurements in permanent and temporary well: will be used to constrain the local hydrogeology and groundwater flow directions.

- Surface-water and sediment samples: will be used to characterize small bodies of water that have not previously been sampled.

Field observations

During sample collection, the field teams will observe and make note of the conditions at the Site and observe the presence of surface water bodies, the terrain, and the wildlife present. The field teams will also take PID readings during drilling and well cap removal.

Source of information:

The required information will be obtained by sample collection and analysis, and will be supported by existing information on the site.

Information Needed to Meet Performance Criteria

Performance Criteria	Information Need to Meet Performance Criteria
Use of approved sampling procedures	Field notes and sample logs
Collecting an adequate sample volume	Field notes and laboratory notes
Collecting an adequate number of samples	Field notes; comparison of laboratory results report to work plan
Proper sample packing, shipping, and handling	Field notes and laboratory notes
Appropriate analytical procedures	Laboratory notes in analytical results report; all data will be validated.

4. Define the Boundaries of the Study

Geographic Area

The geographic area of the study is the Rolling Knolls Landfill and adjacent areas, including areas in the GSNWR. The depth of the study is to approximately 15 feet bgs, which is anticipated to be the approximate depth of temporary and permanent monitoring wells. In addition, the study includes evaluation of the existing Hunt Club supply well, the depth of which is unknown.

Time Frame for Collecting the Data

This study includes collection of soil, sediment, groundwater, surface water and pore water. Sampling is proposed to begin in October when the temperatures will be moderate but the brush will begin to die back increasing visibility and site accessibility. The initial phase of field investigation should be completed in November 2014. Data will be evaluated over the winter, and the second phase of investigation (installation and sampling of permanent monitoring wells) will be implemented in April and May 2015, before vegetation has reached its full size.

The data will provide a current picture of site conditions, suitable for the risk assessments and feasibility study which will be completed when this investigation is complete.

Appropriate Scale for Decision Making

The purpose of the data gaps sampling is to target specific areas of the site that need further evaluation (See Data Gaps Sampling and Analysis Plan and Worksheets # 17 and 18). Soil, and sediment results represent the local area of the sample. Surface water, pore water, and groundwater results represent the area local to the sampling point, but because the water flows, the results also represent upgradient areas and can be used to estimate potential future impacts to downgradient areas.

5. Develop the Analytic Approach

Population Parameters

For delineation, individual soil and groundwater sample results will be compared to state regulatory standards.

For risk assessments, the data will be segregated by exposure pathway (for example, surface water). Maximum and 95 percent upper confidence limit concentrations of the data will be compared to the appropriate risk screening level.

Action Levels

The action levels for soil, surface water, and groundwater data are contained in N.J.A.C. 7:26D, Remediation Standards. In addition, the data will be used in risk assessments for comparison to the appropriate risk screening levels.

6. Specify Performance or Acceptance Criteria.

The sampling program covered by this QAPP has been developed to address certain data gaps in the investigation previously described in the SCSR, which was approved by the USEPA. This sampling is not the only or entire effort to characterize the site. The scope of sampling and analysis was determined by the Settling Parties and the USEPA project team to answer specific

and limited questions about the site. Therefore, the statistical analysis proposed in the USEPA guidance (USEPA, February 2006) is not applicable to this scope of sampling.

For acceptance criteria, it is expected that representative, valid data will be obtained from at least 90% of the proposed sample locations. Field conditions, such as a lack of groundwater in certain monitoring wells, access restrictions, or other conditions, may limit the completion of sampling at certain proposed sample locations. To the extent practical, sample locations will be relocated as needed to ensure completion of the proposed sampling. However, at some locations, an alternative location may not be available.

7. Develop the Detailed Plan for Obtaining Data.

In its letter of March 7, 2013, the USEPA identified several data gaps related to the delineation of constituents in environmental media (USEPA 2013). To address these data gaps, ARCADIS prepared a Preliminary Plan to Address Data Gaps (April 30, 2013; ARCADIS 2013). The work proposed in this Preliminary Plan was to be conducted during the design of the site remedy. However, during subsequent scoping of the BERA, USEPA offered the Group the option of assessing the data gaps before implementing the BERA so that the additional data could be used in scoping the BERA (USEPA letter of July 30, 2014; USEPA 2014). The objectives of the data gaps sampling, as described in item 3 above and in Worksheet #17, were to further characterize constituents in soil, groundwater, pore water, surface water, and sediment.

A complete Data Gaps Sampling and Analysis Plan (SAP) developed in conjunction with USEPA has been prepared to detail the sampling and analyses proposed to for the data gaps investigation. This SAP has been submitted to the USEPA and is currently under review.

QAPP Worksheet #12: Measurement Performance Criteria

Quality Assurance Project Plan Worksheet #12-1 – Measurement Performance Criteria (Semivolatile Organic Compounds in Water by SOM01.2 and SOM01.2-SIM)

Matrix	Water
Analytical Group	SVOCs
Concentration Level	All

Sampling Procedure[1]	Analytical Method/Standard Operating Procedure (SOP)[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SOP 2, SOP 7, SOP 8, SOP 20	SOM01.2/SOM01.2-SIM/TAB-3	Precision – Overall	Relative percent difference (RPD) < 35%	Field duplicate	S&A
		Accuracy/Bias	% Relative abundance, see SOM01.2 – Exhibit D Semivolatiles Table 1	Instrument performance check: decafluorotriphenylphosphine (DFTPP)	A
		Accuracy/Bias Contamination	All target compounds < Contract Required Quantitation Limit (CRQL)	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	Percent recovery (%R), see see SOM01.2 – Exhibit D Semivolatiles Tables 6 (%),7 (associated target compounds), and 8 (associated target compounds, SIM)	Deuterated monitoring compounds (DMC)	A
		Accuracy/Bias	%R, see see SOM01.2 – Exhibit D Semivolatiles Table 5	Matrix spike (MS)[3]	A
		Accuracy/Bias	%R, see see SOM01.2 – Exhibit D Semivolatiles Table 5	Matrix spike duplicate (MSD)[3]	A
		Precision	%RPD, see see SOM01.2 – Exhibit D Semivolatiles Table 5	MS/MSD[3]	A

Quality Assurance Project Plan Worksheet #12-1 – Measurement Performance Criteria (Semivolatile Organic Compounds in Water by SOM01.2 and SOM01.2-SIM)

Matrix	Water
Analytical Group	SVOCs
Concentration Level	All

Sampling Procedure[1]	Analytical Method/Standard Operating Procedure (SOP)[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
		Precision	Area response 50.0% to 200% and retention time (RT) ±30.0 seconds from associated 12-hour calibration standard; see SOM01.2 – Exhibit D Semivolatiles Table 2 (associated target compounds)	Internal standard	A

Notes:
[1] Reference number from Quality Assurance Project Plan Worksheet #21.
[2] Reference number from Quality Assurance Project Plan Worksheet #23.
[3] MS and MSD must be client-provided.

Quality Assurance Project Plan Worksheet #12-2 – Measurement Performance Criteria (Volatile Organic Compounds in Water by SOM01.2)

Matrix	Water
Analytical Group	VOCs
Concentration Level	All

Sampling Procedure[1]	Analytical Method/Standard Operating Procedure (SOP)[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SOP 2, SOP 7, SOP 8, SOP 20	SOM01.2/TAB-11	Precision – Overall	Relative percent difference (RPD) < 35%	Field duplicate	S&A
		Accuracy/Bias	% Relative abundance, see SOM01.2 – Exhibit D Low/Medium Volatiles Table 1	Instrument performance check: bromofluorobenzene (BFB)	A
		Accuracy/Bias Contamination	All target compounds < Contract Required Quantitation Limit (CRQL)	Blanks (trip, field, equipment, method)	S&A
		Accuracy/Bias	Percent recovery (%R), see SOM01.2 – Exhibit D Low/Medium Volatiles Table 5 (%R) and Table 7 (associated target compounds)	Deuterated monitoring compounds (DMC)	A
		Accuracy/Bias	%R, see SOM01.2 – Exhibit D Low/Medium Volatiles Table 6	Matrix spike (MS)[3]	A
		Accuracy/Bias	%R, see SOM01.2 – Exhibit D Low/Medium Volatiles Table 6	Matrix spike duplicate (MSD)[3]	A
		Precision	%RPD, see SOM01.2 – Exhibit D Low/Medium Volatiles Table 6	MS/MSD[3]	A
		Precision	Area response 50.0% to 200% and retention time (RT) ±30.0 seconds from associated 12-hour calibration standard; see SOM01.2 – Exhibit D Low/Medium Volatiles Table 3 (associated target compounds)	Internal standard	A

Notes:
[1] Reference number from Quality Assurance Project Plan Worksheet #21.
[2] Reference number from Quality Assurance Project Plan Worksheet #23.
[3] MS and MSD must be client-provided.

Quality Assurance Project Plan Worksheet #12-3 – Measurement Performance Criteria (Pesticides in Water by SOM01.2)

Matrix	Water
Analytical Group	Pesticides
Concentration Level	All

Sampling Procedure[1]	Analytical Method/SOP[2]	DQIs	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SOP 2, SOP 7, SOP 8, SOP 20	SOM01.2/TAB-2	Precision – Overall	RPD < 35%	Field duplicate	S&A
		Accuracy/Bias Contamination	< CRQL	Blanks (field, equipment, method, instrument)	S&A
		Accuracy/Bias	%R: 30-150%	Surrogate spikes: tetrachloro-m-xylene (TCX) and decachlorobiphenyl (DCB)	A
		Accuracy/Bias	%R, see SOM01.2 – Exhibit D Pesticides Table 3	MS[3]	A
		Accuracy/Bias	%R, see SOM01.2 – Exhibit D Pesticides Table 3	MSD[3]	A
		Precision	%RPD, see SOM01.2 – Exhibit D Pesticides Table 3	MS/MSD[3]	A
		Accuracy/Bias	%R, see SOM01.2 – Exhibit D Pesticides Table 2	LCS	A
		Accuracy/Bias and Precision	Retention times, see SOM01.2 – Exhibit D Pesticides Table 1	Retention time windows	A

Notes:

[1] Reference number from Quality Assurance Project Plan Worksheet #21.

[2] Reference number from Quality Assurance Project Plan Worksheet #23.

[3] MS and MSD analysis must be client-provided.

Quality Assurance Project Plan Worksheet #12-4 – Measurement Performance Criteria (Polychlorinated Biphenyls (PCBs) in Water by SOM01.2)

Matrix	Water
Analytical Group	PCBs
Concentration Level	All

Sampling Procedure[1]	Analytical Method/SOP[2]	DQIs	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SOP 2, SOP 7, SOP 8, SOP 20	SOM01.2/TAB-1	Precision – Overall	RPD < 35%	Field duplicate	S&A
		Accuracy/Bias Contamination	< CRQL	Blanks (field, equipment, method, instrument)	S&A
		Accuracy/Bias	%R: 30-150%	Surrogate spikes: tetrachloro-m-xylene (TCX) and decachlorobiphenyl (DCB)	A
		Accuracy/Bias	%R, see SOM01.2 – Exhibit D Aroclors Table 1	MS[3]	A
		Accuracy/Bias	%R, see SOM01.2 – Exhibit D Aroclors Table 1	MSD[3]	A
		Precision	%RPD, see SOM01.2 – Exhibit D Aroclors Table 1	MS/MSD[3]	A
		Accuracy/Bias	%R, see SOM01.2 – Exhibit D Aroclors Table 2	LCS	A
		Accuracy/Bias and Precision	Retention times, see analytical SOP	Retention time windows	A

Notes:

[1] Reference number from Quality Assurance Project Plan Worksheet #21.

[2] Reference number from Quality Assurance Project Plan Worksheet #23.

[3] MS and MSD analysis must be client-provided.

Quality Assurance Project Plan Worksheet #12-5 – Measurement Performance Criteria (Metals, Mercury, and Cyanide in Water by ISM01.3)

Matrix	Water
Analytical Group	Metals/Mercury/Cyanide
Concentration Level	All

Sampling Procedure[1]	Analytical Method/SOP[2]	DQIs	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SOP 2, SOP 7, SOP 8, SOP 20	ISM01.3/TAB-5, TAB-6, TAB-7	Precision – Overall	RPD < 35%	Field duplicate	S&A
		Accuracy/Bias Contamination	< CRQL	Blanks (field, equipment, calibration, method)	S&A
		Precision	RPD < 20% for original and duplicate sample values ≥5x the CRQL; control limit of the CRQL used if either the sample or duplicate value is <5x the CRQL	Matrix duplicate (MD)[3]	A
		Accuracy/Bias	%R: 75-125%; does not apply when the sample concentration is ≥4x the spike added	MS[3]	A
		Precision – lab	Percent recovery (%R) ±20% of true value	Interference check sample (A and AB) (ICP metals analysis only)	A
		Accuracy/Bias	%R 70-130% (50-150% for antimony and silver)	Laboratory control sample (LCS) (ICP metals analysis only)	A
		Precision	Percent difference (%D) < 10%	Serial dilution (ICP metals analysis only)[4]	A

Notes:

[1] Reference number from Quality Assurance Project Plan Worksheet #21.
[2] Reference number from Quality Assurance Project Plan Worksheet #23.
[3] MD and MS must be client-provided.
[4] Performed as needed only for analytes with concentration > 50 times the method detection limit (MDL).

Quality Assurance Project Plan Worksheet #12-6 – Measurement Performance Criteria (Mercury in Water by EPA 1631E)

Matrix	Water
Analytical Group	Mercury
Concentration Level	Low

Sampling Procedure[1]	Analytical Method/SOP[2]	DQIs	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SOP 2, SOP 7, SOP 8, SOP 20	EPA 1613E/TANC-12	Precision – Overall	RPD < 35%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, calibration, method)	S&A
		Precision	RPD < method specified limit	Matrix duplicate (MD)[3]	A
		Accuracy/Bias	%R, method specified limit	MS[4]	A
		Accuracy/Bias	%R, method specified limit	Continuing calibration verification	A
		Accuracy/Bias	%R, method specified limit	Laboratory control sample	A

Notes:

[1] Reference number from Quality Assurance Project Plan Worksheet #21.

[2] Reference number from Quality Assurance Project Plan Worksheet #23.

[3] MD and MS must be client-provided.

Quality Assurance Project Plan Worksheet #12-7 – Measurement Performance Criteria (Semivolatile Organic Compounds in Soil and Sediment by SOM01.2 and SOM01.2-SIM)

Matrix	Soil/Sediment
Analytical Group	SVOCs
Concentration Level	All

Sampling Procedure[1]	Analytical Method/Standard Operating Procedure (SOP)[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SOP 5, SOP 14	SOM01.2/SOM01.2-SIM/TAB-3	Precision – Overall	Relative percent difference (RPD) < 50%	Field duplicate	S&A
		Accuracy/Bias	% Relative abundance, see SOM01.2 – Exhibit D Semivolatiles Table 1	Instrument performance check: decafluorotriphenylphosphine (DFTPP)	A
		Accuracy/Bias Contamination	All target compounds < Contract Required Quantitation Limit (CRQL)	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	Percent recovery (%R), see see SOM01.2 – Exhibit D Semivolatiles Tables 6 (%),7 (associated target compounds), and 8 (associated target compounds, SIM)	Deuterated monitoring compounds (DMC)	A
		Accuracy/Bias	%R, see see SOM01.2 – Exhibit D Semivolatiles Table 5	Matrix spike (MS)[3]	A
		Accuracy/Bias	%R, see see SOM01.2 – Exhibit D Semivolatiles Table 5	Matrix spike duplicate (MSD)[3]	A
		Precision	%RPD, see see SOM01.2 – Exhibit D Semivolatiles Table 5	MS/MSD[3]	A
		Precision	Area response 50.0% to 200% and retention time (RT) ±30.0 seconds from associated 12-hour calibration standard; see SOM01.2 – Exhibit D Semivolatiles Table 2 (associated target compounds)	Internal standard	A

Notes:
[1] Reference number from Quality Assurance Project Plan Worksheet #21.
[2] Reference number from Quality Assurance Project Plan Worksheet #23.
[3] MS and MSD must be client-provided.

Quality Assurance Project Plan Worksheet #12-8 – Measurement Performance Criteria (Volatile Organic Compounds in Soil and Sediment by SOM01.2)

Matrix	Soil/Sediment
Analytical Group	VOCs
Concentration Level	All

Sampling Procedure[1]	Analytical Method/Standard Operating Procedure (SOP)[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SOP 5, SOP 14	SOM01.2/TAB-4	Precision – Overall	Relative percent difference (RPD) < 50%	Field duplicate	S&A
		Accuracy/Bias	% Relative abundance, see SOM01.2 – Exhibit D Low/Medium Volatiles Table 1	Instrument performance check: bromofluorobenzene (BFB)	A
		Accuracy/Bias Contamination	All target compounds < Contract Required Quantitation Limit (CRQL)	Blanks (trip, field, equipment, method)	S&A
		Accuracy/Bias	Percent recovery (%R), see SOM01.2 – Exhibit D Low/Medium Volatiles Table 5 (%R) and Table 7 (associated target compounds)	Deuterated monitoring compounds (DMC)	A
		Accuracy/Bias	%R, see SOM01.2 – Exhibit D Low/Medium Volatiles Table 6	Matrix spike (MS)[3]	A
		Accuracy/Bias	%R, see SOM01.2 – Exhibit D Low/Medium Volatiles Table 6	Matrix spike duplicate (MSD)[3]	A
		Precision	%RPD, see SOM01.2 – Exhibit D Low/Medium Volatiles Table 6	MS/MSD[3]	A
		Precision	Area response 50.0% to 200% and retention time (RT) ±30.0 seconds from associated 12-hour calibration standard; see SOM01.2 – Exhibit D Low/Medium Volatiles Table 3	Internal standard	A

Quality Assurance Project Plan Worksheet #12-8 – Measurement Performance Criteria (Volatile Organic Compounds in Soil and Sediment by SOM01.2)

Matrix	Soil/Sediment
Analytical Group	VOCs
Concentration Level	All

Sampling Procedure[1]	Analytical Method/Standard Operating Procedure (SOP)[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
			(associated target compounds)		

Notes:
[1] Reference number from Quality Assurance Project Plan Worksheet #21.
[2] Reference number from Quality Assurance Project Plan Worksheet #23.
[3] MS and MSD must be client-provided.

Quality Assurance Project Plan Worksheet #12-9 – Measurement Performance Criteria (Pesticides in Soil and Sediment by SOM01.2)

Matrix	Soil/Sediment
Analytical Group	Pesticides
Concentration Level	All

Sampling Procedure[1]	Analytical Method/SOP[2]	DQIs	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SOP 5, SOP 14	SOM01.2/TAB-2	Precision – Overall	RPD < 50%	Field duplicate	S&A
		Accuracy/Bias Contamination	< CRQL	Blanks (field, equipment, method, instrument)	S&A
		Accuracy/Bias	%R: 30-150%	Surrogate spikes: tetrachloro-m-xylene (TCX) and decachlorobiphenyl (DCB)	A
		Accuracy/Bias	%R, see SOM01.2 – Exhibit D Pesticides Table 3	MS[3]	A
		Accuracy/Bias	%R, see SOM01.2 – Exhibit D Pesticides Table 3	MSD[3]	A
		Precision	%RPD, see SOM01.2 – Exhibit D Pesticides Table 3	MS/MSD[3]	A
		Accuracy/Bias	%R, see SOM01.2 – Exhibit D Pesticides Table 2	LCS	A
		Accuracy/Bias and Precision	Retention times, see SOM01.2 – Exhibit D Pesticides Table 1	Retention time windows	A

Notes:
[1] Reference number from Quality Assurance Project Plan Worksheet #21.
[2] Reference number from Quality Assurance Project Plan Worksheet #23.
[3] MS and MSD analysis must be client-provided.

Quality Assurance Project Plan Worksheet #12-10 – Measurement Performance Criteria (Polychlorinated Biphenyls (PCBs) in Soil and Sediment by SOM01.2)

Matrix	Soil/Sediment
Analytical Group	PCBs
Concentration Level	All

Sampling Procedure[1]	Analytical Method/SOP[2]	DQIs	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SOP 5, SOP 14	SOM01.2/TAB-1	Precision – Overall	RPD < 50%	Field duplicate	S&A
		Accuracy/Bias Contamination	< CRQL	Blanks (field, equipment, method, instrument)	S&A
		Accuracy/Bias	%R: 30-150%	Surrogate spikes: tetrachloro-m-xylene (TCX) and decachlorobiphenyl (DCB)	A
		Accuracy/Bias	%R, see SOM01.2 – Exhibit D Aroclors Table 1	MS[3]	A
		Accuracy/Bias	%R, see SOM01.2 – Exhibit D Aroclors Table 1	MSD[3]	A
		Precision	%RPD, see SOM01.2 – Exhibit D Aroclors Table 1	MS/MSD[3]	A
		Accuracy/Bias	%R, see SOM01.2 – Exhibit D Aroclors Table 2	LCS	A
		Accuracy/Bias and Precision	Retention times, see analytical SOP	Retention time windows	A

Notes:
[1] Reference number from Quality Assurance Project Plan Worksheet #21.
[2] Reference number from Quality Assurance Project Plan Worksheet #23.
[3] MS and MSD analysis must be client-provided.

Quality Assurance Project Plan Worksheet #12-11 – Measurement Performance Criteria (Metals, Mercury, and Cyanide in Soil and Sediment by ISM01.3)

Matrix	Soil/Sediment
Analytical Group	Metals/Mercury/Cyanide
Concentration Level	All

Sampling Procedure[1]	Analytical Method/SOP[2]	DQIs	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SOP 5, SOP 14	ISM01.3/TAB-5, TAB-6, TAB-7	Precision – Overall	RPD < 50%	Field duplicate	S&A
		Accuracy/Bias Contamination	< CRQL	Blanks (field, equipment, calibration, method)	S&A
		Precision	RPD < 20% for original and duplicate sample values ≥5x the CRQL; control limit of the CRQL used if either the sample or duplicate value is <5x the CRQL	Matrix duplicate (MD)[3]	A
		Accuracy/Bias	%R: 75-125%; does not apply when the sample concentration is ≥4x the spike added	MS[3]	A
		Precision – lab	Percent recovery (%R) ±20% of true value	Interference check sample (A and AB) (ICP metals analysis only)	A
		Accuracy/Bias	%R 70-130% (50-150% for antimony and silver)	Laboratory control sample (LCS) (ICP metals analysis only)	A
		Precision	Percent difference (%D) < 10%	Serial dilution (ICP metals analysis only)[4]	A

Notes:

[1] Reference number from Quality Assurance Project Plan Worksheet #21.
[2] Reference number from Quality Assurance Project Plan Worksheet #23.
[3] MD and MS must be client-provided.
[4] Performed as needed only for analytes with concentration > 50 times the method detection limit (MDL).

QAPP Worksheet #12-12 Measurement Performance Criteria (Total Organic Carbon in Soil and Sediment by Lloyd Kahn)

Matrix	Soil/Sediment
Analytical Group	TOC
Concentration Level	All

Sampling Procedure[1]	Analytical Method/SOP[2]	DQIs	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SOP 5, SOP 14	Lloyd Kahn/TAB-9	Precision — Overall	RPD < 50%	Field duplicate	S&A
		Accuracy/Bias	%R, laboratory generated limits	LCS	A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, laboratory generated limits	Matrix Spike (MS)[3]	A
		Precision	RPD, laboratory generated limits	MS/MSD or Laboratory Duplicate[3]	A

Notes:

[1] Reference number from QAPP Worksheet #21.

[2] Reference number from QAPP Worksheet #23.

[3] Sufficient sample size for MS and laboratory duplicate analysis must be client-provided.

Quality Assurance Project Plan Worksheet #12-13 – Measurement Performance Criteria (PCB Congeners in Soil and Sediment by EPA 1668A)

Matrix	Soil/Sediment
Analytical Group	PCB Congeners
Concentration Level	All

Sampling Procedure[1]	Analytical Method/SOP[2]	DQIs	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SOP 5, SOP 14	EPA 1668A/TAWS-1	Precision – Overall	RPD < 50%	Field duplicate	S&A
		Accuracy/Bias	%R, method specified limit	Labeled Compounds/Internal Standard	A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, method specified limit	OPR/LCS	A
		Accuracy/Bias	%R, method specified limit	MS[3]	A
		Accuracy/Bias	%R, method specified limit	MSD or LCSD[3]	A
		Precision	RPD, method specified limit	MS/MSD or LCS/LCSD [3]	A

Notes:

[1]Reference number from Quality Assurance Project Plan Worksheet #21.

[2]Reference number from Quality Assurance Project Plan Worksheet #23.

[3]Sufficient sample size for MS and MSD analysis must be client-provided. LCS/LCSD performed when no MS/MSD are supplied.

Quality Assurance Project Plan Worksheet #12-14 – Measurement Performance Criteria (Dioxins and Furans in Soil and Sediment by EPA 1613)

Matrix	Soil/Sediment
Analytical Group	Dioxins and Furans
Concentration Level	All

Sampling Procedure[1]	Analytical Method/ Standard Operating Procedure (SOP)[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	Quality Control (QC) Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SOP 5, SOP 14	EPA 1613/TAWS-2	Precision – Overall	Relative percent difference (RPD) < 50%	Field duplicate	S&A
		Precision	Percent recovery (%R), method specified limit	Labeled Compounds/Internal Standard	A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, method specified limit	Laboratory control sample (LCS) and laboratory control sample duplicate (LCSD)[3]	A
		Accuracy/Bias and Precision	Method specified limit	Instrument performance check: Perfluorokerosene (PKF)	A
		Precision	%RPD method specified limit	LCS/LCSD	A

Notes:
[1]Reference number from Quality Assurance Project Plan Worksheet #21.
[2]Reference number from Quality Assurance Project Plan Worksheet #23.

QAPP Worksheet #13: Secondary Data Uses and Limitations

Data type	Source	Data uses relative to current project	Factors affecting the reliability of data and limitations on data use
Visual observation of surface water bodies	Field personnel	Better describe the occurrence of surface water in wetlands areas, potentially including observations of bed and back morphology, and when/if surface water is present.	Observations will be made concurrent with sampling so will not include all areas of the landfill, and will be limited in duration.
Visual observation of landfill materials and soil	Field personnel	Add to our understanding of waste materials in the landfill, and the thickness/quality of soil cover.	Observations will be made concurrent with sampling so will not include all areas of the landfill.
Field screening data of monitoring and temporary wells with PID	Field personnel	Add to our understanding of the volatiles that are concentrated in the headspace of the well over time.	Observations will be made concurrent with sampling so will not include all areas of the landfill. This method may also have varying consistency due to tightness of the well cap.

QAPP Worksheet #14/16: Project Tasks & Schedule

Activity	Responsible party	Planned start date	Planned completion date	Deliverable(s)	Deliverable due date
Mobilization	ARCADIS	13 October 2014	13 October 2014	Field notes	13 October 2014
Vegetation clearing	ARCADIS	13 October 2014	14 October 2014	Field notes	13 October 2014
Underground utility clearing	ARCADIS	14 October 2014	14 October 2014	Field notes of New Jersey One-Call utility mark outs	14 October 2014
Sample collection – soil	ARCADIS	20 October 2014	31 October 2014	Field notes, map of boring locations, and soil logs	28 October 2014
Installation of temporary monitoring wells	ARCADIS	27 October 2014	28 October 2014	Field notes, map of well locations, and soil logs	29 October 2014
Sample collection – groundwater from temporary and permanent wells	ARCADIS	28 October 2014	31 October 2014	Field notes, groundwater purge logs, and chain of custodies	3 November 2014
Installation of pore water samplers	ARCADIS	29 October 2014	29 October 2014	Field notes and chain of custodies	1 November 2014
Sample collection – pore water	ARCADIS	12 November 2014	12 November 2014	Field notes and chain of custodies	19 November 2014
Sample collection – surface water and sediment	ARCADIS	27 October 2014	31 October 2014	Field notes and chain of custodies	3 November 2014

Activity	Responsible party	Planned start date	Planned completion date	Deliverable(s)	Deliverable due date
Assess Hunt Club Well HC-1	ARCADIS	22 October 2014	22 October 2014	Field notes, groundwater purge logs, and chain of custodies	29 October 2014
Analysis of Phase One samples	TestAmerica	22 October 2014	10 December 2014	Report of Analyses/Data package	10 December 2014
Validation of Phase One data	ARCADIS	10 December 2014	17 January 2015	Validation Summary report	17 January 2015
Usability assessment	Project Team	December 2014	December 2014	Meeting minutes/Usability assessment summary report	December 2014
Preparation of Interim Technical Memo	ARCADIS	3 November 2014	5 January 2015	Interim Technical Memorandum	5 January 2015
USEPA review and approval of Interim Technical Memorandum	USEPA	6 January 2015	27 January 2015	Approval of proposed permanent monitoring well locations	28 January 2015
Obtain well permits	ARCADIS	29 January 2015	28 February 2015	Permit approvals	28 February 2015
Install and develop permanent wells	ARCADIS	2 March 2015	11 March 2015	Field notes and well logs	24 March 2015
Redevelop existing wells	ARCADIS	12 March 2015	17 March 2015	Field notes	18 March 2015
First groundwater sampling event (all new and existing wells)	ARCADIS	6 April 2015	17 April 2015	Field notes and purge logs	24 April 2015
Second groundwater sampling event (all new wells)	ARCADIS	18 May 2015	22 May 2015	Field notes and purge logs	29 May 2015
Groundwater sample	TestAmerica	7 April 2015	12 June 2015	Laboratory data	12 June 2015

Activity	Responsible party	Planned start date	Planned completion date	Deliverable(s)	Deliverable due date
analysis				packages	
Data validation	ARCADIS	13 June 2015	13 July 2015	Validation summary report	13 July 2015
Final report	ARCADIS	14 July 2015	30 August 2015	Final report	30 August 2015

Analysis Tasks

- Soil and sediment samples will be processed, prepared and analyzed by:
  - i. TestAmerica Burlington for volatile organic compounds (VOCs) by SOM01.2, semivolatile organic compounds (SVOCs) by SOM01.2, polynuclear aromatic hydrocarbons (PAHs) by SIM by SOM01.2, polychlorinated biphenyls (PCBs) Aroclors by SOM01.2, pesticides by SOM01.2, metals by ISM01.3, mercury by ISM01.3, cyanide by ISM01.3, total organic carbon (TOC) by Lloyd Kahn, and pH by SW-846 9045C.
  - ii. TestAmerica West Sacramento for polychlorinated biphenyl (PCB) congeners by EPA 1668A, and dioxins and furans by EPA 1613B.
- Surface water and groundwater samples will be processed, prepared and analyzed by:
  - i. TestAmerica Burlington for VOCs by SOM01.2, SVOCs by SOM01.2, PAHs by SIM by SOM01.2, PCB Aroclors by SOM01.2, pesticides by SOM01.2, metals by ISM01.3, mercury by ISM01.3, low level mercury by EPA 1631E, cyanide by ISM01.3, TOC by EPA SW846 9060, and pH by SW-846 9045C.
  - ii. TestAmerica West Sacramento for polychlorinated biphenyl (PCB) congeners by EPA 1668A, and dioxins and furans by EPA 1613B.

Quality Control Tasks

The samples will be collected and processed, and waste will be disposed of as documented in the field Standard Operating Procedures (SOPs). The quality assurance (QA) samples are described in Worksheet #20.

Secondary Data

See Worksheet #13.

Data Management Tasks

The purpose of data management is to confirm that the necessary data are accurate and readily accessible to meet the analytical and reporting objectives of the project. The field investigations will include a significant number of samples that require a structured, comprehensive and efficient program for management of data.

The data management program established for the project includes field documentation and sample QA/quality control (QC) procedures, methods for tracking and managing the data, and a system for filing all site-related information. More specifically, data management procedures will be employed to efficiently process the information collected, such that the data are readily accessible and accurate. These procedures are described in detail in the following section.

The data management plan has five elements: 1) sample designation system, 2) field activities, 3) sample tracking and management, 4) data management system, and 5) document control and inventory.

Sample Designation System

A concise and easily understandable sample designation system is an important part of project sampling activities. It provides a unique sample number that will facilitate both sample tracking and easy resampling of select locations to evaluate data gaps, if necessary. The sample designation system to be employed during the sampling activities will be consistent, yet flexible enough to accommodate unforeseen sampling events or conditions. A combination of letters and numbers will be used to yield a unique sample number for each field sample collected, as outlined below.

Sample Codes

Each sample will be identified by a unique identification number in the logbook, sampling log, and chain-of-custody (COC) record using an alphanumeric code. Field samples will be linked to geographic location via location codes. All field samples will be identified using the following convention in the order presented below:

The alphanumeric sample designation code prefix will indicate the sampling method and/or sample matrix, subarea from which the sample was collected, and a numeric code corresponding to the location number. The sample depth interval, in feet, will follow the location number, and provide unique identification for that sample. Location numbering will be designated using the following codes:

- Soil Sample – “SS”
- Surface-Water Sample – “SW”
- Sediment Sample – “SD”

- Groundwater Sample – “TW” if from a temporary monitoring well, or “MW” if from a permanent monitoring well
- Pore-Water Sample – “PW”
- Trip Blank Sample – “TB”
- Field Duplicate Sample – “DUP”
- Equipment Blank Sample – “EB”
- Matrix Spike and Matrix Spike Duplicate – “MS” and MSD”

The location code, consisting of a two to five digit designation, will follow the sample type code. For subsurface soil samples, the designation will also consist of the sample depth in feet. For example, a subsurface soil sample collected from a depth of 2 to 4 ft from SB02 would be designated SS-SB02 (2-4). For groundwater, surface-water, and pore-water samples, the sample code will also include a six-digit number indicating the month, day, and year the sample was obtained. For example, a groundwater sample collected from temporary monitoring well TW-2 on October 30, 2014 will be designated GW-TW-2(103014).

QA/QC samples will be designated by a three-letter code followed by the six-digit sample collection date. For field and equipment blanks, a two-letter sample type code will precede the blank designation to indicate which medium the blank was intended to represent. For example, a field blank collected on October 30, 2014 during surface soil samples collection would be designated SS-FB1-103014. The sampling point associations for field duplicates must be recorded in the field log.

Sample identification and labeling procedures may be modified as needed to supplement specific investigation objectives and any deviations identified in site-specific work plans.

Field Activities

Field activities require consistent documentation and accurate record keeping. During site activities, standardized procedures will be used for documentation of field activities, data security and QA. These procedures are described in further detail in the following subsections.

Field Documentation

Complete and accurate record keeping is a critical component of the field investigation activities. When interpreting analytical results and identifying data trends, investigators realize that field notes are an important part of the review and validation process. To confirm that the field investigation is thoroughly documented, several different information records, each with its own specific reporting requirements, will be maintained, including:

- field logs
- chain-of-custody (COC) forms
- instrument calibration records

Each of these types of field documentation is described below.

Field Logs

Personnel performing the field activities will keep field logs that detail observations and measurements made during the site work. Data will be recorded directly into site-dedicated, bound notebooks, with each entry dated and signed. To determine, at a future date, that notebook pages are not missing, each page will be sequentially numbered. Erroneous entries will be corrected by crossing out the original entry, initialing it and then documenting the proper information. In addition, certain media sample locations will be surveyed to accurately record their locations. The survey crew will use its own field logs and will supply the sampling location coordinates to the Database Administrator.

Chain-of-Custody Forms

COC forms are used to document and track sample possession from time of collection to the time of disposal. A COC form will accompany each field sample collected, and one copy of the form will be filed in the field office. Field personnel will be briefed on the proper use of the COC procedure.

Instrument Calibration Records

As part of data QA procedures, field monitoring and detection equipment will be routinely calibrated. Instrument calibration confirms that equipment used is of the proper type, range, accuracy and precision to provide data compatible with the specified requirements and desired results. Calibration procedures for the various types of field instrumentation are described in Worksheet 22. To demonstrate that established calibration procedures have been followed, calibration records will be prepared and maintained to include, as appropriate, the following:

- calibration date and time
- type and identification number of equipment
- calibration frequency and acceptable tolerances
- identification of individual(s) performing calibration
- reference standards used
- calibration data
- information on calibration success or failure

The calibration record will serve as a written account of monitoring or detection equipment QA. Erratic behavior or failures of field equipment will be subsequently recorded in the calibration log.

Data Security

Measures will be taken during the field investigation to confirm that samples and records are not lost, damaged or altered. When not in use, field notebooks will be stored at the field office or locked in the field vehicle. Access to these files will be limited to the field personnel who use them.

Sample Management and Tracking

A record of all field documentation will be maintained to confirm the validity of data used in the site analysis. To effectively execute such documentation, specific sample tracking and data management procedures will be used throughout the sampling program.

Sample tracking will begin with the completion of COC forms. The completed COC forms will be faxed to the ARCADIS Project Manager or their designee Copies of all completed COC forms will be maintained in the project file. The laboratory will verify receipt of the samples electronically (via e-mail) on the following day.

When analytical data are received from the laboratory, the Project QA Manager or designee will review the incoming analytical data packages against the information on the COCs to confirm that the correct analyses were performed for each sample and that results for all samples

submitted for analysis were received. Any discrepancies noted will be promptly followed up by the Project QA Manager or designee.

Data Management System

In addition to the sample tracking system, a data management system will be implemented. The central focus of the data management system will be the development of a personal computer-based project database. The project database, to be maintained by the Project Database Manager, will combine pertinent geographical, field and analytical data. Information that will be used to populate the database will be derived from three primary sources: surveying of sampling locations, field observations and analytical results. Each of these sources is discussed in the following sections.

Computer Hardware

The database will be constructed on personal computer work stations connected through a network server. The network will provide access to various hardware peripherals, such as laser printers, backup storage devices, image scanners and modems. Computer hardware will be upgraded to industrial and corporate standards, as necessary, in the future.

Computer Software

The individual electronic data deliverables (EDDs), supplied by the laboratory in either an ASCII comma separated value (CSV) format or in a Microsoft® Excel worksheet, will be loaded into the appropriate database table via a custom-designed user interface Visual Basic program. Any analytical data that cannot be provided by the laboratory in electronic format will be entered manually. After entry into the database, the EDD data will be compared to the field information previously entered into the database to confirm that all requested analytical data have been received.

Survey Information

In general, each location sampled as part of the work plan will be surveyed to confirm accurate documentation of sample locations for mapping and GIS purposes (if appropriate), to facilitate resampling of select sample locations during future monitoring programs, if needed, and for any potential remediation activities. Field books associated with the surveying activities will be stored as a record of the project activities. The collection and reporting of locational data must include the GPS accuracy.

Field Observations

An important part of the information that will ultimately reside in the data management system for use during the project will originate in the observations that are recorded in the field.

Following each sampling event, a status memorandum may be prepared by the field personnel who performed the sampling activities. The purpose of the status memo is to summarize and provide a record of the sampling event. Topics to be discussed include the locations sampled, blind duplicate and MS/MSD sample identification numbers, personnel involved in the activity, and any other noteworthy events or observations that occurred.

Tables are typically attached to the memorandum and are used to summarize measurements that were recorded in the field books. It is anticipated that these tables will be developed using a personal computer spreadsheet program to reduce possible transcription error and to facilitate the transfer of information to the data management system.

All pertinent field data will be manually entered into the appropriate database tables from the COC forms and field notebooks.

Analytical Results

Analytical results will be provided by the laboratory in a digital (pdf) or a hard copy format. The data packages will be examined to confirm that the correct analyses were performed for each sample submitted and that all of the analyses requested on the COC form were performed. If discrepancies are noted, the Project QA Manager will be notified and will promptly follow up with the laboratory to resolve any issues.

Each data package will be validated in accordance with procedures outlined in Worksheet #37. Data that do not meet the specified standards will be flagged pending resolution of the issue. The flag will not be removed from the data until the issue associated with the sample results is resolved. Although flags may remain for certain data, the use of the data may not necessarily be restricted.

Following completion of the data validation, the digital files will be used to populate the appropriate database tables. This format specifies one data record for each constituent for each sample analyzed. Specific fields include:

- sample identification number
- date sampled
- date analyzed
- parameter name
- analytical result

- units
- detection limit
- qualifier(s)

The individual EDDs, supplied by the laboratory in a Microsoft Excel worksheet, will be loaded into the appropriate database table. If dilutions or re-analyses are included in the EDD, the laboratory must designate which set of results are considered reportable. Any analytical data that cannot be provided by the laboratory in electronic format will be entered manually. After entry into the database, the EDD data will be compared to the field information previously entered into the database to confirm that all requested analytical data have been received.

Data Analysis and Reporting

The database management system will have several functions to facilitate the review and analysis of project data. Data entry screens will be developed to assist in the keypunching of field observations. Routines will also be developed to permit the user to scan analytical data from a given site for a given medium. Several output functions that have been developed by ARCADIS will be appropriately modified for use in the data management system.

A valuable function of the data management system will be the generation of tables of analytical results from the project database. The capability of the data management system to directly produce tables reduces the redundant manual entry of analytical results during report preparation and precludes transcription errors that may occur otherwise. This data management system function has the ability to process the data and generate tables. Tables of analytical data will be produced as part of data interpretation, data reporting, and generation of the Final Report.

For certain comparisons, PCB Aroclors may be summed to obtain a total PCB concentration for each sample location. Undetected Aroclors will be considered to be zero during this summation.

Some sample locations will be submitted for analysis of PCB congeners. These methods may have congeners that co-elute. The co-elution scheme for these analyses will be as described in the laboratory SOP. In the instance where co-eluting congener values may be reported multiple times, the result was included only once in the sum.

Another function of the data management system will be to create digital files of analytical results and qualifiers suitable for transfer to mapping/ presentation software. A function has been created by ARCADIS that creates a digital file consisting of sample location number, state plane coordinates, sampling date and detected constituents, and associated concentrations and analytical qualifiers. The file is then transferred to an AutoCAD work station, where another program has been developed to plot a location’s analytical data in a "box" format at the sample location

(represented by the state plane coordinates). This routine greatly reduces the redundant keypunching of analytical results and facilitates the efficient production of interpretative and presentation graphics.

The data management system also has the capability of producing a digital file of select parameters that exists in one or more of the databases. This type of custom function is accomplished on an interactive basis and is best used for transferring select information into a number of analysis tools, such as statistical or graphing programs.

Documentation and Records

Field Documentation. Field personnel will provide comprehensive documentation covering all aspects of field sampling, field analysis and sample COC. This documentation constitutes a record that allows reconstruction of all field events to aid in the data review and interpretation process. All documents, records and information relating to the performance of the field work will be retained in the project file.

The various forms of documentation to be maintained throughout the action include:

- *Daily Production Documentation*. A field notebook consisting of a waterproof, bound notebook that will contain a record of all activities performed at the site.

- *Sampling Information*. Sampling locations, physical observations and weather conditions (as appropriate) will be described in the field notes.

- *Sample COC*. COC forms will provide the record of responsibility for sample collection, transport and submittal to the laboratory. COC forms will be filled out at each sampling site, at a group of sampling sites or at the end of each day of sampling by ARCADIS' field personnel designated to be responsible for sample custody. If the samples are relinquished by the designated sampling person to other sampling or field personnel, the COC form will be signed and dated by the appropriate personnel to document the sample transfer. The original COC form will accompany the samples to the laboratory, and copies will be forwarded to the project files.

  Persons will have custody of samples when the samples are in their physical possession, in their view after being in their possession, or in their physical possession and secured so they cannot be tampered with. In addition, when samples are secured in a restricted area accessible only to authorized personnel, they will be deemed to be in the custody of such authorized personnel.

- *Field Equipment, Calibration and Maintenance Logs*. To document the calibration and maintenance of field instrumentation, calibration

and maintenance logs will be maintained for each piece of field equipment that is not factory-calibrated.

Laboratory Project Files. The laboratory will establish a file for pertinent data. The file will include correspondence, faxed information, phone logs and COC forms. The laboratory will retain project files and data packages for a period to be determined by the Settling Parties.

Laboratory Logbooks. Workbooks, bench sheets, instrument logbooks and instrument printouts will be used to trace the history of samples through the analytical process and to document important aspects of the work, including the associated QCs. As such, logbooks, bench sheets, instrument logs and instrument printouts will be part of the permanent record of the laboratory. Each page or entry will be dated and initialed by the analyst at the time of entry. Errors in entry will be crossed out in indelible ink with one stroke, corrected without the use of white-out or by obliterating or writing directly over the erroneous entry, and initialed and dated by the individual making the correction. Pages of logbooks that are not used will be completed by lining out unused portions. Information regarding the sample, analytical procedures performed and results of the testing will be recorded on laboratory forms or personal notebook pages by the analyst. These notes will be dated and will also identify the analyst, instrument used and instrument conditions. Laboratory notebooks will be periodically reviewed by the laboratory group leaders for accuracy, completeness and compliance with this QAPP. All entries and calculations will be verified by the laboratory group leader. If all entries on the pages are correct, the laboratory group leader will initial and date the pages. Corrective action will be taken for incorrect entries before the laboratory group leader signs.

Computer and Hard Copy Storage. All electronic files and deliverables and hard copy data packages (or electronic copies) will be retained for a period to be determined by the Settling Parties.

Field Data Reporting. Information collected in the field through visual observation, manual measurement and/or field instrumentation will be recorded in field notebooks or data sheets and/or on forms. Such data will be reviewed by the ARCADIS Project Manager or their designee for adherence to the Work Plan and for consistency. Concerns identified as a result of this review will be discussed with the field personnel, corrected if possible and (as necessary) incorporated into the data evaluation process. If applicable, field data forms and calculations will be processed and included in appendices to the appropriate reports (when generated). The original field logs documents and data reductions will be kept in the project file at the ARCADIS office in Cranbury, New Jersey.

Laboratory Data Reporting. Data reports for all parameters will include, at a minimum, the following items:

Narrative: Summary of activities that took place during sample analysis, including the following information:

- laboratory name and address
- date of sample receipt

- cross reference of laboratory identification number to contractor sample identification
- analytical methods used
- deviations from specified protocol
- corrective actions taken

Included with the narrative will be any sample handling documents, including field and internal COC forms, air bills, and shipping tags.

Analytical Results: These will be reported according to analysis type and include the following information, as applicable:

- sample identification (ID)
- laboratory ID
- date of collection
- date of receipt
- date of extraction
- date of analysis
- method detection and reporting limits

Sample results on the report forms will be corrected for dilutions. Sediment and soil data will be reported on a dry weight basis. Unless otherwise specified, all results will be reported uncorrected for blank contamination.

The analyses performed will be reported as Contract Laboratory Program (CLP)-equivalent Level 4 data package which will include supporting documentation. This additional documentation will include, but not be limited to, raw data required to recalculate any result, including instrument printouts and quantitation reports. The report also will include standards used in calibration and calculation of analytical results; sample extraction, digestion and other preparation logs; standard preparation logs; instrument run logs; and moisture content calculations.

Data reporting levels are as follows:

- **Level 2** — **Modified Reporting**: Modified reporting is used for analyses that are performed following standard USEPA-approved methods and QA/QC protocols. Based on the intended data use, modified reporting may require some supporting documentation, but not full CLP or CLP-type reporting.

- **Level 4** — **Full Reporting**: Full CLP or CLP-type reporting is used for those analyses that, based on the intended data use, require full documentation.

Assessment/Audit Tasks

Performance and systems audits will be completed in the field and laboratory during the data gap investigations, as described below and in Worksheets #31 and #32.

1. ***Field Audits***. The following field performance and systems audits will be completed during this project.
   The ARCADIS Project Manager or their designee will monitor field performance. Field performance audit summaries will contain an evaluation of field activities to verify that the activities are performed according to established procedures as described in field SOPs. Field performance audits may be performed by the ARCADIS Project Manager (or her designee). The auditor(s) will review field reports and communicate concerns to the ARCADIS Project Manager and/or Field Task Manager, as appropriate.

   The number and frequency of field performance audits conducted will be determined independently by the Field Task Manager. The ARCADIS Project Manager will administer field performance audits at a frequency of approximately one per month during field activities. The observations made during field performance audits and any recommended changes/deviations to the field procedures will be recorded and documented.

   In addition, the Project QA Manager will review the rinse and trip blank data to identify potential deficiencies in field sampling and cleaning procedures. In addition, systems audits comparing scheduled QA/QC activities from this QAPP with actual QA/QC activities completed will be performed. The Field Task Manager and Project QA Manager will periodically confirm that work is being performed consistent with this QAPP.

2. **Laboratory Audits**

   Internal laboratory audits are conducted periodically by the Laboratory QA Manager. As part of the audit, the overall performance of the laboratory staff is evaluated and compared to the performance criteria outlined in the laboratory QA manual and SOPs. Results of the

audits are summarized and issued to each department supervisor, Laboratory Manager and Laboratory Director. A systems audit of each laboratory is also performed by the Project QA Manager to determine whether the procedures implemented by each laboratory comply with the QA manual and SOPs.

As a participant in state and federal certification programs, the laboratory is audited by representatives of the regulatory agency issuing certification, in addition to the laboratory's internal audits. Audits are usually conducted annually and focus on laboratory conformance to the specific program protocols for which the laboratory is seeking certification. The auditor reviews sample handling and tracking documentation, analytical methodologies, analytical supportive documentation and final reports. The audit findings are formally documented and submitted to the laboratory for corrective action, if necessary.

ARCADIS reserves the right to conduct an on-site audit of the laboratory prior to the start of analyses for the project. Additional audits may be performed during the project, as deemed necessary.

3. Corrective Action

Corrective actions are required when field or analytical data are not within the objectives specified in this QAPP. Corrective actions include procedures to promptly investigate, document, evaluate and correct data collection and/or analytical procedures. Field and laboratory corrective action procedures for the actions are described below.

a. Field Procedures

If, during field work, a condition is noted by the field crew that would have an adverse effect on data quality, corrective action will be taken so as not to repeat this condition. Condition identification, cause and corrective action implemented by the Field Task Manager or a designee will be documented on a Corrective Action Form and reported to the appropriate ARCADIS Project QA Manager and Project Manager.

Examples of situations that would require corrective actions are provided below:

- protocols as defined by the QAPP and/or field SOPs have not been followed
- equipment is not in proper working order or is not properly calibrated
- QC requirements have not been met

- issues resulting from performance or systems audits have not been resolved

Project personnel will continuously monitor ongoing work performance as part of daily responsibilities.

b. Laboratory Procedures

In the laboratory, when a condition is noted to have an adverse effect on data quality, corrective action will be taken so as not to repeat this condition. Condition identification, cause and corrective action taken will be documented and reported to the Project Manager and Project QA Manager.

Corrective action may be initiated, at a minimum, under the following conditions:

- protocols as defined by this QAPP have not been followed
- predetermined data acceptance standards are not obtained
- equipment is not in proper working order or calibrated
- sample and test results are not completely traceable
- QC requirements have not been met
- issues resulting from performance or systems audits have not been resolved

Laboratory personnel will continuously monitor ongoing work performance as part of daily responsibilities. Corrective action will be initiated at the point where the problem has been identified. At whatever level this occurs (analyst, supervisor, data review, or quality control), it will be brought to the attention of the Laboratory QA Manager and, ultimately, the Laboratory Director. Final approval of any action deemed necessary is subject to the approval of the Laboratory Director.

Any corrective action deemed necessary based on system or performance audits, the analytical results of split samples, or the results of data review will be implemented. The corrective action may include sample re-extraction, re-preparation, re-analysis, cleanup, dilution, matrix modification or other activities.

Data Review Tasks

See Worksheets #36 and #37.

QAPP Worksheet #15: Project Action Limits and Laboratory-Specific Detection/Quantitation Limits

Project action limits and laboratory-specific detection/quantitation limits are provided in Table 1 (attached).

QAPP Worksheet #17: Sampling Design and Rationale

Physical boundaries for the area under study

- Figure 1 depicts the boundaries of the landfill and surface debris area based on observations during test pit activities. Eastern and southern portions of the landfill are located within the GSNWR.

Time period being represented by the collected data

- Sampling will occur in two phases, beginning in October 2014 and ending in May 2015. Data can be compared to the previous sampling event to constrain annual and seasonal variations. All data will represent current conditions.

Description of the sampling area

- The sampling areas were selected to address specific data gaps in the previous investigation.
- They include soil near the southern perimeter of the landfill, groundwater across the landfill and adjacent areas, surface water and sediment in ponds both on and near the landfill, and pore water in wetlands on the west side of the landfill.

Sample locations

Sample locations are shown on Figures 2a and 2b.

Soil samples (20 samples, with 20 additional samples contingent on the results)

a. Basis for the number and placement of samples: Soil sampling will be conducted in a step-out manner. Soil samples will be collected in two lines: an inner line approximately 25 feet from the edge of the landfill, and an outer line approximately 50 feet from the edge of the landfill. The inner samples will be analyzed for the specific constituents that exceeded SRSs in the initial sample on the landfill. If the results of these analyses exceed the SRSs, samples from the outer line will be analyzed for those specific constituents. If the results from the outer line also exceed the SRSs, additional sampling may be needed to complete delineation.

b. How sample positions will be located: Sample locations were selected in consultation with USEPA. They will be located using site landmarks (e.g, monitoring wells or other permanent features) and global positioning system (GPS).

c. If a soil sample cannot be collected then the location may be moved to another location within 10 feet of the proposed location.

Groundwater samples (9 samples total) from temporary monitoring wells

a. Basis for the number and placement of samples: Temporary wells were placed upgradient and downgradient of well MW-3 and MW-10 to help identify potential sources of VOCs and to help delineate their downgradient extent.

b. How sample positions will be located: Sample locations were selected in consultation with USEPA. They will be located using site landmarks (e.g, monitoring wells or other permanent features) and GPS.

c. If a sample cannot be collected where planned, the temporary wells may be relocated or may be replaced with surface water samples.

Groundwater samples (31 samples total) from permanent monitoring wells

a. Basis for the number and placement of samples: The locations of wells include 17 historical permanent wells and 7 new wells. All 24 wells will be sampled once. The new wells will be sampled a second time, resulting in a total of 31 samples.

b. How sample positions will be located: Sample locations were selected in consultation with USEPA. Locations for the new permanent wells will be selected in consultation with USEPA based on the results of soil samples and temporary monitoring wells.

c. If a sample cannot be collected (e.g., the well is dry) then the field staff will return later during the sampling event to check the conditions and collect the sample if possible.

Pore-water samples (2 samples total)

a. Basis for the number and placement of samples: Pore-water sample locations were selected to delineate potential migration of VOCs in groundwater from the area of monitoring well MW-10 to the southwest.

b. How sample positions will be located: Sample locations were selected in consultation with USEPA. They will be located using site landmarks (e.g, monitoring wells or other permanent features) and GPS.

c. If a sample cannot be collected where planned, the locations may be relocated within 10 feet of the proposed location.

Surface-water samples (11 samples total)

a. Basis for the number and placement of samples: Surface-water samples will be collected from surface water bodies on the landfill that were not sampled during the previous investigations.

b. How sample positions will be located: Sample locations were selected in consultation with USEPA. They will be located using site landmarks (e.g, monitoring wells or other permanent features) and GPS.

c. If a sample cannot be collected where planned, the location may be adjusted. Some of the water bodies where sampling is proposed are small and have not been directly observed during previous activities. They may be ephemeral or smaller than shown in Figures 2a and 2b. In such cases, the samples may be collected elsewhere or eliminated.

Sediment samples (11 samples total)

a. Basis for the number and placement of samples: Sediment samples will be collected from surface water bodies on the landfill that were not sampled during the previous investigations.

b. How sample positions will be located: Sample locations were selected in consultation with USEPA. They will be located using site landmarks (e.g, monitoring wells or other permanent features) and GPS.

c. If a sample cannot be collected where planned, the location may be adjusted. Some of the water bodies where sampling is proposed are small and have not been directly observed during previous activities. They may be ephemeral or smaller than shown in Figures 2a and 2b. In such cases, the samples may be collected elsewhere or eliminated.

QAPP Worksheet #18: Sampling Locations and Methods

Sample ID	Matrix	Depth (ft bgs)	Type	Analyte/Analytical Group	Sampling SOP	Comments
SS-125	Soil	0.0-1.0	Macrocore	PCBs (as Aroclors)	SOP 5	
SS-126	Soil	0.0-1.0	Macrocore	PCBs (as Aroclors)	SOP 5	Contingent sample
SS-127	Soil	0.0-1.0	Macrocore	SVOCs, SVOCs SIM, PCBs (as Aroclors), PCB (as Congeners), Dioxins, Furans, TAL Metals & Cyanide	SOP 5	
SS-128	Soil	0.0-1.0	Macrocore	SVOCs, SVOCs SIM, PCBs (as Aroclors), PCB (as Congeners), Dioxins, Furans, TAL Metals & Cyanide	SOP 5	Contingent sample
SS-129	Soil	0.0-1.0	Macrocore	SVOCs, SVOCs SIM, PCBs (as Aroclors), PCB (as Congeners), Dioxins, Furans, TAL Metals & Cyanide	SOP 5	
SS-130	Soil	0.0-1.0	Macrocore	SVOCs, SVOCs SIM, PCBs (as Aroclors), PCB (as Congeners), Dioxins, Furans, TAL Metals & Cyanide	SOP 5	Contingent sample
SS-131	Soil	0.0-1.0	Macrocore	PCBs (as Aroclors)	SOP 5	

Sample ID	Matrix	Depth (ft bgs)	Type	Analyte/Analytical Group	Sampling SOP	Comments
SS-132	Soil	0.0-1.0	Macrocore	PCBs (as Aroclors)	SOP 5	Contingent sample
SS-133	Soil	0.0-1.0	Macrocore	SVOCs, SVOCs SIM, TAL Metals & Cyanide	SOP 5	
SS-134	Soil	0.0-1.0	Macrocore	SVOCs, SVOCs SIM, TAL Metals & Cyanide	SOP 5	Contingent sample
SS-135	Soil	0.0-1.0	Macrocore	PCBs (as Aroclors), TAL Metals & Cyanide	SOP 5	
SS-136	Soil	0.0-1.0	Macrocore	PCBs (as Aroclors), TAL Metals & Cyanide	SOP 5	Contingent sample
SS-137	Soil	0.0-1.0	Macrocore	PCBs (as Aroclors), TAL Metals & Cyanide, PCBs (as Congeners), Dioxins, Furans	SOP 5	
SS-138	Soil	0.0-1.0	Macrocore	PCBs (as Aroclors), TAL Metals & Cyanide, PCBs (as Congeners), Dioxins, Furans	SOP 5	Contingent sample
SS-139	Soil	0.0-1.0	Macrocore	PCBs (as Aroclors), TAL Metals & Cyanide, PCBs (as Congeners), Dioxins, Furans	SOP 5	
SS-140	Soil	0.0-1.0	Macrocore	PCBs (as Aroclors), TAL Metals & Cyanide, PCBs (as Congeners), Dioxins, Furans	SOP 5	Contingent sample

Sample ID	Matrix	Depth (ft bgs)	Type	Analyte/Analytical Group	Sampling SOP	Comments
SS-141	Soil	0.0-1.0	Macrocore	PCBs (as Aroclors), TAL Metals & Cyanide	SOP 5	
SS-142	Soil	0.0-1.0	Macrocore	PCBs (as Aroclors), TAL Metals & Cyanide	SOP 5	Contingent sample
SS-143	Soil	0.0-1.0	Macrocore	TAL Metals & Cyanide	SOP 5	
SS-144	Soil	0.0-1.0	Macrocore	TAL Metals & Cyanide	SOP 5	Contingent sample
SS-145	Soil	0.0-1.0	Macrocore	SVOCs	SOP 5	
SS-146	Soil	0.0-1.0	Macrocore	SVOCs	SOP 5	Contingent sample
SS-147	Soil	0.0-1.0	Macrocore	SVOCs, PCBs (as Aroclors), Pesticides, TAL Metals & Cyanide	SOP 5	
SS-148	Soil	0.0-1.0	Macrocore	SVOCs, PCBs (as Aroclors), Pesticides, TAL Metals & Cyanide	SOP 5	Contingent sample
SS-149	Soil	0.0-1.0	Macrocore	SVOCs, PCBs (as Aroclors), TAL Metals & Cyanide	SOP 5	
SS-150	Soil	0.0-1.0	Macrocore	SVOCs, PCBs (as Aroclors), TAL Metals & Cyanide	SOP 5	Contingent sample
SS-151	Soil	0.0-1.0	Macrocore	SVOCs	SOP 5	

Sample ID	Matrix	Depth (ft bgs)	Type	Analyte/Analytical Group	Sampling SOP	Comments
SS-152	Soil	0.0-1.0	Macrocore	SVOCs	SOP 5	Contingent sample
SS-153	Soil	0.0-1.0	Macrocore	SVOCs	SOP 5	
SS-154	Soil	0.0-1.0	Macrocore	SVOCs	SOP 5	Contingent sample
SS-155	Soil	0.0-1.0	Macrocore	PCBs (as Aroclors), TAL Metals & Cyanide	SOP 5	
SS-156	Soil	0.0-1.0	Macrocore	PCBs (as Aroclors), TAL Metals & Cyanide	SOP 5	Contingent sample
SS-157	Soil	0.0-1.0	Macrocore	PCBs (as Aroclors), TAL Metals & Cyanide	SOP 5	
SS-158	Soil	0.0-1.0	Macrocore	PCBs (as Aroclors), TAL Metals & Cyanide	SOP 5	Contingent sample
SS-159	Soil	0.0-1.0	Macrocore	Full TCL/TAL, SVOCs SIM, PCBs (as Congeners), Dioxins, Furans	SOP 5	

Sample ID	Matrix	Depth (ft bgs)	Type	Analyte/Analytical Group	Sampling SOP	Comments
SS-160	Soil	0.0-1.0	Macrocore	Full TCL/TAL, SVOCs SIM, PCBs (as Congeners), Dioxins, Furans	SOP 5	Contingent sample
SS-161	Soil	0.0-1.0	Macrocore	Full TCL/TAL, SVOCs SIM, PCBs (as Congeners), Dioxins, Furans	SOP 5	
SS-162	Soil	0.0-1.0	Macrocore	Full TCL/TAL, SVOCs SIM, PCBs (as Congeners), Dioxins, Furans	SOP 5	Contingent sample
SS-163	Soil	0.0-1.0	Macrocore	Full TCL/TAL, SVOCs SIM, PCBs (as Congeners), Dioxins, Furans	SOP 5	
SS-164	Soil	0.0-1.0	Macrocore	Full TCL/TAL, SVOCs SIM, PCBs (as Congeners), Dioxins, Furans	SOP 5	Contingent sample
MW-1	Groundwater	TBD	Low flow	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 7	Existing well
MW-2	Groundwater	TBD	Low flow	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 7	Existing well
MW-3	Groundwater	TBD	Low flow	VOCs, SVOCs, SVOCs SIM, Pesticides, TAL	SOP 7	Existing well

Sample ID	Matrix	Depth (ft bgs)	Type	Analyte/Analytical Group	Sampling SOP	Comments
				Metals & Cyanide (filtered & unfiltered)		
MW-4	Groundwater	TBD	Low flow	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 7	Existing well
MW-5	Groundwater	TBD	Low flow	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 7	Existing well
MW-6	Groundwater	TBD	Low flow	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 7	Existing well
MW-7	Groundwater	TBD	Low flow	VOCs, SVOCs, SVOCs SIM, TAL Metals & Cyanide (filtered & unfiltered)	SOP 7	Existing well
MW-8	Groundwater	TBD	Low flow	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 7	Existing well
MW-9	Groundwater	TBD	Low flow	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 7	Existing well

Sample ID	Matrix	Depth (ft bgs)	Type	Analyte/Analytical Group	Sampling SOP	Comments
MW-10	Groundwater	TBD	Low flow	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 7	Existing well
MW-11	Groundwater	TBD	Low flow	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 7	Proposed new well
MW-12	Groundwater	TBD	Low flow	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 7	Proposed new well
MW-13	Groundwater	TBD	Low flow	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 7	Proposed new well
MW-14	Groundwater	TBD	Low flow	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 7	Proposed new well
MW-15	Groundwater	TBD	Low flow	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 7	Proposed new well
MW-16	Groundwater	TBD	Low flow	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 7	Proposed new well
MW-17	Groundwater	TBD	Low flow	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 7	Proposed new well
X-1	Groundwater	TBD	Low flow	VOCs, TAL Metals & Cyanide (filtered &	SOP 7	Existing well

Sample ID	Matrix	Depth (ft bgs)	Type	Analyte/Analytical Group	Sampling SOP	Comments
				unfiltered)		
X-2	Groundwater	TBD	Low flow	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 7	Existing well
X-3	Groundwater	TBD	Low flow	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 7	Existing well
X-4	Groundwater	TBD	Low flow	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 7	Existing well
X-5	Groundwater	TBD	Low flow	Full TCL/TAL, SVOCs SIM, TAL Metals & Cyanide (filtered)	SOP 7	Existing well
X-6	Groundwater	TBD	Low flow	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 7	Existing well
X-7	Groundwater	TBD	Low flow	Full TCL/TAL, SVOCs SIM, TAL Metals & Cyanide (filtered)	SOP 7	Existing well

Sample ID	Matrix	Depth (ft bgs)	Type	Analyte/Analytical Group	Sampling SOP	Comments
TWP-1	Groundwater	TBD	Macrocore	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 2	Temporary well
TWP-2	Groundwater	TBD	Macrocore	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 2	Temporary well
TWP-3	Groundwater	TBD	Macrocore	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 2	Temporary well
TWP-4	Groundwater	TBD	Macrocore	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 2	Temporary well
TWP-5	Groundwater	TBD	Macrocore	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 2	Temporary well
TWP-6	Groundwater	TBD	Macrocore	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 2	Temporary well
TWP-7	Groundwater	TBD	Macrocore	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 2	Temporary well
TWP-8	Groundwater	TBD	Macrocore	VOCs, TAL Metals & Cyanide (filtered & unfiltered)	SOP 2	Temporary well
TWP-9	Groundwater	TBD	Macrocore	VOCs, TAL Metals & Cyanide (filtered &	SOP 2	Temporary well

Sample ID	Matrix	Depth (ft bgs)	Type	Analyte/Analytical Group	Sampling SOP	Comments
				unfiltered)		
PWS -1	Pore Water	TBD	PDB	VOCs	SOP 20	Passive Sampler
PWS-2	Pore Water	TBD	PDB	VOCs	SOP 20	Passive Sampler
SW-34	Surface Water	TBD	Bailer/direct dip	SVOCs SIM, Full TCL/TAL, TAL Metals & Cyanide (filtered), LL Hg, Hardness, pH, TOC	SOP 8	Teflon-lined bailer
SW-35	Surface Water	TBD	Bailer/direct dip	Full TCL/TAL, SVOCs SIM, TAL Metals & Cyanide (filtered), LL Hg, Hardness, pH, TOC	SOP 8	Teflon-lined bailer
SW-36	Surface Water	TBD	Bailer/direct dip	Full TCL/TAL, SVOCs SIM, TAL Metals & Cyanide (filtered), LL Hg, Hardness, pH, TOC	SOP 8	Teflon-lined bailer

Sample ID	Matrix	Depth (ft bgs)	Type	Analyte/Analytical Group	Sampling SOP	Comments
SW-37	Surface Water	TBD	Bailer/direct dip	Full TCL/TAL, SVOCs SIM, TAL Metals & Cyanide (filtered), LL Hg, Hardness, pH, TOC	SOP 8	Teflon-lined bailer
SW-38	Surface Water	TBD	Bailer/direct dip	Full TCL/TAL, SVOCs SIM, TAL Metals & Cyanide (filtered), LL Hg, Hardness, pH, TOC	SOP 8	Teflon-lined bailer
SW-39	Surface Water	TBD	Bailer/direct dip	Full TCL/TAL, SVOCs SIM, TAL Metals & Cyanide (filtered), LL Hg, Hardness, pH, TOC	SOP 8	Teflon-lined bailer
SW-40	Surface Water	TBD	Bailer/direct dip	Full TCL/TAL, SVOCs SIM, TAL Metals & Cyanide (filtered), LL Hg, Hardness, pH, TOC	SOP 8	Teflon-lined bailer
SW-41	Surface Water	TBD	Bailer/direct dip	Full TCL/TAL, SVOCs SIM, TAL Metals & Cyanide (filtered), LL Hg, Hardness, pH, TOC	SOP 8	Teflon-lined bailer

Sample ID	Matrix	Depth (ft bgs)	Type	Analyte/Analytical Group	Sampling SOP	Comments
SW-42	Surface Water	TBD	Bailer/direct dip	Full TCL/TAL, SVOCs SIM, TAL Metals & Cyanide (filtered), LL Hg, Hardness, pH, TOC	SOP 8	Teflon-lined bailer
SW-43	Surface Water	TBD	Bailer/direct dip	Full TCL/TAL, SVOCs SIM, TAL Metals & Cyanide (filtered), LL Hg, Hardness, pH, TOC	SOP 8	Teflon-lined bailer
SW-44	Surface Water	TBD	Bailer/direct dip	Full TCL/TAL, SVOCs SIM, TAL Metals & Cyanide (filtered), LL Hg, Hardness, pH, TOC	SOP 8	Teflon-lined bailer
SD-34	Sediment	TBD	Grab sample	Full TCL/TAL, SVOCs SIM, pH, TOC, Grain size	SOP 14	
SD-35	Sediment	TBD	Grab sample	Full TCL/TAL, SVOCs SIM, pH, TOC, Grain size	SOP 14	
SD-36	Sediment	TBD	Grab sample	Full TCL/TAL, SVOCs SIM, pH, TOC, Grain size	SOP 14	

Sample ID	Matrix	Depth (ft bgs)	Type	Analyte/Analytical Group	Sampling SOP	Comments
SD-37	Sediment	TBD	Grab sample	Full TCL/TAL, SVOCs SIM, pH, TOC, Grain size	SOP 14	
SD-38	Sediment	TBD	Grab sample	Full TCL/TAL, SVOCs SIM, pH, TOC, Grain size	SOP 14	
SD-39	Sediment	TBD	Grab sample	Full TCL/TAL, SVOCs SIM, pH, TOC, Grain size	SOP 14	
SD-40	Sediment	TBD	Grab sample	Full TCL/TAL, SVOCs SIM, pH, TOC, Grain size	SOP 14	
SD-41	Sediment	TBD	Grab sample	Full TCL/TAL, SVOCs SIM, pH, TOC, Grain size	SOP 14	
SD-42	Sediment	TBD	Grab sample	Full TCL/TAL, SVOCs SIM, pH, TOC, Grain size	SOP 14	
SD-43	Sediment	TBD	Grab sample	Full TCL/TAL, SVOCs SIM, pH, TOC, Grain size	SOP 14	
SD-44	Sediment	TBD	Grab sample	Full TCL/TAL, SVOCs SIM, pH, TOC, Grain size	SOP 14	

QAPP Worksheet #19 & 30: Sample Containers, Preservation, and Hold Times

Laboratory: TestAmerica, Inc. 30 Community Dr, Suite 11 S. Burlington, VT 05403 Attn: Sample Receiving

List any required accreditations/certifications: Active CLP Routine Analytical Services Laboratory with contract number EPW11036 (Organic Multi - SOM01.2) and EPW09044 (Inorganic - ISM01.3); NJ NELAP VT972 Expires 06/30/15

Back-up Laboratory: Not identified

Sample Delivery Method: FedEx Overnight

Analyte/ Analyte Group	Matrix	Method/ SOP	Container (number, size & type per sample)	Preservation	Preparation Holding Time	Analytical Holding Time	Data Package Turnaround
Pesticides	Soil/sediment	SOM01.2/TAB-2	1x 4-ounce (oz) glass jar with Teflon®-lined lid	Cool to <6°C	10 days from verified time of sample receipt (VTSR)	40 days from extraction date	4 weeks
PCB Aroclors	Soil/sediment	SOM01.2/TAB-1	1x 4-oz glass jar with Teflon®-lined lid	Cool to <6°C	10 days from VTSR	40 days from extraction date	4 weeks
PCB Congeners	Soil/sediment	EPA 1668/TAWS-1	1x 4-oz glass jar with Teflon®-lined lid	Cool to <6°C	1 year from VTSR	40 days from extraction date	4 weeks
Metals/Cyanide	Soil/sediment	ISM01.3/TAB-5, TAB-6, TAB-7	1x 4-oz glass jar with Teflon®-lined lid	Cool to <6°C	NA	180 days VTSR – ICP, 26 days VTSR – Hg, 12 days VTSR	4 weeks

Analyte/ Analyte Group	Matrix	Method/ SOP	Container (number, size & type per sample)	Preservation	Preparation Holding Time	Analytical Holding Time	Data Package Turnaround
						- CN	
VOCs	Soil/Sediment	SOM01.2/TAB -4	2 x 40-milliliter (mL) vial 5ml DI water & 1 40mL vial 5mL MeOH	Cool to <6°C	NA	10 day VTSR (vials must be frozen with 48 hours)	4 weeks
SVOCs/ SVOC SIM	Soil/Sediment	SOM01.2/ SOM01.2-SIM/TAB-3	1 – 4oz amber glass	Cool to <6°C	10 days from VTSR	40 days from extraction date	4 weeks
Dioxins, furans	Soil/sediment	EPA 1613/TAWS-14	1x 8-ounce glass jar with Teflon®-lined lid or stainless steel liner	Cool to <6°C	1 year from VTSR	40 days	4 weeks
TOC	Soil/sediment	Lloyd Kahn/TAB-9	1x 2-oz glass jar with Teflon®-lined lid	Cool to <6°C	NA	28 days from collection date	4 weeks
VOCs	Water	SOM01.2/TAB -11	3 x 40-mL vials	No headspace; HCl to pH <2; Cool to <6°C	NA	10 days VTSR	4 weeks

Analyte/ Analyte Group	Matrix	Method/ SOP	Container (number, size & type per sample)	Preservation	Preparation Holding Time	Analytical Holding Time	Data Package Turnaround
SVOCs/ SVOC SIM	Water	SOM01.2/SOM01.2-SIM/TAB-3	2 x 1-liter (L) amber bottles	Cool to <6°C	5 days VTSR	40 days from extraction date	4 weeks
TAL Metals	Water	ISM01.3/TAB-5, TAB-6	1 x 500-mL high density polyethylene (HDPE)	HNO_3 to pH <2; Cool to <6°C	NA	180 days VTSR – ICP, 26 days VTSR - Hg	4 weeks
Cyanide	Water	ISM01.3/TAB-7	1 x 250-mL HDPE	NaOH to pH >12; Cool to <6°C	NA	12 days VTSR	4 weeks
Pesticides	Water	SOM01.2/TAB-2	2 x 1-L amber bottles	Cool to <6°C	5 days VTSR	40 days from extraction date	4 weeks
PCB Aroclors	Water	SOM01.2/TAB-1	2 x 1-L amber bottles	Cool to <6°C	5 days VTSR	40 days from extraction date	4 weeks
Mercury LL	Water	1631E/TANC-12	4 – 40 mL Vials	Cool to <6°C	Unpreserved sample – preserve or analyze within 48 hours of collection; Preserved sample – 28 days	28 days from collection	4 weeks

QAPP Worksheet #20: Field QC Summary

Matrix	Analyte/Analytical Group	Method/ SOP	Field Samples	Field Duplicates	Matrix Spikes	Matrix Spike Duplicates	Equipment Blanks	Trip Blanks	Total # analyses
Soil	SVOCs	SOM01.2/TAB-3	22	1	1	1	1	0	26
Soil	SVOCs SIM	SOM01.2-SIM/TAB-3	12	1	1	1	1	0	16
Soil	Pesticides	SOM01.2/TAB-3	8	1	1	1	1	0	12
Soil	PCBs Aroclors	SOM01.2/TAB-1	30	2	1	1	1	0	35
Soil	TAL Metals	ISM01.3/TAB-5, TAB-6	30	2	1	1	1	0	35
Soil	PCB Congeners	EPA 1668/TAWS-1	14	1	1	1	1	0	18
Soil	Dioxins and Furans	EPA 1613/TAWS-2	14	1	1	1	1	0	18
Groundwater (temporary wells)	VOCs	SOM01.2/TAB-11	9	1	1	1	1	2	15
Groundwater (temporary wells)	TAL Metals and Cyanide (unfiltered)	ISM01.3/TAB-5, TAB-6, TAB-7	9	1	1	1	1	0	13
Groundwater (temporary wells)	TAL Metals and Cyanide (filtered)	ISM01.3/TAB-5, TAB-6, TAB-7	9	1	1	1	1	0	13
Groundwater (permanent wells)	VOCs	SOM01.2/TAB-11	31	3[a]	2[b]	2[b]	7	5	50
Groundwater (permanent	SVOCs	SOM01.2/TAB-3	4	1[a]	1[b]	1[b]	1	0	8

Matrix	Analyte/Analytical Group	Method/ SOP	Field Samples	Field Duplicates	Matrix Spikes	Matrix Spike Duplicates	Equipment Blanks	Trip Blanks	Total # analyses
wells)									
Groundwater (permanent wells)	SVOCs SIM	SOM01.2-SIM/TAB-3	4	1[a]	1[b]	1[b]	1	0	8
Groundwater (permanent wells)	Pesticides	SOM01.2/TAB-2	3	1[a]	1[b]	1[b]	1	0	7
Groundwater (permanent wells)	PCB Aroclors	SOM01.2/TAB-1	2	1[a]	1[b]	1[b]	1	0	6
Groundwater (permanent wells)	TAL Metals and Cyanide (unfiltered)	ISM01.3/TAB-5, TAB-6, TAB-7	31	3[a]	2[b]	2[b]	7	0	45
Groundwater (permanent wells)	TAL Metals and Cyanide (filtered)	ISM01.3/TAB-5, TAB-6, TAB-7	31	3[a]	2[b]	2[b]	7	0	45
Pore Water	VOCs	SOM01.2/TAB-11	2	1	0[c]	0[c]	0[c]	1	4
Surface Water	VOCs	SOM01.2/TAB-11	11	1	1	1	1	2	17
Surface Water	SVOCs	SOM01.2/TAB-3	11	1	1	1	1	0	15
Surface Water	SVOCs SIM	SOM01.2-SIM/TAB-3	11	1	1	1	1	0	15
Surface Water	Pesticides	SOM01.2-TAB-2	11	1	1	1	1	0	15
Surface Water	PCBs Aroclors	SOM01.2/TAB-1	11	1	1	1	1	0	15
Surface	TAL Metals and	ISM01.3/TAB-5,	11	1	1	1	1	0	15

Matrix	Analyte/Analytical Group	Method/ SOP	Field Samples	Field Duplicates	Matrix Spikes	Matrix Spike Duplicates	Equipment Blanks	Trip Blanks	Total # analyses
Water	Cyanide (unfiltered)	TAB-6, TAB-7							
Surface Water	TAL Metals and Cyanide (Filtered)	ISM01.3/TAB-5, TAB-6, TAB-7	11	1	1	1	1	0	15
Surface Water	Low-Level Mercury	EPA 1631E/TANC-12	11	1	1	1	1	0	15
Surface Water	Hardness	Calculation	11	0	0	0	0	0	11
Sediment	VOCs	SOM01.2/TAB-4	11	1	1	1	1	2	17
Sediment	SVOCs	SOM01.2/TAB-3	11	1	1	1	1	0	15
Sediment	SVOCs SIM	SOM01.2-SIM/TAB-3	11	1	1	1	1	0	15
Sediment	Pesticides	SOM01.2-TAB-2	11	1	1	1	1	0	15
Sediment	PCBs Aroclors	SOM01.2/TAB-1	11	1	1	1	1	0	15
Sediment	TAL Metals and Cyanide	ISM01.3/TAB-5, TAB-6, TAB-7	11	1	1	1	1	0	15
Sediment	pH, TOC, grain size	Lloyd Kahn/TAB-9	11	0	0	0	0	0	11

[a] Two field duplicate samples will be collected during the first groundwater event and one field duplicate sample will be collected during the second groundwater event.

[b] One matrix spike and matrix spike duplicate sample will be collected during the first groundwater event and one matrix spike and matrix spike duplicate sample will be collected during the second groundwater event.

[c] No matrix spike or matrix spike duplicate samples were collected as the sample matrix consists of deionized water. No equipment blank is required because the samples are transferred directly from the pore water Permeable Diffusion Bag to the sample bottles.

QAPP Worksheet #21: Field SOPs

SOP # or reference	Title, Revision, Date, and URL (if available)	Originating Organization	SOP option or Equipment Type (if SOP provides different options)	Modified for Project? Y/N	Comments
SOP 1	Water Level Measurement	ARCADIS		N	
SOP 2	Standard GW Sampling for Monitoring Wells	ARCADIS		N	
SOP 3	Monitoring Well Installation	ARCADIS		N	
SOP 4	Monitoring Well Development	ARCADIS		N	
SOP 5	Drilling Procedures for Collecting and Screening of Soil Samples	ARCADIS		N	
SOP 6	Soil Description	ARCADIS		N	
SOP 7	Low-Flow Groundwater Purging and Sampling Procedures for Monitoring Wells	ARCADIS		N	
SOP 8	Surface Water Sampling	ARCADIS		N	
SOP 9	Chain-of-Custody, Handling, Packing and Shipping	ARCADIS		N	
SOP 10	Investigation-Derived Waste Handling and Storage	ARCADIS		N	
SOP 11	Field Equipment Decontamination	ARCADIS		N	

SOP # or reference	Title, Revision, Date, and URL (if available)	Originating Organization	SOP option or Equipment Type (if SOP provides different options)	Modified for Project? Y/N	Comments
SOP 12	Measuring Basic Water Quality Parameters In-situ	ARCADIS		N	
SOP 13	Sediment Core Collection	ARCADIS		N	
SOP 14	Sediment Sampling	ARCADIS		N	
SOP 15	Extraction/Preservation of Soil/ Sediment Samples for VOCs	ARCADIS		N	
SOP 16	Compositing or Homogenizing Samples	ARCADIS		N	
SOP 17	Surface and Subsurface Soil Sampling Using Manual Methods	ARCADIS		N	
SOP 18	Soil Drilling and Sample Collection	ARCADIS		N	
SOP 19	Field Log Book Entries	ARCADIS		N	
SOP 20	Pore Water Sampling	ARCADIS		N	

QAPP Worksheet #22: Field Equipment Calibration, Maintenance, Testing, and Inspection

Field Equipment	Activity	SOP Reference	Title or position of responsible person	Frequency	Acceptance Criteria	Corrective Action
Water Quality meter	Check all membranes and sensors, cable and check battery charge	SOP 12	Field Staff	See SOP 12	See SOP 12	See SOP 12
Photoionization Detector (PID)	Calibrate	SOP 5	Field Staff	See SOP 5	See SOP 5	See SOP 5
Water-Level Meter	Check battery	SOP 1	Field Staff	See SOP 1	See SOP 1	See SOP 1
GPS	As required by manufacturer specification	NA	Field Staff	NA	NA	NA

QAPP Worksheet #23: Analytical SOP's

SOP #	Title, Date, and URL (if available)	Definitive or Screening Data	Matrix/Analytical Group	SOP Option or Equipment Type	Modified for Project? Y/N
F-4	FSP – Water Column Sampling Procedures	Definitive	Temperature, pH, turbidity, conductivity, dissolved oxygen (DO)	Water quality meter	N
F-3	FSP – Sediment Sampling Procedures	Screening	Water surface elevation	Water level meter	N
F-3	FSP – Sediment Sampling Procedures	Screening	Core characterization	Unified Soil Classification System (USCS) or United States Department of Agriculture (USDA) soil classification system	N
Agriculture (USDA) soil classificati on systemNT AWS-1	'PCB Analysis by HRGC/HRMS',WS-ID-0013, Rev 4.4, 5/07/14 and 'PCB Preparation for Analysis by HRGC/HRMS' WS-IDP-0013, Rev 3.0, 9/12/14	Definitive	PCB Congeners in Water, Soil and Sediment	High Resolution Gas Chromatography/ High Resolution/Mass Spectrometry (HRGC/HRMS)	N
TAWS-2	'Analysis of Tetra- through Octa Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS by Method 1613B', WS-ID-0007, Rev 3.7, 2/07/14 and 'Preparation of Samples for Tetra- through Octa Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS by Method 1613B' WS-IDP-0007, Rev 1.9, 4/11/2014	Definitive	Dioxins and Furans in Water, Soil and Sediment	HRGC/HRMS	N
TAB-1	'Determination of Aroclors by GC/ECD (CLP SOW SOM01.2)', BR-GC-010, Rev 1, 6/02/08 and 'Extraction and Cleanup Procedure for the Determination of Aroclors	Definitive	PCB Aroclors in Water, Soil and Sediment	Gas Chromatography/ Electron Capture Dectector (GC/ECD)	N

	(CLP SOW SOM01.2)', BR-EX-013, Rev 2, 2/21/14				
TAB-2	'Determination of Pesticides by GC/ECD (CLP SOW SOM01.2)', BR-GC-011, Rev 1, 6/02/08 and 'Sample Preparation and Cleanup Procedure for Pesticides (CLP SOW SOM01.2)', BR-EX-014, Rev 2, 02/24/14	Definitive	Pesticides in Water, Soil and Sediment	GC/ECD	N
TAB-3	'SVOCs by GC/MS and GC/MS SIM (CLP SOM01.2)', BR-MS-006, Rev 1, 11/10/10 and 'Sample Preparation and Cleanup Procedure for SVOCs (CLP SOW SOM01.2)',BR-EX-015 Rev 2, 02/24/14	Definitive	SVOCs in Water, Soil and Sediment	Gas Chromatography/ Mass Spectrometry (GC/MS)	N
TAB-4	'Analytical Method for Low/Medium Volatiles (CLP SOW SOM01.2)', BR-MV-009 Rev 0, 1/01/08	Definitive	VOCs in Water, Soil and Sediment	GC/MS	N
TAB-5	'Determination of Trace Metals by ICP-OES (CLP SOW ISM01.3)', BR-ME-019, Rev 1, 10/29/12	Definitive	Metals, except mercury in Water, Soil and Sediment	Inductively coupled atomic plasma-optical emission spectroscopy (ICP-OES)	N
TAB-6	'Determination of Mercury by Cold Vapor Analysis (CLP SOW ISM01.2)', BR-ME-018, Rev 0, 08/06/10	Definitive	Mercury in Water, Soil, and Sediment	Mercury autoanalyzer	N
TAB-7	'Determination of Total Cyanide'(CLP SOW ISM01.3), BR-WC-023, Rev 0, 08/06/10		Cyanide in Water, Soil, and Sediment		
TAB-9	'Total Organic Carbon in Soils & Sediments (Lloyd Kahn)', BR-WC-008, Rev 14, 03/18/14	Definitive	TOC	TOC analyzer	N
TAB-11	'Analytical Method for Trace Volatiles (CLP SOW SOM01.2)', BR-MV-010, Rev 0, 1/1/2008	Definitive	VOCs in Water	GC/MS	N
TANC-12	'Preparation and Analysis of Mercury in Aqueous and Solid Samples by Cold Vapor Atomic Fluorescence Method 1631E', NC-MT-001, Rev 6, 9/27/13	Definitive	Low level Mercury in Water	Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS)	N

QAPP Worksheet #24: Analytical Instrument Calibration

Instrument	Calibration Procedure	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/position responsible for CA	SOP Reference
GC/MS for VOCs by SOM01.2	Instrument performance check: Bromofluorobenzene (BFB)	Once at the beginning of each 12-hour period during which samples or standards are analyzed.	% Relative abundance, see SOM01.2 Exhibit D Low/Medium Volatiles Section 17 Table 1	Retune instrument.	TestAmerica Analyst	See TAB-4 and TAB-11
	Initial calibration (ICAL) – minimum of five concentrations	Prior to sample analysis, after instrument performance check acceptance criteria have been met.	Relative standard deviation (RSD) and RRF, see SOM01.2 Exhibit D Low/Medium Volatiles Section 17 Table 4	Inspect system, correct problem, rerun calibration and affected samples.		
	Continuing calibration verification (CCV) – opening	Prior to sample analysis and after instrument performance check and ICAL acceptance criteria and have been met.	Percent difference (%D) and RRF, see SOM01.2 Exhibit D Low/Medium Volatiles Section 17 Table 4	Inspect system, correct problem, rerun calibration and affected samples.		
	CCV – closing	After all samples and blanks have been analyzed, and before the	%D ±50% for all compounds and RRF ≥ 0.010 for all compounds.	Inspect system, correct problem, rerun calibration and affected samples.		

Instrument	Calibration Procedure	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/position responsible for CA	SOP Reference
		end of the 12-hour time period. May be used as the opening CCV for a new 12-hour analytical sequence.				
GC/MS for SVOCs by SOM01.2 and SOM01.2 SIM (PAHs)	Instrument performance check: Decafluorotriphenylphosphine (DFTPP)	Once at the beginning of each 12-hour period during which samples or standards are analyzed.	% Relative abundance, see SOM01.2 Exhibit D Semivolatiles Section 17 Table 1	Retune instrument.	TestAmerica Analyst	See TAB-3
	Initial calibration (ICAL) – minimum of five concentrations	Prior to sample analysis, after instrument performance check acceptance criteria have been met.	Relative standard deviation (RSD) and RRF, see SOM01.2 Exhibit D Semivolatiles Section 17 Table 4	Inspect system, correct problem, rerun calibration and affected samples.		
	Continuing calibration verification (CCV) – opening	Prior to sample analysis and after instrument performance check and ICAL acceptance criteria and have been met.	Percent difference (%D) and RRF, see SOM01.2 Exhibit D Semivolatiles Section 17 Table 4	Inspect system, correct problem, rerun calibration and affected samples.		
	CCV - closing	After all samples and blanks have been analyzed, and before the end of the 12-hour time period. May be used as	%D ±50% for all compounds and RRF ≥ 0.010 for all compounds.	Inspect system, correct problem, rerun calibration and affected samples.		

Instrument	Calibration Procedure	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/position responsible for CA	SOP Reference
		the opening CCV for a new 12-hour analytical sequence.				
HRGC/HRMS for EPA 1668 and 1613	Instrument performance check (tune).	Prior to initial and continuing calibration.	As per method.	Retune instrument.	TestAmerica Analyst	See TAWS-1 and TAWS-2
	Initial calibration — a minimum of five concentration levels for all compounds.	Prior to sample analysis; minimum of annually.	Each compound RRF RSD ≤ 35% for all compounds and RF RSD ≤ 20%.	Inspect system, correct problem, rerun calibration and affected samples if RSD > 50%.		
	Continuing calibration — before sample analysis; one midpoint standard.	Before sample analysis and every 12 hours.	Each compound RRF %D ≤ 35% and RF %D ≤20%.	Inspect system, correct problem, rerun calibration and affected samples if %D > 80%.		
GC/ECD for PCB Aroclors by SOM01.2	ICAL – minimum of five concentrations for Aroclors 1016 and 1260; single mid-point calibration for other Aroclors	Prior to sample analysis. If any Aroclors other than 1016 and 1260 are detected in a sample, a five-point initial calibration is required for the detected Aroclor.	RSD ≤ 20% for any Aroclor analyzed at a five-point calibration.	Inspect system, correct problem, rerun calibration and affected samples.	TestAmerica Analyst	See TAB-1
	CCV – opening; mid-point concentration for Aroclor 1016/1260 and any other Aroclor detected in a sample	At the beginning of the analytical sequence.	Retention time (RT) within the RT window established for the ICAL. %D within ±15.0%.	Inspect system, correct problem, rerun calibration and affected samples.		
	CCV – closing; mid-point concentration for Aroclor 1016/1260 and any other Aroclor detected in a sample	At the beginning of the analytical sequence.	RT within the RT window established for the ICAL. %D within ±50.0%.	Inspect system, correct problem, rerun calibration and affected samples.		
GC/ECD for Pesticides by SOM01.2	ICAL – single-component compounds – minimum of five concentrations	Prior to sample analysis.	Initial Calibration RSD ≤ 20% for compounds or linear $r^2 \geq 0.99$, except for	Inspect system, correct problem, and rerun calibration.	TestAmerica Analyst	See TAB-2

Instrument	Calibration Procedure	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/position responsible for CA	SOP Reference
			alpha-BHC and delta-BHC must be ≤ 25.0%, %RSD of the two surrogates must be ≤ 30.0%.			
	ICAL – Toxaphene (multi-component compound) – minimum of five concentrations	Prior to sample analysis.	The %RSD of the CFs for each Toxaphene peak and surrogates must be ≤ 30.0%	Inspect system, correct problem, and rerun calibration.		
	Opening CCV – before sample analysis; one midpoint standard. Toxaphene CCV analyzed if detected in sample.	Prior to sample analysis.	The %D for compounds and surrogates in the PEM ± 25.0%; %D in the calibration verification standard (CS) ± 20.0%	Inspect system, correct problem, and rerun calibration.		
	Closing CCV	After 12 hours.	Same as Opening CCV	Inspect system, correct problem, rerun calibration and affected samples.		
ICP-AES for ISM01.3	ICAL: blank and at least five standards; one standard shall be at or below	Daily, prior to sample analysis.	Correlation coefficient r ≥ 0.995.	Terminate analysis, correct problem, and re-verify calibration	TestAmerica Analyst	See TAB-5
	Initial calibration verification (ICV)	Following each instrument calibration.	Within ±10% of the true value.	Terminate analysis, correct problem, and re-verify calibration.		
	CCV	Every 2 hours of analytical run, and at the beginning and end of each run.	Within ±10% of the true value.	Terminate analysis, correct problem, re-verify calibration, and reanalyze all samples analyzed since the last compliant CCV.		
	Initial and continuing calibration blank (ICB/CCB)	ICB: Following each instrument calibration, immediately after the ICV. CCB: Every 2 hours of a run,	< CRQL	Terminate analysis, correct problem, recalibrate instrument, re-verify calibration, and reanalyze all samples analyzed since the lab compliant CCB.		

Instrument	Calibration Procedure	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/position responsible for CA	SOP Reference
		and at the beginning and end of each run. Performed immediately after the CCV.				
CVAA for ISM01.3 (mercury)	ICAL: blank and at least five standards; one standard shall be at or below	Daily or each time instrument is set up, after ICV or CCV failures, and after major instrument adjustment.	Correlation coefficient r ≥ 0.995.	Terminate analysis, correct problem, and re-verify calibration.	TestAmerica Analyst	See TAB-6
	Initial calibration verification (ICV)	Following each instrument calibration.	Within ±15% of the true value.	Terminate analysis, correct problem, and re-verify calibration.		
	CCV	Every hour of a run, and at the beginning and end of each run.	Within ±15% of the true value.	Terminate analysis, correct problem, re-verify calibration, and reanalyze all samples analyzed since the last compliant CCV.		
	Initial and continuing calibration blank (ICB/CCB)	ICB: Following each instrument calibration, immediately after the ICV. CCB: Every 2 hours of a run, and at the beginning and end of each run. Performed immediately after the CCV.	< CRQL	Terminate analysis, correct problem, recalibrate instrument, re-verify calibration, and reanalyze all samples analyzed since the lab compliant CCB.		
CVAFS for Low Level Mercury Analysis by EPA 1631E	Initial calibration (ICAL) per manufacturer's instructions, with a minimum of six standards and three calibration blanks.	Daily initial calibration prior to sample analysis	Calibration factors must have < 15% RSD, and the low standard must calculate back to +	Evaluate standard and instrument response. Repeat ICAL.	TestAmerica Analyst	See TANC-12

Instrument	Calibration Procedure	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/position responsible for CA	SOP Reference
			25% of the true value.			
	Second-source ICV (QCS)	Beginning of every analytical sequence.	80% - 120% Recovery	Terminate analysis, correct the problem, recalibrate, or re-prep with calibration curve.		
	Continuing calibration verification (CCV or OPR)	Following ICV/ICB, after every 10 samples and the end of the sequence	77% - 123% recovery	Evaluate standard and instrument response. If problem with instrument (autosampler failure, response poor, etc.) or standards, correct as appropriate, then repeat. If still fails, repeat initial calibration. Re-analyze all samples since the last successful calibration verification.		
	Calibration blank (ICB/CCB)	After ICAL, after CCV calibration, after every 10 samples, and at the end of the sequence	No target analytes ≥ RL in accordance with requirements	Terminate analysis, correct problem, recalibrate instrument, re-verify calibration, and reanalyze all samples analyzed since the lab compliant CCB.		
pH Meter	Initial calibration with two buffers that bracket pH of samples at room temperature.	Daily.	Slope reading after calibration should be between 94-102%.	If slope falls out of range of slope reading, troubleshoot and fix problem according to user's manual.	TestAmerica Analyst	See laboratory QAM
Analytical Balance	See laboratory Quality Assurance Manual (QAM)	Daily.	Not applicable	Inspect system, correct problem, rerun calibration and affected samples.	TestAmerica Analyst	See laboratory QAM

Note: the analytical laboratory, TestAmerica, has a SOP review cycle related to the CLP SOW methods. This review cycle only occurs as the EPA CLP SOW methods are updated and promulgated.

Worksheet #25: Analytical Instrument and Equipment Maintenance, Testing, and Inspection

Instrument /Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/ position responsible for CA	Reference
CVAFS	Check argon flow, pump tubing, drain, soda lime drying tube.	Sensitivity check	Instrument performance and sensitivity	Daily	CCV pass criteria	Troubleshoot and correct problem	TestAmerica Chemist	NC-MT-001
CVAFS	Check Hg lamp intensity	Sensitivity check	Instrument performance and sensitivity	Semi-annually	CCV pass criteria	Troubleshoot and correct problem	TestAmerica Chemist	NC-MT-001
CVAFS	Change Hg lamp, liquid/gas separator, Nafion dryer	General maintenance	Instrument performance and sensitivity	As Needed	CCV pass criteria	Troubleshoot and correct problem	TestAmerica Chemist	NC-MT-001
GC/MS	Clean Injection Port and Liner, Change Septa, Replace or clip Guard Column and or Analytical Column, and Fill		Check Injection Port and Liner, Check Septa, Check Guard Column and or Analytical Column, and Check	As required	Passing calibration	Perform maintenance, check standards, recalibrate	Laboratory Analyst	SOP BR-QAM

Instrument /Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/ position responsible for CA	Reference
	Autosampler rinse vials		Autosampler rinse vials					
GC	Replace Septa, Clean and replace Injection Port Liner, Replace or clip Guard Column Replace or clip Analytical Column Bake, Re-foil, Refurbish Detector		Instrument performance and sensitivity	As required	Passing calibration	Perform maintenance, check standards, recalibrate	Laboratory Analyst	SOP BR-QAM
ICP-AES	Replace Peristaltic Pump tubing, Clean Torch and Cones, Fill Rinse, Internal Standard, and Standards Vessels, Empty Waste Vessels		Check Peristaltic Pump tubing, Check Torch and Cones, Check Level of Rinse, Internal Standard, and Standards Vessels, Check	As required	Passing calibration	Perform maintenance, check standards, recalibrate	Laboratory Analyst	SOP BR-QAM

Instrument /Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/ position responsible for CA	Reference
			Waste Vessels					
CVAA	Lubricate Autosampler rods, Clean Autosampler Fill Rinse Vessel, Fill Stannous Chloride, and Empty Waste Vessel		Check Peristaltic Pump tubing, Check/ Rinse Vessel, Check Stannous Chloride, and Check Waste Vessel	As required	Passing calibration	Perform maintenance, check standards, recalibrate	Laboratory Analyst	SOP BR-QAM
GC/HRMS	Parameter Setup	Physical check	Physical check	Initially; prior to DCC	Correct Parameters	Reset if incorrect	TestAmerica Chemist	WS-ID-0007
GC/HRMS	Tune Check	Instrument Performance	Conformance to instrument tuning.	Initially; prior to DCC	Compliance to ion abundance criteria	Correct the problem and repeat tune check	TestAmerica Chemist	WS-ID-0007

Worksheet #26 & 27: Sample Handling, Custody, and Disposal

Worksheet #26 – Sample Handling System

Sample Collection, Packaging and Shipment
Sample Collection (Personnel/Organization): Field Personnel/ARCADIS
Sample Packaging (Personnel/Organization): Field Personnel/ARCADIS
Coordination of Shipment (Personnel/Organization): Field Personnel/ARCADIS
Type of Shipment/Carrier: pick-up at site by TestAmerica courier, or Federal Express to TestAmerica
Sample Receipt and Analysis
Sample Receipt (Personnel/Organization): Sample Custodian/TestAmerica
Sample Custody and Storage (Personnel/Organization): Sample Custodian/TestAmerica
Sample Preparation (Personnel/Organization): Lab Analysts/TestAmerica
Sample Determinative Analysis (Personnel/Organization): Lab Analysts/TestAmerica
Sample Archiving
Field Sample Storage: 30 days from submittal of laboratory final report
Sample Extract/Digestate Storage (number of days from extraction/digestion): 60 days
Sample Disposal
Personnel/Organization: Sample Custodian/TestAmerica
Number of Days from Analysis: 30-day minimum from submittal of laboratory final report

Worksheet #27 – Sample Custody Requirements

Sample Handling and Custody Requirements
At all times, field and laboratory personnel will be aware of the need to maintain all samples, whether in the field or in the laboratory, under strict chain-of-custody and in a manner to retain physical properties and chemical composition. This Worksheet details sample handling and custody requirements from collection to ultimate disposal.
Sample Handling
Sample packaging and shipment procedures are designed so that the samples will arrive at the laboratory, with the chain-of-custody, intact. Samples will be packaged for shipment as outlined below: • Securely affix the sample label to the container with clear packing tape. • Check the cap on the sample container to confirm that it is properly sealed. • Wrap the sample container cap with clear packing tape to prevent the label from becoming loose. • Complete the chain-of-custody form with the required sampling information and confirm that the recorded information matches the sample labels. **Note:** If the designated sampler relinquishes the samples to other sampling or field personnel for packing or other purposes, the sampler will complete the chain-of-custody prior to this transfer. The appropriate personnel will sign and date the chain-of-custody form to document the sample custody transfer. • Using duct tape, secure the outside drain plug at the bottom of the cooler. • Wrap sample containers in bubble wrap or other cushioning material. • Place 1 to 2 inches of cushioning material at the bottom of the cooler. • Place the sealed sample containers into the cooler. • Place ice in plastic bags and seal. Place loosely in the cooler. • Fill the remaining space in the cooler with cushioning material. • Place chain-of-custody forms in a plastic bag and seal. Tape the forms to the inside of the cooler lid. • Close the lid of the cooler, lock and secure with duct tape. • Wrap strapping tape around both ends of the cooler at least twice. • Mark the cooler on the outside with the shipping address and return address, affix “Fragile” labels and draw (or affix) arrows indicating “this side up.” Cover the labels with clear plastic tape. • Place a signed custody seal over the sample cooler lid.
Shipping Procedures
Samples will be packaged by field personnel and transported as low-concentration environmental samples. Samples will be hand delivered or delivered by an express carrier within 48 hours of the time of collection. Shipments will be accompanied by the chain-of-custody form identifying the contents. The original form will accompany the shipment; copies will be retained by the sampler for the sampling office records. If the

Worksheet #27 – Sample Custody Requirements

samples are sent by common carrier, a bill of lading will be used. Receipts or bills of lading will be retained as part of the permanent project documentation. Commercial carriers are not required to sign off on the chain-of-custody form as long as the forms are sealed inside the sample cooler and the custody seals remain intact.

Sample custody seals and packing materials for filled sample containers will be provided by the analytical laboratory. The filled, labeled and sealed containers will be placed in a cooler on ice and carefully packed to eliminate the possibility of container breakage.

Field Custody Procedures

The objective of field sample custody is to protect samples from tampering from the time of sample collection through time of transport to the analytical laboratory. Persons will have custody of samples when the samples are in their physical possession, in their view after being in their possession, or in their physical possession and secured so they cannot be tampered with. In addition, when samples are secured in a restricted area accessible only to authorized personnel, they will be deemed to be in the custody of such authorized personnel.

Field custody documentation consists of both field logbooks and field chain-of-custody forms.

Field logbooks will provide the means of recording the data collecting activities that are performed. As such, entries will be described in as much detail as possible so that persons going to the site could reconstruct a particular situation without reliance on memory.

Field logbooks will be bound field survey books or notebooks. Logbooks will be assigned to field personnel, but will be stored in a secure location when not in use. Each logbook will be identified by the project-specific document number. The title page of each logbook will contain the following:

- person to whom the logbook is assigned
- logbook number
- project name
- project start date
- end date

Entries into the logbook will contain a variety of information. At the beginning of each entry, the date, start time, weather conditions, names of all sampling team members present, level of personal protection being used, and signature of the person making the entry will be provided. The names of visitors to the site and field sampling or investigation team personnel, as well as the purpose of their visit, will also be recorded in the field logbook.

Measurements made and samples collected will be recorded. Entries will be made in ink, with no erasures. If an incorrect entry is made, the information will be crossed out with one strike mark. Whenever a sample is collected or a measurement is made, a detailed description of the location of the station will be recorded. The number of the photographs taken, if any, will also be noted. All equipment used to make

Worksheet #27 – Sample Custody Requirements

measurements will be identified, along with the date of calibration.

Samples will be collected following the sampling procedures documented in the Standard Operating Procedures in Appendix A and Worksheet #14. The equipment used to collect samples will be noted, along with the time of sampling, sample description, depth at which the sample was collected, volume and number of containers. Sample identification numbers will be assigned prior to sample collection. Field duplicate samples, which will receive an entirely separate sample identification number, will be noted under sample description.

Sample Labels

Sample labels will be affixed to sample bottles prior to delivery at the sampling site. The following information is required on each sample label:

- project name
- date collected
- time collected
- location
- name of sampler
- analysis to be performed
- preservative
- sample number

Chain-of-Custody Record

Completed chain-of-custody forms will be required for all samples to be analyzed. Chain-of-custody forms will be initiated by the sampling crew in the field. The chain-of-custody forms will contain the unique sample identification number, sample date and time, sample description, sample type, preservation (if any) and analyses required. The original chain-of-custody form will accompany the samples to the laboratory. Copies of the chain-of-custody will be made prior to shipment (or multiple copy forms will be used) for field documentation. The chain-of-custody forms will remain with the samples at all times. The samples and signed chain-of-custody forms will remain in the possession of the sampling crew until the samples are delivered to the express carrier (e.g., Federal Express), hand delivered to a mobile or permanent laboratory, or placed in secure storage.

Sample labels will be completed for each sample using waterproof ink. The labels will include the information listed in the previous section (Sample Labels). The completed sample labels will be affixed to each sample bottle and covered with clear tape.

Whenever samples are split with a government agency or other party, a separate chain-of-custody will be prepared for those samples and marked to identify the party with whom the samples are being split. The person relinquishing the samples to the facility or agency should request the representative's signature acknowledging sample receipt. If the representative is unavailable or refuses, note this in the "Received By" space.

Worksheet #27 – Sample Custody Requirements

Laboratory Custody Procedures
Upon sample receipt, laboratory personnel will be responsible for sample custody. The original field chain-of-custody form will accompany all samples requiring laboratory analysis. The laboratory will use chain-of-custody guidelines described in the United States Environmental Protection Agency guidance documents. Samples will be kept secured in the laboratory until all stages of analysis are complete. All laboratory personnel having samples in their custody will be responsible for documenting and maintaining sample integrity. Immediately upon sample receipt, the laboratory sample custodian will verify the integrity of the cooler seal, open the cooler, and compare the contents against the field chain-of-custody. If a sample container is missing, a sample container is received broken, the sample is in an inappropriate container, or the sample has not been preserved by appropriate means, ARCADIS will be notified. The laboratory sample custodian will be responsible for logging the samples in, assigning a unique laboratory identification number to each sample, labeling the sample bottle with the laboratory identification number, and moving the sample to an appropriate storage location to await analysis. The project name, field sample code, date sampled, date received, analysis required, storage location and date, and action for final disposition will be recorded in the laboratory tracking system. Relevant custody documentation will be placed in the project file.

QAPP Worksheet #28: Analytical Quality Control and Corrective Action

Quality Assurance Project Plan Worksheet #28-1 – Quality Control Samples (Semivolatile Organic Compounds in Water by SOM01.2 and SOM01.2-SIM)

Matrix	Water	**Analytical Method/ SOP Reference**	SOM01.2/SOM01.2-SIM/TAB-3	**No. of Sample Locations**	Numerous	
Analytical Group	SVOCs	**Sampler's Name**	NA			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling SOP	SOP 2, SOP 7, SOP 8, SOP 20	**Analytical Organization**	Test America			
Quality Control (QC) Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Field duplicate	One per 10 field samples of similar matrix	RPD < 35%	Qualify data as needed.	Data validator	Precision – overall	RPD < 35%
DMC	Added to all samples and blanks	%R, see SOM01.2 – Exhibit D Semivolatiles Tables 6 (%R) 7 (associated target compounds), and 8 (associated target compounds – SIM)	Check calculations, sample preparation logs, DMC standard spiking solution, and instrument operation. Re-extract/reanalyze samples. Qualify data as needed.	Laboratory analyst and/or data validator	Accuracy/bias	%R, see SOM01.2 – Exhibit D Semivolatiles Tables 6 (%R) 7 (associated target compounds), and 8 (associated target compounds – SIM)
Method blanks	One per analytical batch	< CRQL	Investigate source of contamination and re-extract/reanalyze associated samples. Qualify data as needed.	Laboratory analyst and/or data validator	Accuracy/bias contamination	< CRQL

Quality Assurance Project Plan Worksheet #28-1 – Quality Control Samples (Semivolatile Organic Compounds in Water by SOM01.2 and SOM01.2-SIM)

Matrix	Water	**Analytical Method/ SOP Reference**	SOM01.2/SOM01.2-SIM/TAB-3	**No. of Sample Locations**	Numerous	
Analytical Group	SVOCs	**Sampler's Name**	NA			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling SOP	SOP 2, SOP 7, SOP 8, SOP 20	**Analytical Organization**	Test America			
Quality Control (QC) Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Equipment blanks	One per 20 field samples	< CRQL	Qualify data as needed.	Data validator	Accuracy/bias contamination	< CRQL
Instrument check: DFTPP	One per calibration	%R, see SOM01.2 – Exhibit D Semivolatiles Table 1	Re-tune the instrument and reanalyze associated samples.	Laboratory analyst	Accuracy/bias	%R, see SOM01.2 – Exhibit D Semivolatiles Table 1
Internal standard	Added to all samples and blanks	Area response 50.0% to 200% and retention time (RT) ±30.0 seconds from associated 12-hour calibration standard, see SOM01.2 – Exhibit D Semivolatiles Table 2 (associated target compounds)	Check calculations, internal standard solutions, and instrument operation. Re-extract/reanalyze samples. Qualify data as needed.	Laboratory analyst and/or data validator	Precision	Area response 50.0% to 200% and retention time (RT) ±30.0 seconds from associated 12-hour calibration standard, see SOM01.2 – Exhibit D Semivolatiles Table 2 (associated target compounds)

Quality Assurance Project Plan Worksheet #28-1 – Quality Control Samples (Semivolatile Organic Compounds in Water by SOM01.2 and SOM01.2-SIM)

Matrix	Water	**Analytical Method/ SOP Reference**	SOM01.2/SOM01.2-SIM/TAB-3	**No. of Sample Locations**	Numerous	
Analytical Group	SVOCs	**Sampler's Name**	NA			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling SOP	SOP 2, SOP 7, SOP 8, SOP 20	**Analytical Organization**	Test America			
Quality Control (QC) Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
MS[2]	One per batch	%R, see SOM01.2 - Exhibit D Semivolatile Table 5	Re-extract/reanalyze samples. Qualify data as needed	Laboratory analyst and/or data validator	Accuracy/bias	%R, see SOM01.2 - Exhibit D Semivolatile Table 5
MSD[2]	One per batch	%R, see SOM01.2 - Exhibit D Semivolatile Table 5	Re-extract/reanalyze samples. Qualify data as needed	Laboratory analyst and/or data validator	Accuracy/bias	%R, see SOM01.2 - Exhibit D Semivolatile Table 5
MS/MSD[2]	One per batch	%R, see SOM01.2 - Exhibit D Semivolatile Table 5	Re-extract/reanalyze samples. Qualify data as needed	Laboratory analyst and/or data validator	Precision	%R, see SOM01.2 - Exhibit D Semivolatile Table 5

Note:

[1] An analytical batch is defined as no more than 20 analytical samples including field samples and field blanks.

[2] MS and MSD must be client-provided.

Quality Assurance Project Plan Worksheet #28-2 – Quality Control Samples (Volatile Organic Compounds in Water by SOM01.2)

Matrix	Water	**Analytical Method/ SOP Reference**	SOM01.2/TAB-11	**No. of Sample Locations**	Numerous	
Analytical Group	VOCs	**Sampler's Name**	NA			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling SOP	SOP 2, SOP 7, SOP 8, SOP 20	**Analytical Organization**	Test America			
Quality Control (QC) Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Field duplicate	One per 10 field samples of similar matrix	RPD < 35%	Qualify data as needed.	Data validator	Precision – overall	RPD < 35%
DMC	Added to all samples and blanks	%R, see SOM01.2 – Exhibit D Low/Medium Volatiles Tables 5 (%R) and 7 (associated target compounds)	Check calculations, sample preparation logs, DMC standard spiking solution, and instrument operation. Re-extract/reanalyze samples. Qualify data as needed.	Laboratory analyst and/or data validator	Accuracy/bias	%R, see SOM01.2 – Exhibit D Low/Medium Volatiles Tables 5 (%R) and 7 (associated target compounds)
Method blanks	One per analytical batch	< CRQL	Investigate source of contamination and re-extract/reanalyze associated samples. Qualify data as needed.	Laboratory analyst and/or data validator	Accuracy/bias contamination	< CRQL
Equipment blanks	One per 20 field samples	< CRQL	Qualify data as needed.	Data validator	Accuracy/bias contamination	< CRQL

Quality Assurance Project Plan Worksheet #28-2 – Quality Control Samples (Volatile Organic Compounds in Water by SOM01.2)

Matrix	Water	**Analytical Method/ SOP Reference**	SOM01.2/TAB-11	**No. of Sample Locations**	Numerous	
Analytical Group	VOCs	**Sampler's Name**	NA			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling SOP	SOP 2, SOP 7, SOP 8, SOP 20	**Analytical Organization**	Test America			
Quality Control (QC) Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Instrument check: BFB	One per calibration	%R, see SOM01.2 – Exhibit D Low/Medium Volatiles Table 1	Re-tune the instrument and reanalyze associated samples.	Laboratory analyst	Accuracy/bias	%R, see SOM01.2 – Exhibit D Low/Medium Volatiles Table 1
Internal standard	Added to all samples and blanks	Area response 50.0% to 200% and retention time (RT) ±30.0 seconds from associated 12-hour calibration standard, see SOM01.2 – Exhibit D Low/Medium Volatiles Table 3 (associated target compounds)	Check calculations, internal standard solutions, and instrument operation. Re-extract/reanalyze samples. Qualify data as needed.	Laboratory analyst and/or data validator	Precision	Area response 50.0% to 200% and retention time (RT) ±30.0 seconds from associated 12-hour calibration standard, see SOM01.2 – Exhibit D Semivolatiles Table 2 (associated target compounds)
MS[2]	One per batch	%R, see SOM01.2 - Exhibit D Low/Medium Volatiles Table 6	Re-extract/reanalyze samples. Qualify data as needed	Laboratory analyst and/or data validator	Accuracy/bias	%R, see SOM01.2 - Exhibit D Low/Medium Volatiles Table 6

Quality Assurance Project Plan Worksheet #28-2 – Quality Control Samples (Volatile Organic Compounds in Water by SOM01.2)

Matrix	Water	**Analytical Method/ SOP Reference**	SOM01.2/TAB-11	**No. of Sample Locations**	Numerous	
Analytical Group	VOCs	**Sampler's Name**	NA			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling SOP	SOP 2, SOP 7, SOP 8, SOP 20	**Analytical Organization**	Test America			
Quality Control (QC) Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
MSD[2]	One per batch	%R, see SOM01.2 - Exhibit D Low/Medium Volatiles Table 6	Re-extract/reanalyze samples. Qualify data as needed	Laboratory analyst and/or data validator	Accuracy/bias	%R, see SOM01.2 - Exhibit D Low/Medium Volatiles Table 6
MS/MSD[2]	One per batch	%R, see SOM01.2 - Exhibit D Low/Medium Volatiles Table 6	Re-extract/reanalyze samples. Qualify data as needed	Laboratory analyst and/or data validator	Precision	%R, see SOM01.2 - Exhibit D Low/Medium Volatiles Table 6

Note:

[1] An analytical batch is defined as no more than 20 analytical samples including field samples and field blanks.

[2] MS and MSD must be client-provided.

Quality Assurance Project Plan Worksheet #28-3 – Quality Control Samples (Pesticides in Water by SOM01.2)

Matrix	Water	**Analytical Method/ SOP Reference**	SOM01.2/TAB-2	**No. of Sample Locations**	Numerous	
Analytical Group	Pesticides	**Sampler's Name**	NA			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling SOP	SOP 2, SOP 7, SOP 8, SOP 20	**Analytical Organization**	Test America			
QC Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits[3]**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**DQI**	**Measurement Performance Criteria**
Field duplicate	One per 10 field samples of similar matrix	RPD < 35%	Qualify data as needed	Data validator	Precision – overall	RPD < 35%
Surrogate spikes	Added to all samples and blanks	%R: 30-150%	Check calculations, sample preparation logs, surrogate spiking solution, and instrument operation. Re-extract/reanalyze samples. Qualify data as needed.	Laboratory analyst and/or data validator	Accuracy/bias	%R: 30-150%
Method blanks	One per analytical batch	< CRQL	Investigate source of contamination and re-extract/reanalyze associated samples. Qualify data as needed.	Laboratory analyst and/or data validator	Accuracy/bias contamination	< CRQL
Equipment blanks	One per 20 field samples	< CRQL	Qualify data as needed	Data validator	Accuracy/bias contamination	< CRQL

Quality Assurance Project Plan Worksheet #28-3 – Quality Control Samples (Pesticides in Water by SOM01.2)

Matrix	Water	**Analytical Method/ SOP Reference**	SOM01.2/TAB-2	**No. of Sample Locations**	Numerous	
Analytical Group	Pesticides	**Sampler's Name**	NA			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling SOP	SOP 2, SOP 7, SOP 8, SOP 20	**Analytical Organization**	Test America			
QC Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits[3]**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**DQI**	**Measurement Performance Criteria**
LCS	One per analytical batch	%R, see SOM01.2 - Exhibit D Pesticides Table 2	Re-extract/reanalyze associated samples. Qualify data as needed	Laboratory analyst and/or data validator	Accuracy/bias	%R, see SOM01.2 - Exhibit D Pesticides Table 2
MS[2]	One per analytical batch	%R, see SOM01.2 - Exhibit D Pesticides Table 3	Re-extract/reanalyze samples. Qualify data as needed	Laboratory analyst and/or data validator	Accuracy/bias	%R, see SOM01.2 - Exhibit D Pesticides Table 3
MSD[2]	One per analytical batch	%R, see SOM01.2 - Exhibit D Pesticides Table 3	Re-extract/reanalyze samples. Qualify data as needed	Laboratory analyst and/or data validator	Accuracy/bias	%R, see SOM01.2 - Exhibit D Pesticides Table 3
MS/MSD[2]	One per analytical batch	%R, see SOM01.2 - Exhibit D Pesticides Table 3	Re-extract/reanalyze samples. Qualify data as needed	Laboratory analyst and/or data validator	Precision	%R, see SOM01.2 - Exhibit D Pesticides Table 3

Note:
[1] An analytical batch is defined as no more than 20 analytical samples including field samples and field blanks.
[2] MS and MSD must be client-provided.

Quality Assurance Project Plan Worksheet #28-4 – Quality Control Samples (PCBs in Water by SOM01.2)

Matrix	Water	**Analytical Method/ SOP Reference**	SOM01.2/TAB-1	**No. of Sample Locations**	Numerous	
Analytical Group	PCBs	**Sampler's Name**	NA			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling SOP	SOP 2, SOP 7, SOP 8, SOP 20	**Analytical Organization**	Test America			
QC Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits[3]**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**DQI**	**Measurement Performance Criteria**
Field duplicate	One per 10 field samples of similar matrix	RPD < 35%	Qualify data as needed	Data validator	Precision – overall	RPD < 35%
Surrogate spikes	Added to all samples and blanks	%R: 30-150%	Check calculations, sample preparation logs, surrogate spiking solution, and instrument operation. Re-extract/reanalyze samples. Qualify data as needed.	Laboratory analyst and/or data validator	Accuracy/bias	%R: 30-150%
Method blanks	One per analytical batch	< CRQL	Investigate source of contamination and re-extract/reanalyze associated samples. Qualify data as needed.	Laboratory analyst and/or data validator	Accuracy/bias contamination	< CRQL
Equipment blanks	One per 20 field samples	< CRQL	Qualify data as needed	Data validator	Accuracy/bias contamination	< CRQL
LCS	One per analytical batch	%R, see SOM01.2 - Exhibit D Aroclors Table 2	Re-extract/reanalyze associated samples. Qualify data as needed	Laboratory analyst and/or data validator	Accuracy/bias	%R, see SOM01.2 - Exhibit D Aroclors Table 2
MS[2]	One per analytical batch	%R, see SOM01.2 - Exhibit D Aroclors Table 1	Re-extract/reanalyze samples. Qualify data as needed	Laboratory analyst and/or data validator	Accuracy/bias	%R, see SOM01.2 - Exhibit D Aroclors Table 1

Quality Assurance Project Plan Worksheet #28-4 – Quality Control Samples (PCBs in Water by SOM01.2)

Matrix	Water	**Analytical Method/ SOP Reference**	SOM01.2/TAB-1	**No. of Sample Locations**	Numerous	
Analytical Group	PCBs	**Sampler's Name**	NA			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling SOP	SOP 2, SOP 7, SOP 8, SOP 20	**Analytical Organization**	Test America			
QC Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits[3]**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**DQI**	**Measurement Performance Criteria**
MSD[2]	One per analytical batch	%R, see SOM01.2 - Exhibit D Aroclors Table 1	Re-extract/reanalyze samples. Qualify data as needed	Laboratory analyst and/or data validator	Accuracy/bias	%R, see SOM01.2 - Exhibit D Aroclors Table 1
MS/MSD[2]	One per analytical batch	%R, see SOM01.2 - Exhibit D Aroclors Table 1	Re-extract/reanalyze samples. Qualify data as needed	Laboratory analyst and/or data validator	Precision	%R, see SOM01.2 - Exhibit D Aroclors Table 1

Note:
[1] An analytical batch is defined as no more than 20 analytical samples including field samples and field blanks.
[2] MS and MSD must be client-provided.

Quality Assurance Project Plan Worksheet #28-5 – Quality Control Samples (Metals. Mercury, and Cyanide in Water by ISM01.3)

Matrix	Water	**Analytical Method/ SOP Reference**	ISM01.3/TAB-5, TAB-6, TAB-7	**No. of Sample Locations**	Numerous	
Analytical Group	Metals, Mercury, and Cyanide	**Sampler's Name**	To be determined			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling Standard Operating Procedure (SOP)	SOP 2, SOP 7, SOP 8, SOP 20	**Analytical Organization**	Test America			
Quality Control (QC) Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator**	**Measurement Performance Criteria**
Field duplicate	One per 10 field samples of similar matrix	Relative percent difference (RPD) < 35%	Qualify data as needed	Data Validator	Precision – overall	RPD < 35%
Method blanks	One per analytical batch	< CRQL	Qualify data as needed or reanalyze batch	Lab personnel and/or Data Validator	Accuracy/bias contamination	< CRQL
Equipment blanks	One per 20 field samples	< CRQL	Qualify data as needed	Data Validator	Accuracy/bias contamination	< CRQL
Calibration verification standards	Every 10 field samples and at the end of the analysis sequence	Percent recovery (%R) 85-115%	Reanalysis of batch	Lab personnel	Accuracy/bias contamination	%R 85-115%
Interference check sample (A and AB)	Two per run	%R ±20% of true value	Qualify data as needed or reanalysis of batch	Lab personnel	Precision – lab	%R ±20% of true value
Laboratory control sample (LCS) (ICP metals analysis only)	One per batch	%R 70-130% (50-150% for antimony and silver)	Qualify data as needed or reanalyze batch	Lab personnel and/or Data Validator	Precision	%R 70-130% (50-150% for antimony and silver)

Quality Assurance Project Plan Worksheet #28-5 – Quality Control Samples (Metals. Mercury, and Cyanide in Water by ISM01.3)

Matrix	Water	**Analytical Method/ SOP Reference**	ISM01.3/TAB-5, TAB-6, TAB-7	**No. of Sample Locations**	Numerous	
Analytical Group	Metals, Mercury, and Cyanide	**Sampler's Name**	To be determined			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling Standard Operating Procedure (SOP)	SOP 2, SOP 7, SOP 8, SOP 20	**Analytical Organization**	Test America			
Quality Control (QC) Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator**	**Measurement Performance Criteria**
Matrix spike (MS)[2]	One per batch	%R: 75-125%; does not apply when the sample concentration is ≥4x the spike added	Qualify data as needed	Lab personnel and/or Data Validator	Accuracy/bias	%R: 75-125%; does not apply when the sample concentration is ≥4x the spike added
Matrix duplicate (MD)[2]	One per batch	RPD < 20% for original and duplicate sample values ≥5x the CRQL; control limit of the CRQL used if either the sample or duplicate value is <5x the CRQL	Qualify data as needed	Lab personnel and/or Data Validator	Precision	RPD < 20% for original and duplicate sample values ≥5x the CRQL; control limit of the CRQL used if either the sample or duplicate value is <5x the CRQL
Serial dilution (ICP metals analysis only)	One per batch	Percent difference (%D) < 10%	Qualify data as needed	Lab personnel	Precision	Percent difference (%D) < 10%

Notes:

[1]An analytical batch is defined as no more than 20 analytical samples including field samples and field blanks.

[2] MS/MD must be client-supplied.

Quality Assurance Project Plan Worksheet #28-6 – Quality Control Samples (Mercury in Water by EPA 1613E)

Matrix	Water	**Analytical Method/ SOP Reference**	EPA 1613E/TANC-12	**No. of Sample Locations**	Numerous	
Analytical Group	Mercury	**Sampler's Name**	To be determined			
Concentration Level	Low	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling Standard Operating Procedure (SOP)	SOP 2, SOP 7, SOP 8, SOP 20	**Analytical Organization**	Test America			
Quality Control (QC) Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator**	**Measurement Performance Criteria**
Field duplicate	One per 10 field samples of similar matrix	Relative percent difference (RPD) < 35%	Qualify data as needed	Data Validator	Precision – overall	RPD < 35%
Method blanks	One per analytical batch	< RL	Qualify data as needed or reanalyze batch	Lab personnel and/or Data Validator	Accuracy/bias contamination	< RL
Equipment blanks	One per 20 field samples	< RL	Qualify data as needed	Data Validator	Accuracy/bias contamination	< RL
Calibration verification standards	Every 10 field samples and at the end of the analysis sequence	Percent recovery (%R), method specified limit	Reanalysis of batch	Lab personnel	Accuracy/bias contamination	%R 85-115%
Laboratory control sample (LCS)	One per batch	%R, method specified limit	Qualify data as needed or reanalyze batch	Lab personnel and/or Data Validator	Precision	%R, method specified limit
Matrix spike (MS)[2]	One per batch	%R, method specified limit	Qualify data as needed	Lab personnel and/or Data Validator	Accuracy/bias	%R, method specified limit

Quality Assurance Project Plan Worksheet #28-6 – Quality Control Samples (Mercury in Water by EPA 1613E)

Matrix	Water	**Analytical Method/ SOP Reference**	EPA 1613E/TANC-12	**No. of Sample Locations**	Numerous	
Analytical Group	Mercury	**Sampler's Name**	To be determined			
Concentration Level	Low	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling Standard Operating Procedure (SOP)	SOP 2, SOP 7, SOP 8, SOP 20	**Analytical Organization**	Test America			
Quality Control (QC) Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator**	**Measurement Performance Criteria**
Matrix duplicate (MD)[2]	One per batch	RPD, method specified limit	Qualify data as needed	Lab personnel and/or Data Validator	Precision	RPD, method specified limit

Notes:
[1]An analytical batch is defined as no more than 20 analytical samples including field samples and field blanks.
[2] MS/MD must be client-supplied.

Quality Assurance Project Plan Worksheet #28-7 – Quality Control Samples (Semivolatile Organic Compounds in Soil and Sediment by SOM01.2 and SOM01.2-SIM)

Matrix	Soil/Sediment	**Analytical Method/ SOP Reference**	SOM01.2/SOM01.2-SIM/TAB-3	**No. of Sample Locations**	Numerous	
Analytical Group	SVOCs	**Sampler's Name**	NA			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling SOP	SOP 5, SOP 14	**Analytical Organization**	Test America			
Quality Control (QC) Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Field duplicate	One per 10 field samples of similar matrix	RPD < 50%	Qualify data as needed.	Data validator	Precision – overall	RPD < 50%
DMC	Added to all samples and blanks	%R, see SOM01.2 – Exhibit D Semivolatiles Tables 6 (%R) 7 (associated target compounds), and 8 (associated target compounds – SIM)	Check calculations, sample preparation logs, DMC standard spiking solution, and instrument operation. Re-extract/reanalyze samples. Qualify data as needed.	Laboratory analyst and/or data validator	Accuracy/bias	%R, see SOM01.2 – Exhibit D Semivolatiles Tables 6 (%R) 7 (associated target compounds), and 8 (associated target compounds – SIM)
Method blanks	One per analytical batch	< CRQL	Investigate source of contamination and re-extract/reanalyze associated samples. Qualify data as needed.	Laboratory analyst and/or data validator	Accuracy/bias contamination	< CRQL
Equipment blanks	One per 20 field samples	< CRQL	Qualify data as needed.	Data validator	Accuracy/bias contamination	< CRQL
Instrument check: DFTPP	One per calibration	%R, see SOM01.2 – Exhibit D Semivolatiles Table 1	Re-tune the instrument and reanalyze associated samples.	Laboratory analyst	Accuracy/bias	%R, see SOM01.2 – Exhibit D Semivolatiles Table 1

Quality Assurance Project Plan Worksheet #28-7 – Quality Control Samples (Semivolatile Organic Compounds in Soil and Sediment by SOM01.2 and SOM01.2-SIM)

Matrix	Soil/Sediment	**Analytical Method/ SOP Reference**	SOM01.2/SOM01.2-SIM/TAB-3	**No. of Sample Locations**	Numerous	
Analytical Group	SVOCs	**Sampler's Name**	NA			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling SOP	SOP 5, SOP 14	**Analytical Organization**	Test America			
Quality Control (QC) Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Internal standard	Added to all samples and blanks	Area response 50.0% to 200% and retention time (RT) ±30.0 seconds from associated 12-hour calibration standard, see SOM01.2 – Exhibit D Semivolatiles Table 2 (associated target compounds)	Check calculations, internal standard solutions, and instrument operation. Re-extract/reanalyze samples. Qualify data as needed.	Laboratory analyst and/or data validator	Precision	Area response 50.0% to 200% and retention time (RT) ±30.0 seconds from associated 12-hour calibration standard, see SOM01.2 – Exhibit D Semivolatiles Table 2 (associated target compounds)
MS[2]	One per batch	%R, see SOM01.2 - Exhibit D Semivolatile Table 5	Re-extract/reanalyze samples. Qualify data as needed	Laboratory analyst and/or data validator	Accuracy/bias	%R, see SOM01.2 - Exhibit D Semivolatile Table 5
MSD[2]	One per batch	%R, see SOM01.2 - Exhibit D Semivolatile Table 5	Re-extract/reanalyze samples. Qualify data as needed	Laboratory analyst and/or data validator	Accuracy/bias	%R, see SOM01.2 - Exhibit D Semivolatile Table 5
MS/MSD[2]	One per batch	%R, see SOM01.2 - Exhibit D Semivolatile Table 5	Re-extract/reanalyze samples. Qualify data as needed	Laboratory analyst and/or data validator	Precision	%R, see SOM01.2 - Exhibit D Semivolatile Table 5

Note:

[1] An analytical batch is defined as no more than 20 analytical samples including field samples and field blanks.

[2] MS and MSD must be client-provided.

Quality Assurance Project Plan Worksheet #28-8 – Quality Control Samples (Volatile Organic Compounds in Soil and Sediment by SOM01.2)

Matrix	Soil/Sediment	**Analytical Method/ SOP Reference**	SOM01.2-TAB-4	**No. of Sample Locations**	Numerous	
Analytical Group	VOCs	**Sampler's Name**	NA			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling SOP	SOP 5, SOP 14	**Analytical Organization**	Test America			
Quality Control (QC) Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Field duplicate	One per 10 field samples of similar matrix	RPD < 50%	Qualify data as needed.	Data validator	Precision – overall	RPD < 50%
DMC	Added to all samples and blanks	%R, see SOM01.2 – Exhibit D Low/Medium Volatiles Tables 5 (%R) and 7 (associated target compounds)	Check calculations, sample preparation logs, DMC standard spiking solution, and instrument operation. Re-extract/reanalyze samples. Qualify data as needed.	Laboratory analyst and/or data validator	Accuracy/bias	%R, see SOM01.2 – Exhibit D Low/Medium Volatiles Tables 5 (%R) and 7 (associated target compounds)
Method blanks	One per analytical batch	< CRQL	Investigate source of contamination and re-extract/reanalyze associated samples. Qualify data as needed.	Laboratory analyst and/or data validator	Accuracy/bias contamination	< CRQL
Equipment blanks	One per 20 field samples	< CRQL	Qualify data as needed.	Data validator	Accuracy/bias contamination	< CRQL

Quality Assurance Project Plan Worksheet #28-8 – Quality Control Samples (Volatile Organic Compounds in Soil and Sediment by SOM01.2)

Matrix	Soil/Sediment	**Analytical Method/ SOP Reference**	SOM01.2-TAB-4	**No. of Sample Locations**	Numerous	
Analytical Group	VOCs	**Sampler's Name**	NA			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling SOP	SOP 5, SOP 14	**Analytical Organization**	Test America			
Quality Control (QC) Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Instrument check: BFB	One per calibration	%R, see SOM01.2 – Exhibit D Low/Medium Volatiles Table 1	Re-tune the instrument and reanalyze associated samples.	Laboratory analyst	Accuracy/bias	%R, see SOM01.2 – Exhibit D Low/Medium Volatiles Table 1
Internal standard	Added to all samples and blanks	Area response 50.0% to 200% and retention time (RT) ±30.0 seconds from associated 12-hour calibration standard, see SOM01.2 – Exhibit D Low/Medium Volatiles Table 3 (associated target compounds)	Check calculations, internal standard solutions, and instrument operation. Re-extract/reanalyze samples. Qualify data as needed.	Laboratory analyst and/or data validator	Precision	Area response 50.0% to 200% and retention time (RT) ±30.0 seconds from associated 12-hour calibration standard, see SOM01.2 – Exhibit D Semivolatiles Table 2 (associated target compounds)
MS[2]	One per batch	%R, see SOM01.2 - Exhibit D Low/Medium Volatiles Table 6	Re-extract/reanalyze samples. Qualify data as needed	Laboratory analyst and/or data validator	Accuracy/bias	%R, see SOM01.2 - Exhibit D Low/Medium Volatiles Table 6
MSD[2]	One per batch	%R, see SOM01.2 - Exhibit D Low/Medium Volatiles Table 6	Re-extract/reanalyze samples. Qualify data as needed	Laboratory analyst and/or data validator	Accuracy/bias	%R, see SOM01.2 - Exhibit D Low/Medium Volatiles Table 6

Quality Assurance Project Plan Worksheet #28-8 – Quality Control Samples (Volatile Organic Compounds in Soil and Sediment by SOM01.2)

Matrix	Soil/Sediment	**Analytical Method/ SOP Reference**	SOM01.2-TAB-4	**No. of Sample Locations**	Numerous	
Analytical Group	VOCs	**Sampler's Name**	NA			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling SOP	SOP 5, SOP 14	**Analytical Organization**	Test America			
Quality Control (QC) Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
MS/MSD[2]	One per batch	%R, see SOM01.2 - Exhibit D Low/Medium Volatiles Table 6	Re-extract/reanalyze samples. Qualify data as needed	Laboratory analyst and/or data validator	Precision	%R, see SOM01.2 - Exhibit D Low/Medium Volatiles Table 6

Note:

[1] An analytical batch is defined as no more than 20 analytical samples including field samples and field blanks.

[2] MS and MSD must be client-provided.

Quality Assurance Project Plan Worksheet #28-9 – Quality Control Samples (Pesticides in Soil and Sediment by SOM01.2)

Matrix	Soil/Sediment	**Analytical Method/ SOP Reference**	SOM01.2/TAB-2	**No. of Sample Locations**	Numerous	
Analytical Group	Pesticides	**Sampler's Name**	NA			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling SOP	SOP 5, SOP 14	**Analytical Organization**	Test America			
QC Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits[3]**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**DQI**	**Measurement Performance Criteria**

Quality Assurance Project Plan Worksheet #28-9 – Quality Control Samples (Pesticides in Soil and Sediment by SOM01.2)

Matrix	Soil/Sediment	**Analytical Method/ SOP Reference**	SOM01.2/TAB-2	**No. of Sample Locations**	Numerous	
Analytical Group	Pesticides	**Sampler's Name**	NA			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling SOP	SOP 5, SOP 14	**Analytical Organization**	Test America			
QC Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits[3]**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**DQI**	**Measurement Performance Criteria**
Field duplicate	One per 10 field samples of similar matrix	RPD < 50%	Qualify data as needed	Data validator	Precision – overall	RPD < 50%
Surrogate spikes	Added to all samples and blanks	%R: 30-150%	Check calculations, sample preparation logs, surrogate spiking solution, and instrument operation. Re-extract/reanalyze samples. Qualify data as needed.	Laboratory analyst and/or data validator	Accuracy/bias	%R: 30-150%
Method blanks	One per analytical batch	< CRQL	Investigate source of contamination and re-extract/reanalyze associated samples. Qualify data as needed.	Laboratory analyst and/or data validator	Accuracy/bias contamination	< CRQL
Equipment blanks	One per 20 field samples	< CRQL	Qualify data as needed	Data validator	Accuracy/bias contamination	< CRQL
LCS	One per analytical batch	%R, see SOM01.2 - Exhibit D Pesticides Table 2	Re-extract/reanalyze associated samples. Qualify data as needed	Laboratory analyst and/or data validator	Accuracy/bias	%R, see SOM01.2 - Exhibit D Pesticides Table 2
MS[2]	One per analytical batch	%R, see SOM01.2 - Exhibit D Pesticides Table 3	Re-extract/reanalyze samples. Qualify data as needed	Laboratory analyst and/or data validator	Accuracy/bias	%R, see SOM01.2 - Exhibit D Pesticides Table 3

Quality Assurance Project Plan Worksheet #28-9 – Quality Control Samples (Pesticides in Soil and Sediment by SOM01.2)

Matrix	Soil/Sediment	**Analytical Method/ SOP Reference**	SOM01.2/TAB-2	**No. of Sample Locations**	Numerous	
Analytical Group	Pesticides	**Sampler's Name**	NA			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling SOP	SOP 5, SOP 14	**Analytical Organization**	Test America			
QC Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits[3]**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**DQI**	**Measurement Performance Criteria**
MSD[2]	One per analytical batch	%R, see SOM01.2 - Exhibit D Pesticides Table 3	Re-extract/reanalyze samples. Qualify data as needed	Laboratory analyst and/or data validator	Accuracy/bias	%R, see SOM01.2 - Exhibit D Pesticides Table 3
MS/MSD[2]	One per analytical batch	%R, see SOM01.2 - Exhibit D Pesticides Table 3	Re-extract/reanalyze samples. Qualify data as needed	Laboratory analyst and/or data validator	Precision	%R, see SOM01.2 - Exhibit D Pesticides Table 3

Note:
[1] An analytical batch is defined as no more than 20 analytical samples including field samples and field blanks.
[2] MS and MSD must be client-provided.

Quality Assurance Project Plan Worksheet #28-10 – Quality Control Samples (PCBs in Soil and Sediment by SOM01.2)

Matrix	Soil/Sediment	**Analytical Method/ SOP Reference**	SOM01.2/TAB-1	**No. of Sample Locations**	Numerous	
Analytical Group	PCBs	**Sampler's Name**	NA			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling SOP	SOP 5, SOP 14	**Analytical Organization**	Test America			
QC Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits[3]**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**DQI**	**Measurement Performance Criteria**
Field duplicate	One per 10 field samples of similar matrix	RPD < 50%	Qualify data as needed	Data validator	Precision – overall	RPD < 50%
Surrogate spikes	Added to all samples and blanks	%R: 30-150%	Check calculations, sample preparation logs, surrogate spiking solution, and instrument operation. Re-extract/reanalyze samples. Qualify data as needed.	Laboratory analyst and/or data validator	Accuracy/bias	%R: 30-150%
Method blanks	One per analytical batch	< CRQL	Investigate source of contamination and re-extract/reanalyze associated samples. Qualify data as needed.	Laboratory analyst and/or data validator	Accuracy/bias contamination	< CRQL
Equipment blanks	One per 20 field samples	< CRQL	Qualify data as needed	Data validator	Accuracy/bias contamination	< CRQL
LCS	One per analytical batch	%R, see SOM01.2 - Exhibit D Aroclors Table 2	Re-extract/reanalyze associated samples. Qualify data as needed	Laboratory analyst and/or data validator	Accuracy/bias	%R, see SOM01.2 - Exhibit D Aroclors Table 2
MS[2]	One per analytical batch	%R, see SOM01.2 - Exhibit D Aroclors Table 1	Re-extract/reanalyze samples. Qualify data as needed	Laboratory analyst and/or data validator	Accuracy/bias	%R, see SOM01.2 - Exhibit D Aroclors Table 1

Quality Assurance Project Plan Worksheet #28-10 – Quality Control Samples (PCBs in Soil and Sediment by SOM01.2)

Matrix	Soil/Sediment	**Analytical Method/ SOP Reference**	SOM01.2/TAB-1	**No. of Sample Locations**	Numerous	
Analytical Group	PCBs	**Sampler's Name**	NA			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling SOP	SOP 5, SOP 14	**Analytical Organization**	Test America			
QC Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits[3]**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**DQI**	**Measurement Performance Criteria**
MSD[2]	One per analytical batch	%R, see SOM01.2 - Exhibit D Aroclors Table 1	Re-extract/reanalyze samples. Qualify data as needed	Laboratory analyst and/or data validator	Accuracy/bias	%R, see SOM01.2 - Exhibit D Aroclors Table 1
MS/MSD[2]	One per analytical batch	%R, see SOM01.2 - Exhibit D Aroclors Table 1	Re-extract/reanalyze samples. Qualify data as needed	Laboratory analyst and/or data validator	Precision	%R, see SOM01.2 - Exhibit D Aroclors Table 1

Note:
[1] An analytical batch is defined as no more than 20 analytical samples including field samples and field blanks.
[2] MS and MSD must be client-provided.

Quality Assurance Project Plan Worksheet #28-11 – Quality Control Samples (Metals. Mercury, and Cyanide in Soil and Sediment by ISM01.3)

Matrix	Soil/Sediment	**Analytical Method/ SOP Reference**	ISM01.3/TAB-5, TAB-6, TAB-7	**No. of Sample Locations**	Numerous	
Analytical Group	Metals, Mercury, and Cyanide	**Sampler's Name**	To be determined			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling Standard Operating Procedure (SOP)	SOP 5, SOP 14	**Analytical Organization**	Test America			
Quality Control (QC) Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator**	**Measurement Performance Criteria**
Field duplicate	One per 10 field samples of similar matrix	Relative percent difference (RPD) < 50%	Qualify data as needed	Data Validator	Precision – overall	RPD < 50%
Method blanks	One per analytical batch	< CRQL	Qualify data as needed or reanalyze batch	Lab personnel and/or Data Validator	Accuracy/bias contamination	< CRQL
Equipment blanks	One per 20 field samples	< CRQL	Qualify data as needed	Data Validator	Accuracy/bias contamination	< CRQL
Calibration verification standards	Every 10 field samples and at the end of the analysis sequence	Percent recovery (%R) 85-115%	Reanalysis of batch	Lab personnel	Accuracy/bias contamination	%R 85-115%
Interference check sample (A and AB)	Two per run	%R ±20% of true value	Qualify data as needed or reanalysis of batch	Lab personnel	Precision – lab	%R ±20% of true value
Laboratory control sample (LCS) (ICP metals analysis only)	One per batch	%R 70-130% (50-150% for antimony and silver)	Qualify data as needed or reanalyze batch	Lab personnel and/or Data Validator	Precision	%R 70-130% (50-150% for antimony and silver)

Quality Assurance Project Plan Worksheet #28-11 – Quality Control Samples (Metals. Mercury, and Cyanide in Soil and Sediment by ISM01.3)

Matrix	Soil/Sediment	**Analytical Method/ SOP Reference**	ISM01.3/TAB-5, TAB-6, TAB-7	**No. of Sample Locations**	Numerous	
Analytical Group	Metals, Mercury, and Cyanide	**Sampler's Name**	To be determined			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling Standard Operating Procedure (SOP)	SOP 5, SOP 14	**Analytical Organization**	Test America			
Quality Control (QC) Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator**	**Measurement Performance Criteria**
Matrix spike (MS)[2]	One per batch	%R: 75-125%; does not apply when the sample concentration is ≥4x the spike added	Qualify data as needed	Lab personnel and/or Data Validator	Accuracy/bias	%R: 75-125%; does not apply when the sample concentration is ≥4x the spike added
Matrix duplicate (MD)[2]	One per batch	RPD < 20% for original and duplicate sample values ≥5x the CRQL; control limit of the CRQL used if either the sample or duplicate value is <5x the CRQL	Qualify data as needed	Lab personnel and/or Data Validator	Precision	RPD < 20% for original and duplicate sample values ≥5x the CRQL; control limit of the CRQL used if either the sample or duplicate value is <5x the CRQL
Serial dilution (ICP metals analysis only)	One per batch	Percent difference (%D) < 10%	Qualify data as needed	Lab personnel	Precision	Percent difference (%D) < 10%

Notes:
[1]An analytical batch is defined as no more than 20 analytical samples including field samples and field blanks.
[2] MS/MD must be client-supplied.

Quality Assurance Project Plan Worksheet #28-12 Quality Control Samples (Total Organic Carbon in Soil and Sediment by Lloyd Kahn)

Matrix	Soil/Sediment	**Analytical Method/ SOP Reference**	Lloyd Kahn/TAB-12	**No. of Sample Locations**	Numerous	
Analytical Group	TOC	**Sampler's Name**	Not Available			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling SOP	SOP 5, SOP 14	**Analytical Organization**	Test America			
QC Sample	**Frequency/Number**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**DQI**	**Measurement Performance Criteria**
Field duplicate	One per 10 field samples of similar matrix	RPD < 50%	Qualify data as needed	Data validator	Precision – overall	RPD < 50%
LCS	One per analytical batch	%R, laboratory specific limits	Re-prepare/reanalyze samples. Qualify data as needed.	Laboratory analyst and/or data validator	Accuracy/bias	%R, laboratory specific limits
Laboratory duplicate[2]	One per analytical batch	RPD, laboratory specific limits	Re-prepare/reanalyze samples. Qualify data as needed.	Laboratory analyst and/or data validator	Precision – overall	RPD, laboratory specific limits
MS[2]	One per analytical batch	%R, laboratory specific limits	Re-prepare/reanalyze samples. Qualify data as needed.	Laboratory analyst and/or data validator	Accuracy/bias	%R, laboratory specific limits

Note:
[1] An analytical batch is defined as no more than 20 analytical samples including field samples and field blanks.
[2] Sufficient sample size for MS and laboratory duplicate analysis must be client-provided.

Quality Assurance Project Plan Worksheet #28-13 – Quality Control Samples (PCB Congeners in Soil and Sediment by EPA 1668A)

Matrix	Soil/Sediment	**Analytical Method/ SOP Reference**	EPA 1668A/TAWS-1	**No. of Sample Locations**	Numerous	
Analytical Group	PCB Congeners	**Sampler's Name**	NA			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling SOP	SOP 5, SOP 14	**Analytical Organization**	Test America			
QC Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**DQI**	**Measurement Performance Criteria**
Field duplicate	One per 10 field samples of similar matrix	RPD < 50%	Qualify data as needed	Data validator	Precision – overall	RPD < 50%
Ongoing precision and recovery (OPR)	One per analytical batch	%R, method specified limits	Correct the problem. Re-prepare, extract, and clean-up the sample batch and repeat the OPR.	Laboratory analyst and/or data validator	Accuracy/bias	%R, method specified limits
Method blanks	One per analytical batch	< RL	Investigate source of contamination and re-extract/reanalyze associated samples. Qualify data as needed.	Laboratory analyst and/or data validator	Accuracy/bias contamination	< RL
Equipment blanks	One per 20 field samples	< RL	Qualify data as needed.	Data validator	Accuracy/bias contamination	< RL
Internal standards	Added to all samples	%R, method specified limits	Reanalyze sample. Qualify data as needed.	Laboratory analyst and/or data validator	Accuracy/bias	%R, method specified limits
MS[2]	One per analytical batch	%R, method specified limits	Re-extract/reanalyze associated samples. Qualify data as needed.	Laboratory analyst and/or data validator	Accuracy/bias	%R, method specified limits

Quality Assurance Project Plan Worksheet #28-13 – Quality Control Samples (PCB Congeners in Soil and Sediment by EPA 1668A)

Matrix	Soil/Sediment	**Analytical Method/ SOP Reference**	EPA 1668A/TAWS-1	**No. of Sample Locations**	Numerous	
Analytical Group	PCB Congeners	**Sampler's Name**	NA			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling SOP	SOP 5, SOP 14	**Analytical Organization**	Test America			
QC Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**DQI**	**Measurement Performance Criteria**
MSD or LCSD[2]	One per analytical batch	%R, method specified limits	Re-extract/reanalyze samples. Qualify data as needed.	Laboratory analyst and/or data validator	Accuracy/bias	%R, method specified limits
MS/MSD and LCS/LCSD[2]	One per analytical batch	RPD, method specified limits	Re-extract/reanalyze samples. Qualify data as needed.	Laboratory analyst and/or data validator	Precision	RPD, method specified limits

Note:
[1] An analytical batch is defined as no more than 20 analytical samples including field samples and field blanks.
[2] LCS/LCSD used when MS/MSD are not client-supplied.

Quality Assurance Project Plan Worksheet #28-14 – Quality Control Samples (Dioxins and Furans in Soil and Sediment by EPA 1613)

Matrix	Soil	**Analytical Method/ SOP Reference**	EPA 1613/TAWS-2	**No. of Sample Locations**	Numerous	
Analytical Group	Dioxins and Furans	**Sampler's Name**	TBD			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling Standard Operating Procedure (SOP)	SOP 5, SOP 14	**Analytical Organization**	Test America			
Quality Control (QC) Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Field duplicate	One per 10 field samples of similar matrix	Relative percent difference (RPD) < 50%	Qualify data as needed	Data Validator	Precision – overall	RPD < 50%
Internal standards/ recovery standards	9 IS/2 RS per sample and lab QC samples	Percent recovery (%R), method specified limit	Reanalysis or re-extraction/reanalysis of sample	Lab personnel	Accuracy/bias	%R, method specified limit
Method blanks	One per analytical batch	< RL	Qualify data as needed or re-extraction/reanalysis of batch	Lab personnel and/or Data Validator	Accuracy/bias contamination	< RL
Equipment blanks	One per 20 field samples	< RL	Qualify data as needed	Data Validator	Accuracy/bias contamination	< RL
Laboratory control sample/laboratory control sample duplicate (LCS/LCSD)[2]	One per analytical batch	%R, method specified limit	Reanalysis or re-extraction/ reanalysis of batch	Lab personnel and/or Data Validator	Accuracy/bias	%R, method specified limit
Instrument performance check: Perfluorokerosene (PKF)	One per calibration	Method specified limit	Reanalyze batch	Lab personnel	Accuracy/bias	%R, method specified limit

Quality Assurance Project Plan Worksheet #28-14 – Quality Control Samples (Dioxins and Furans in Soil and Sediment by EPA 1613)

Matrix	Soil	**Analytical Method/ SOP Reference**	EPA 1613/TAWS-2	**No. of Sample Locations**	Numerous	
Analytical Group	Dioxins and Furans	**Sampler's Name**	TBD			
Concentration Level	All	**Field Sampling Organization**	ARCADIS Sampling Personnel			
Sampling Standard Operating Procedure (SOP)	SOP 5, SOP 14	**Analytical Organization**	Test America			
Quality Control (QC) Sample	**Frequency/Number[1]**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Matrix spike/matrix spike duplicate (MS/MSD)[2]	One per batch	%R, method specified limit	Qualify data as needed	Lab personnel and/or Data Validator	Accuracy/bias	%R, method specified limit
MS/MSD and LCS/LCSD[2]	One per batch	%RPD, method specified limit	Qualify data as needed	Lab personnel and/or Data Validator	Precision	%RPD, method specified limit

Note: [1]An analytical batch is defined as no more than 20 analytical samples including field samples and field blanks.
[2]LCS/LCSD used when MS/MSD are not client-supplied.

QAPP Worksheet #29: Project Documents and Records

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 - Sampling Logs - Chain-of-Custody Records - Air Bills - Custody Seals	- Equipment Calibration Logs - Field Data Records - Field Instrument Maintenance Logs	- Sample Receipt, Custody and Tracking Records - Standard Traceability Logs - Equipment Calibration Logs - Sample Prep Logs - Run Logs - Equipment Maintenance, Testing and Inspection Logs - Corrective Action Forms - Reported Field Sample Results - Reported Results for Standards, Quality Control (QC) Checks and QC Samples - Instrument PDF of (raw data) for Field Samples, Standards, QC Checks and QC Samples - Data Package Completeness Checklists - Sample Disposal Records - Extraction/Cleanup Records - Raw Data (stored on disk or CD-R) - Analytical Reports to ARCADIS	- Data Validation Checklists - Data Quality Assessments	Site-specific Work Plans as needed Site-specific Safety and Health Plan

QAPP Worksheet #31, 32 & 33: Assessments and Corrective Action

Assessments:

Assessment Type	Responsible Party & Organization	Number/Frequency	Estimated Dates	Assessment Deliverable	Deliverable due date
Readiness Review	Suzanne Walls, ARCADIS	One assessment one week prior to mobilization	Approximately 15 October 2014	Readiness Review Memorandum	24 hours following assessment
Field Sampling TSA	Andrew Gutherz, ARCADIS	One each on first day of soil and temporary well groundwater sampling	Approximately 22 October 2014	TSA Memorandum	24 hours following assessment
Management Review	John Persico, ARCADIS	Interim Management Review following site mobilization. Final management review upon completion of field work.	Interim review – approximately 10 November 2014. Final review – approximately 1 February 2015	QA Management Report	48 hours following Management Review

Assessment Response and Corrective Action:

Assessment Type	Responsibility for responding to assessment findings	Assessment Response Documentation	Timeframe for Response	Responsibility for Implementing Corrective Action	Responsible for monitoring Corrective Action implementation
Readiness Review	John Persico, ARCADIS	Readiness Review Corrective Action Response	24 hours from receipt of Readiness Review Memorandum	As directed by PM	As directed by PM
Field Sampling TSA	Suzanne Walls, ARCADIS	Field Sampling Corrective Action Response	24 hours from receipt of Memorandum	Field Task Leader	Field Task Leader
Management Reviews	Suzanne Walls, ARCADIS	QA Management Response	48 hours from receipt of QA Management Report	As assigned in QA Management Response	As assigned in QA Management Response

QAPP Worksheet #34: Data Verification and Validation Inputs

Item	Description	Verification (completeness)	Validation (conformance to specifications)
Planning Documents/Records			
1	Approved QAPP	X	
2	Contract	X	
4	Field SOPs	X	
5	Laboratory SOPs	X	
Field Records			
6	Field logbooks	X	
7	Equipment calibration records	X	
8	Chain-of-Custody Forms	X	
9	Sampling logs	X	
10	Drilling logs	X	
13	Change orders/deviations	X	
14	Field audit reports	X	
15	Field corrective action reports	X	
Analytical Data Package			
16	Cover sheet (laboratory identifying information)	X	X
17	Case narrative	X	X
18	Internal laboratory chain-of-custody	X	X
19	Sample receipt records	X	X
20	Sample chronology (i.e. dates and times of receipt, preparation, & analysis)	X	X
21	Communication records	X	X
22	Project-specific PT sample results	X	X
23	LOD/LOQ establishment and verification	X	X
24	Standards Traceability	X	X
25	Instrument calibration records	X	X
26	Definition of laboratory qualifiers	X	X
27	Results reporting forms	X	X
28	QC sample results	X	X
29	Corrective action reports	X	X
30	Raw data	X	X
31	Electronic data deliverable	X	

QAPP Worksheet #35: Data Verification Procedures

Records Reviewed	Requirement Documents	Process Description	Responsible Person, Organization
Field logbook and purge forms	QAPP	Verify that records are present and complete for each day of field activities. Verify that all planned samples including field QC samples were collected and that sample collection locations are documented. Verify that changes/exceptions are documented and were reported in accordance with requirements. Verify that any required field monitoring was performed and results are documented.	Weekly – Project Manager
Chain-of-custody forms	QAPP	Verify the completeness of chain-of-custody records. Check that appropriate methods and sample preservation have been recorded. Verify that the required volume of sample has been collected and that sufficient sample volume is available for QC samples (e.g., field duplicates, surrogates, blanks, and MS/MSD). Verify that all required signatures and dates are present. Check for transcription errors.	Daily – Field Crew Chief At conclusion of field activities – Project Manager
Laboratory Deliverable		Verify that the laboratory deliverable contains all records specified in the QAPP. Check sample receipt records to ensure sample condition upon receipt was noted, and any missing/broken sample containers were noted and reported according to plan. Compare the data package with the CoCs to verify that results were provided for all collected samples. Review the narrative to ensure all QC exceptions are described. Check for evidence that any required notifications were provided to project personnel as specified in the QAPP. Verify that necessary signatures and dates are present.	Before release – Laboratory QAM Upon receipt – Project Manager

QAPP Worksheet #36
Data Validation Procedures

Quality Assurance Project Plan Worksheet #36 – Validation (Steps IIa and IIb) Summary

Steps IIa and IIb	Matrix	Analytical Group	Data Purpose	Concentration Level	Validation Criteria[1]	Data Validator (title and organizational affiliation)
IIa and IIb	Sediments and Soil	Volatile Organic Compounds (VOCs), Semi-Volatile Organic Compounds (SVOCs) TCL/SIM, Polychlorinated Biphenyls (PCBs), Pesticides, PCBs Congener, Dioxins/Furans, TAL Metals, pH, TOC	Data Gaps	All	USEPA Contract Laboratory Program National Functional Guidelines for Superfund Organic Methods Data Review SOM 1.2 June 2008, and USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Superfund Data Review ISM 1.2 January 2010; EPA Region II Data Validation SOP for Dioxins EPA method 1613 HW-25 September 2008, EPA Region II Data Validation SOP for PCB congeners EPA method 1668 August 2003; Quality Assurance Project Plan (QAPP) criteria; associated analytical methodology, and professional judgment	Lyndi Mott Project Chemist, ARCADIS
IIa and IIb	Water	Volatile Organic Compounds (VOCs), Semi-Volatile Organic Compounds (SVOCs) TCL/SIM, Polychlorinated Biphenyls (PCBs), Pesticides, TAL Metals, LL Mercury, pH, TOC	Data Gaps	All	USEPA Contract Laboratory Program National Functional Guidelines for Superfund Organic Methods Data Review SOM 1.2 June 2008, and USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Superfund Data Review ISM 1.2 January 2010; Quality Assurance Project Plan (QAPP) criteria, associated analytical methodology; and professional judgment	Lyndi Mott Project Chemist, ARCADIS

QAPP Worksheet #37: Data Usability Assessment

Identify personnel (organization and position/title) responsible for participating in the data usability assessment:

- John Persico, ARCADIS Project Coordinator
- Suzanne Walls, ARCADIS Project Manager
- Dennis Capria, ARCADIS QA Manager

The data usability assessment will be performed by the ARCADIS project management staff. Data verification will involve assessing whether analytical data meet the QC objectives and whether the necessary quality control steps were performed during field and laboratory tasks. The key data that will be assessed during data verification include:

- Sample collection, handling and analysis procedures in the field and laboratory
- Laboratory data (laboratory-qualified)
- Data package deliverable completeness
- QC sample data summaries

Quality Assurance Project Plan Worksheet #37 – Usability Assessment

The Data Usability Assessment will be performed by ARCADIS for data associated with the Data QAP Work Plan at the Rolling Knolls site. Documentation generated during the Data Usability Assessment will consist of data validation checklists with a brief summary of overall data usability.

The Data Usability Assessment process involves data verification and validation. Data verification is the process by which laboratory results are checked to provide that the proper quality control (QC) steps were performed and key items have met QC objectives (both analytical and contractual). Key steps of an ARCADIS data verification include:

- identifying sample collection, handling and analysis procedures
- documenting handling and analysis activities (e.g., , QC checklist)
- verifying (internally, at the data generator level) all sampling, handling, on-site analytical laboratory data

Quality Assurance Project Plan Worksheet #37 – Usability Assessment

- verifying laboratory data (e.g., laboratory-qualified data)
- verifying sampling, on-site analytical laboratory data
- verifying data package deliverable completeness
- reviewing the case narrative
- presenting all analytical results
- summarizing QC sample data
- evaluating applicable raw data

All required data deliverables must be present in the data package in order to proceed to the next step of data validation.

Data validation entails a review of the sample collection, handling, QC data, and the raw data to verify that the laboratory was operating within required limits, analytical results were correctly transcribed from the instrument read-outs and which (if any) environmental samples were related to out-of-control QC samples. The objective of data validation is to identify any questionable or invalid laboratory measurements.

The data quality indicators (DQIs) used to evaluate conformance with the project data quality objectives (DQOs) are presented below.

DQIs are generally defined in terms of six parameters:

1. representativeness
2. comparability
3. completeness
4. precision
5. accuracy
6. sensitivity

Quality Assurance Project Plan Worksheet #37 – Usability Assessment

Each parameter is defined below. Specific objectives for the site actions are presented in other sections of this QAPP, as referenced below.

Representativeness

Representativeness is the degree to which sampling data accurately and precisely represent site conditions, and is dependent on sampling and analytical variability and the variability of environmental media at the site. Actions have been designed to assess the presence of chemical constituents at the time of sampling. The QAPP presents the rationale for sample quantities and location. This QAPP presents field sampling and laboratory analytical methodologies. Use of the prescribed field and laboratory analytical methods with associated holding times and preservation requirements are intended to provide representative data.

Comparability

Comparability is the degree of confidence with which one data set can be compared to another. Comparability between phases of the actions (if additional phases are required) will be maintained through consistent use of the sampling and analytical methodologies set forth in this QAPP, established quality assurance/quality control (QA/QC) procedures and use of appropriately trained personnel.

Completeness

Completeness is defined as a measure of the amount of valid data obtained from an event and/or investigation compared to the total amount that was obtained. This will be determined upon final assessment of the analytical results. Completeness of a field or laboratory data set will be calculated by comparing the number of valid sample results generated to the total number of results generated.

$$\text{Completeness} = \frac{\text{Number valid results}}{\text{Total number of results generated}} \times 100$$

As a general guideline, overall project completeness is expected to be at least 90 percent. The assessment of completeness will require professional judgment to determine data usability for intended purposes.

Quality Assurance Project Plan Worksheet #37 – Usability Assessment

Precision

Precision is a measure of the reproducibility of sample results. The goal is to maintain a level of analytical precision consistent with the objectives of the action. To maximize precision, sampling and analytical procedures will be followed. All work for the site actions will adhere to established protocols presented in the QAPP. Checks for analytical precision will include the analysis of matrix spike/matrix spike duplicates (MS/MSDs), laboratory duplicates and field duplicates. Checks for field measurement precision will include duplicate field measurements.

The precision of data will be measured by calculating the Relative Percent Difference (RPD) by the following equation:

$$RPD = \frac{(A-B)}{(A+B)/2} \times 100$$

Where:

A = Analytical result from one of two duplicate measurements.

B = Analytical result from the second measurement.

Accuracy

Accuracy is a measure of how close a measured result is to the true value. Both field and analytical accuracy will be monitored through initial and continuing calibration of instruments. In addition, reference standards, MSs, blank spikes and surrogate standards will be used to assess the accuracy of the analytical data.

Accuracy will be calculated in terms of percent recovery as follows:

$$\% \text{ Recovery} = \frac{A-X}{} \times 100$$

Quality Assurance Project Plan Worksheet #37 – Usability Assessment

B

Where:

A = Value measured in spiked sample or standard.

X = Value measured in original sample.

B = True value of amount added to sample or true value of standard.

Sensitivity

Sensitivity is a quantitative measurement to determine if the analytical laboratory's procedures/methodologies and their associated detection limits can satisfy the project requirements as they relate to the project action limits. DLs are updated annually by the laboratory. The current DLs for the analytical laboratories are presented in Worksheet #15.

1. Data Validation and Usability

ARCADIS will validate data generated using the United States Environmental Protection Agency's (USEPA's) National Functional Guidelines (Organics October 1999 and Inorganics October 2004), USEPA Contract Laboratory Program National Functional Guidelines for Chlorinated Dibenzo-p-Dioxins (CDDs) and Chlorinated Dibenzofurans (CDFs) Data Review, (September 2011), and USEPA Region 2 SOP HW-31, Rev. 6 Analysis of Volatile Organic Compounds in Air Contained in Canisters by Method TO-15, (June 2014) for data validation, available at the time of project initiation. These procedures and criteria may be modified, as necessary, to address project-specific and method-specific criteria. Data validation will consist of data screening, checking, reviewing, editing and interpretation to document analytical data quality and to determine whether the quality is sufficient to meet the DQOs.

The data validator will verify that reduction of laboratory measurements and laboratory reporting of analytical parameters is in accordance with the procedures specified for each analytical method and/or as specified in this QAPP. Any deviations from the analytical method or any special reporting requirements apart from those specified in this QAPP will be detailed on chain-of-custody (COC) forms.

Quality Assurance Project Plan Worksheet #37 – Usability Assessment

Upon receipt of laboratory data, the following procedures will be executed by the data validator:

- Evaluate completeness of data package.
- Verify that field COC forms were completed and that samples were handled properly.
- Verify that holding times were met for each parameter. Holding time exceedances, should they occur, will be documented. Data for all samples exceeding holding time requirements will be flagged as either estimated or rejected. The decision as to which qualifier is more appropriate will be made on a case-by-case basis.
- Verify that parameters were analyzed according to the methods specified.
- Review QA/QC data (i.e., confirm that duplicates, blanks and spikes were analyzed on the required number of samples, as specified in the method and verify that duplicate and MS recoveries are acceptable).
- Investigate anomalies identified during review. When anomalies are identified, they will be discussed with the Project Manager and/or Laboratory Manager, as appropriate.
- If data appear suspect, investigate the specific data of concern. Calculations will be traced back to raw data. If calculations do not agree, the cause will be determined and corrected.

Deficiencies discovered as a result of the data review, as well as the corrective actions implemented in response, will be documented and submitted in the form of a written report addressing the following topics, as applicable to each method:

- assessment of the data package
- description of any protocol deviations
- failures to reconcile reported and/or raw data
- assessment of any compromised data
- overall appraisal of the analytical data

Quality Assurance Project Plan Worksheet #37 – Usability Assessment

- table of site name, sample quantities, matrix and fractions analyzed

It should be noted that qualified results do not necessarily invalidate data. The goal to produce the best possible data does not necessarily mean that data must be produced without QC qualifiers. Qualified data can provide useful information.

During the review process, laboratory qualified and unqualified data are verified against the supporting documentation. Based on this evaluation, qualifier codes may be added, deleted or modified by the data reviewer. Results will be qualified with the following codes in accordance with the USEPA National Functional Guidelines:

Laboratory Data Qualifiers:

J Estimated: The compound was positively identified; however, the associated numerical value is an estimated concentration greater than the DL but less than the LOQ.

B Blank contamination: The analyte was found in an associated blank above one half the LOQ, as well as in the sample.

U Undetected: The analyte/compound was analyzed for, but not detected.

Usability Assessment Data Qualifiers:

R The data are rejected due to deficiencies in meeting QC criteria and may not be used for decision making.

J Estimated: The analyte was positively identified, the quantitation is an estimation due to discrepancies in meeting certain analyte-specific quality control criteria.

UB Blank contamination: The analyte was found in an associated blank above one half the LOQ, as well as in the sample.

UJ The analyte was not detected; however, the result is estimated due to discrepancies in meeting certain analyte-specific quality control criteria.

Two facts will be noted to all data users. First, the "R" flag means that the associated value is unusable. In other words, due to significant QC problems, the analysis is invalid and provides no information as to whether the compound is present or not. Analytes with "R" values should not

Quality Assurance Project Plan Worksheet #37 – Usability Assessment

appear on data tables because they cannot be relied upon for any reason. The second fact is that no compound concentration, even if it has passed all QC tests, is guaranteed to be accurate. Strict QC serves to increase confidence in data, but any value potentially contains error.

Resolution of any issues regarding laboratory performance or deliverables will be handled between the laboratory and the data validator. Suggestions for reanalysis may be made by the Project Chemist at this point.

Validation Reports

The data validation reports will identify all deficiencies and the potential impact on the results. The ARCADIS Project Chemist or designee will amend qualifiers generated during the validation process to the database. The validation checklists and the database will be the primary location of all applicable data qualifiers. Qualifiers will be applied to the hard copy analytical reports.

Field Data Review

Field data are generated from in-field measurement, which may include a geophysical survey, well development and groundwater sampling. The quality objective for the in-field measurement activities is to obtain accurate measurements of sample characteristics, including aqueous pH, conductivity, temperature, turbidity and dissolved oxygen, using appropriate equipment. Data are recorded in field logbooks or on field sampling sheets and calibration logs. Calibration logs will be reviewed by ARCADIS Field Managers with other field documentation to identify any potential impacts to data quality and usability. Field logbooks are reviewed as part of the QC inspections.

Reconciliation with Data Usability Requirements

Data results will be examined to determine the performance that was achieved for each data usability criterion. The performance will then be compared with the project objectives and DQOs. Deviations from objectives will be noted. Data that has been rejected will not be used. Data that has been qualified but not rejected will be considered useable (i.e., qualified as estimated) and definitive data. If there is an instance where further limitations must be placed on qualified data, the data will be additionally qualified with “X.” This would indicate that the associated data is non-definitive data and should be used for screening purposes only.

Additional action may be warranted when performance does not meet performance objectives for critical data. Options for corrective action relating

Quality Assurance Project Plan Worksheet #37 – Usability Assessment

to incomplete information, questionable results or inconsistent data may include any or all of the following:

- retrieval of missing information
- request for additional explanation or clarification
- reanalysis of sample from extract (when appropriate)
- recalculation or reinterpretation of results by the laboratory

These actions may improve the data quality, reduce uncertainty and eliminate the need to qualify or reject data. If these actions do not improve the data quality to an acceptable level, the following additional actions may be taken:

- extrapolation of missing data from existing data points
- use of historical data
- evaluation of the critical/noncritical nature of the sample

If the data gap cannot be resolved by these actions, the data bias and potential for false negatives and positives can be evaluated. If the resultant uncertainty level is unacceptable, the following action must be taken:

- additional sample collection and analysis

Therefore the usability of the analytical data will be assessed based on the quality controls, field and laboratory documentation, and data comparison. The data will be analyzed in the context of the sampling location, groundwater flow patterns, geology, and previous data from the Site Characterization Summary Report. All data acquired will also be reviewed to ensure that sampling was consistent with the pre-designed sampling plan. Any deviations from the sampling plan and any anomalous data will be further examined to constrain what the usability of this data is.

Step 1	**Review the project's objectives and sampling design** The Project Manager and Project Coordinator will review the key outputs defined during systematic planning (i.e., DQOs) to make sure they are still applicable. Review the sampling design for consistency with stated objectives. This provides the context for interpreting the data in subsequent steps. - Verify that required sampling procedures were used

	- Verify that required analytical methods were used - Verify all required QC samples were collected and analyzed - Evaluate QC data
Step 2	**Review the data verification and data validation outputs** The Data Validator will evaluate the completeness of the data package, verify chain of custodies, verify sample holding times were met, verify analysis methods, review QA/QC data, and investigate anomalies. The Project Coordinator and Project Manager will summarize the data using graphs, maps, and tables, and will look for patterns, trends, and anomalies (i.e., unexpected results). Review deviations from planned activities (e.g., number and locations of samples, holding time exceedances, damaged samples, non-compliant PT sample results, and SOP deviations) and determine their impacts on the data usability. Evaluate implications of unacceptable QC sample results.
Step 3	**Document data usability and draw conclusions** Determine if the data can be used as intended, considering implications of deviations and corrective actions. Discuss data quality indicators. Assess the performance of the sampling design and identify limitations on data use. Update the conceptual site model and document conclusions. Prepare the data usability summary report which can be in the form of text and/or a table.

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Tables

Table 1
Sample Locations, Depths, and Analyses
Data Gaps Sampling and Analysis Plan
Rolling Knolls Landfill Superfund Site
Chatham, New Jersey

Sample ID	Sample Media	Depth Interval (Feet)	Sample Collection Method	Laboratory Analyses													Notes
				VOCs	SVOCs	SVOCs - SIM	PCBs (as Aroclors)	Pesticides	TAL Metals and Cyanide	PCB Congeners, Dioxins, Furans	Full TCL/TAL	TAL Metals and Cyanide (unfiltered)	TAL Metals and Cyanide (filtered)	Low-Level Mercury	Hardness	pH, TOC, Grain Size	
Soil Samples																	
SS-125	Soil	0.0-1.0	Macrocore				X										
SS-126	Soil	0.0-1.0	Macrocore														*Contingent on sample SS-125
SS-127	Soil	0.0-1.0	Macrocore		X	X	X		X	X							
SS-128	Soil	0.0-1.0	Macrocore														*Contingent on sample SS-127
SS-129	Soil	0.0-1.0	Macrocore		X	X	X		X	X							
SS-130	Soil	0.0-1.0	Macrocore														*Contingent on sample SS-129
SS-131	Soil	0.0-1.0	Macrocore				X										
SS-132	Soil	0.0-1.0	Macrocore														*Contingent on sample SS-131
SS-133	Soil	0.0-1.0	Macrocore		X	X			X								
SS-134	Soil	0.0-1.0	Macrocore														*Contingent on sample SS-133
SS-135	Soil	0.0-1.0	Macrocore				X		X								
SS-136	Soil	0.0-1.0	Macrocore														*Contingent on sample SS-135
SS-137	Soil	0.0-1.0	Macrocore				X		X	X							
SS-138	Soil	0.0-1.0	Macrocore														*Contingent on sample SS-137
SS-139	Soil	0.0-1.0	Macrocore				X		X	X							
SS-140	Soil	0.0-1.0	Macrocore														*Contingent on sample SS-139
SS-141	Soil	0.0-1.0	Macrocore				X		X								
SS-142	Soil	0.0-1.0	Macrocore														*Contingent on sample SS-141
SS-143	Soil	0.0-1.0	Macrocore						X								

Table 1
Sample Locations, Depths, and Analyses
Data Gaps Sampling and Analysis Plan
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Chatham, New Jersey

Sample ID	Sample Media	Depth Interval (Feet)	Sample Collection Method	Laboratory Analyses													Notes
				VOCs	SVOCs	SVOCs - SIM	PCBs (as Aroclors)	Pesticides	TAL Metals and Cyanide	PCB Congeners, Dioxins, Furans	Full TCL/TAL	TAL Metals and Cyanide (unfiltered)	TAL Metals and Cyanide (filtered)	Low-Level Mercury	Hardness	pH, TOC, Grain Size	
SS-144	Soil	0.0-1.0	Macrocore														*Contingent on sample SS-143
SS-145	Soil	0.0-1.0	Macrocore		X												
SS-146	Soil	0.0-1.0	Macrocore														*Contingent on sample SS-145
SS-147	Soil	0.0-1.0	Macrocore		X		X	X	X								
SS-148	Soil	0.0-1.0	Macrocore														*Contingent on sample SS-147
SS-149	Soil	0.0-1.0	Macrocore		X		X		X								
SS-150	Soil	0.0-1.0	Macrocore														*Contingent on sample SS-149
SS-151	Soil	0.0-1.0	Macrocore		X												
SS-152	Soil	0.0-1.0	Macrocore														*Contingent on sample SS-151
SS-153	Soil	0.0-1.0	Macrocore		X												
SS-154	Soil	0.0-1.0	Macrocore														*Contingent on sample SS-153
SS-155	Soil	0.0-1.0	Macrocore				X		X								
SS-156	Soil	0.0-1.0	Macrocore														*Contingent on sample SS-155
SS-157	Soil	0.0-1.0	Macrocore				X		X								
SS-158	Soil	0.0-1.0	Macrocore														*Contingent on sample SS-157
SS-159	Soil	0.0-1.0	Macrocore			X				X	X						Congeners, dioxins, and furans will be analyzed on up to 2 samples if PCBs are detected in the TAL analysis.
SS-160	Soil	0.0-1.0	Macrocore			X				X	X						
SS-161	Soil	0.0-1.0	Macrocore			X				X	X						
SS-162	Soil	0.0-1.0	Macrocore			X				X	X						
SS-163	Soil	0.0-1.0	Macrocore			X				X	X						
SS-164	Soil	0.0-1.0	Macrocore			X				X	X						

Table 1
Sample Locations, Depths, and Analyses
Data Gaps Sampling and Analysis Plan
Rolling Knolls Landfill Superfund Site
Chatham, New Jersey

Sample ID	Sample Media	Depth Interval (Feet)	Sample Collection Method	Laboratory Analyses													Notes
				VOCs	SVOCs	SVOCs - SIM	PCBs (as Aroclors)	Pesticides	TAL Metals and Cyanide	PCB Congeners, Dioxins, Furans	Full TCL/TAL	TAL Metals and Cyanide (unfiltered)	TAL Metals and Cyanide (filtered)	Low-Level Mercury	Hardness	pH, TOC, Grain Size	
Temporary Monitoring Wells																	
TWP-1	Groundwater	TBD	Macrocore	X								X	X				
TWP-2	Groundwater	TBD	Macrocore	X								X	X				
TWP-3	Groundwater	TBD	Macrocore	X								X	X				
TWP-4	Groundwater	TBD	Macrocore	X								X	X				
TWP-5	Groundwater	TBD	Macrocore	X								X	X				
TWP-6	Groundwater	TBD	Macrocore	X								X	X				
TWP-7	Groundwater	TBD	Macrocore	X								X	X				
TWP-8	Groundwater	TBD	Macrocore	X								X	X				
TWP-9	Groundwater	TBD	Macrocore	X								X	X				
Permanent Monitoring Wells (Existing)																	
MW-1	Groundwater	14.5	Low flow	X								X	X				
MW-2	Groundwater	12.5	Low flow	X								X	X				
MW-3	Groundwater	12.5	Low flow	X	X	X		X				X	X				
MW-4	Groundwater	12.5	Low flow	X								X	X				
MW-5	Groundwater	12.5	Low flow	X								X	X				
MW-6	Groundwater	12.5	Low flow	X								X	X				
MW-7	Groundwater	12.5	Low flow	X	X	X						X	X				
MW-8	Groundwater	12.5	Low flow	X								X	X				
MW-9	Groundwater	12.5	Low flow	X								X	X				
MW-10	Groundwater	12.5	Low flow	X								X	X				
X-1	Groundwater	18	Low flow	X								X	X				

Table 1
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				VOCs	SVOCs	SVOCs - SIM	PCBs (as Aroclors)	Pesticides	TAL Metals and Cyanide	PCB Congeners, Dioxins, Furans	Full TCL/TAL	TAL Metals and Cyanide (unfiltered)	TAL Metals and Cyanide (filtered)	Low-Level Mercury	Hardness	pH, TOC, Grain Size	
X-2	Groundwater	20	Low flow	X								X	X				
X-3	Groundwater	23	Low flow	X								X	X				
X-4	Groundwater	15.5	Low flow	X								X	X				
X-5	Groundwater	13.2	Low flow			X					X		X				This well was not sampled during previous sampling activities due to a lack
X-6	Groundwater	13	Low flow	X								X	X				
X-7	Groundwater	8.7	Low flow			X					X		X				This well was not sampled during previous sampling activities due to a lack of water
Permanent Monitoring Wells (Proposed)																	
MW-11	Groundwater	TBD	Low flow														Analytes for these new permanent wells will be selected based on the results of nearby soil samples and groundwater samples from the temporary wells.
MW-12	Groundwater	TBD	Low flow														
MW-13	Groundwater	TBD	Low flow														
MW-14	Groundwater	TBD	Low flow														
MW-15	Groundwater	TBD	Low flow														
MW-16	Groundwater	TBD	Low flow														
MW-17	Groundwater	TBD	Low flow														
Pore Water Samples																	
PW-1	Pore Water	0.0-0.5	PDB	X													
PW-2	Pore Water	0.0-0.5	PDB	X													
Surface Water Samples																	
SW-34	Surface Water	TBD	Teflon-lined bailer/direct dip			X					X		X	X	X		

Table 1
Sample Locations, Depths, and Analyses
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Chatham, New Jersey

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				VOCs	SVOCs	SVOCs - SIM	PCBs (as Aroclors)	Pesticides	TAL Metals and Cyanide	PCB Congeners, Dioxins, Furans	Full TCL/TAL	TAL Metals and Cyanide (unfiltered)	TAL Metals and Cyanide (filtered)	Low-Level Mercury	Hardness	pH, TOC, Grain Size	
SW-35	Surface Water	TBD	Teflon-lined bailer/direct dip			X					X		X	X	X		
SW-36	Surface Water	TBD	Teflon-lined bailer/direct dip			X					X		X	X	X		
SW-37	Surface Water	TBD	Teflon-lined bailer/direct dip			X					X		X	X	X		
SW-38	Surface Water	TBD	Teflon-lined bailer/direct dip			X					X		X	X	X		
SW-39	Surface Water	TBD	Teflon-lined bailer/direct dip			X					X		X	X	X		
SW-40	Surface Water	TBD	Teflon-lined bailer/direct dip			X					X		X	X	X		
SW-41	Surface Water	TBD	Teflon-lined bailer/direct dip			X					X		X	X	X		
SW-42	Surface Water	TBD	Teflon-lined bailer/direct dip			X					X		X	X	X		
SW-43	Surface Water	TBD	Teflon-lined bailer/direct dip			X					X		X	X	X		
SW-44	Surface Water	TBD	Teflon-lined bailer/direct dip			X					X		X	X	X		

Table 1
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Rolling Knolls Landfill Superfund Site
Chatham, New Jersey

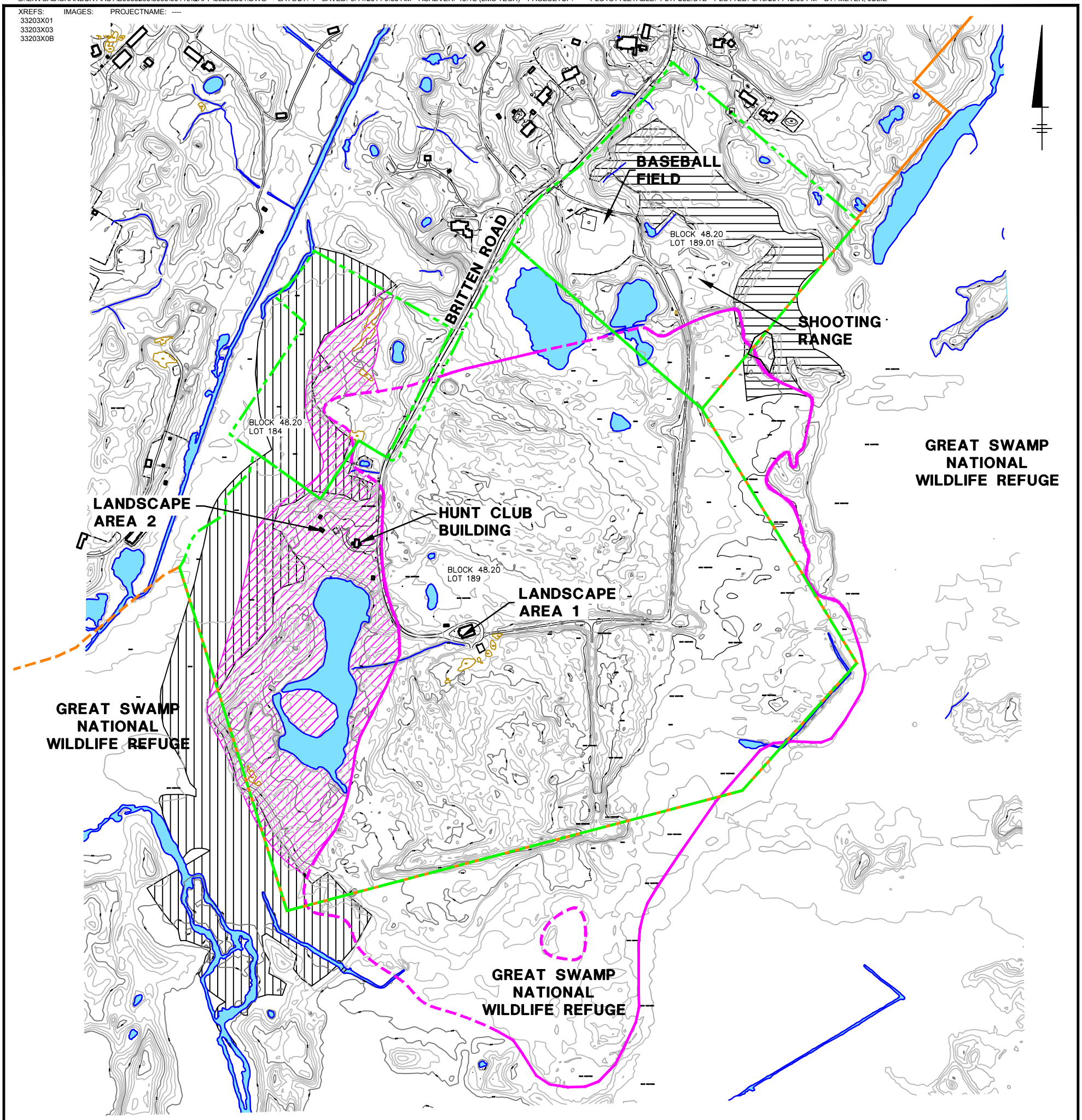
Sample ID	Sample Media	Depth Interval (Feet)	Sample Collection Method	Laboratory Analyses													Notes
				VOCs	SVOCs	SVOCs - SIM	PCBs (as Aroclors)	Pesticides	TAL Metals and Cyanide	PCB Congeners, Dioxins, Furans	Full TCL/TAL	TAL Metals and Cyanide (unfiltered)	TAL Metals and Cyanide (filtered)	Low-Level Mercury	Hardness	pH, TOC, Grain Size	
Sediment Samples																	
SD-34	Sediment	0.0 - 1.0	Grab sample – Encore sampler			X					X					X	
SD-35	Sediment	0.0 - 1.0	Grab sample – Encore sampler			X					X					X	
SD-36	Sediment	0.0 - 1.0	Grab sample – Encore sampler			X					X					X	
SD-37	Sediment	0.0 - 1.0	Grab sample – Encore sampler			X					X					X	
SD-38	Sediment	0.0 - 1.0	Grab sample – Encore sampler			X					X					X	
SD-39	Sediment	0.0 - 1.0	Grab sample – Encore sampler			X					X					X	
SD-40	Sediment	0.0 - 1.0	Grab sample – Encore sampler			X					X					X	
SD-41	Sediment	0.0 - 1.0	Grab sample – Encore sampler			X					X					X	
SD-42	Sediment	0.0 - 1.0	Grab sample – Encore sampler			X					X					X	
SD-43	Sediment	0.0 - 1.0	Grab sample – Encore sampler			X					X					X	
SD-44	Sediment	0.0 - 1.0	Grab sample – Encore sampler			X					X					X	

Abbreviations:

VOCs = volatile organic compounds
SVOCs = semivolatile organic compound
PCBs = polychlorinated biphenyls
PDB = passive diffusion bag
TCL = Target Compound List
TOC = total organic carbon
TAL= Target Analyte List

Sample analyses will be conducted using the following analytical methods:
Target Compound List organics (VOCs, SVOCs, PCBs and pesticides) via SOM01.2, *Contract Laboratory Program (CLP Statement of Work for Organic Ar*
Target Analyte List metals and cyanide via ISM01.3, *CLP Statement of Work for Inorganic Analyses*
PCB Congeners via USEPA Method 1668A, *Chlorinated Biphenyl Congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS*
Dioxins and furans via USEPA Method 1613, *Dioxins and Furans in Water, Soil, Sediment and Tissue by HRGC/HRMS.*
Low-level mercury via USEPA Method 1631, Revision E.
Hardness via SM 2340C.
pH via USEPA Method 9045D.
TOC via the Lloyd Kahn method.
Grain size via ASTM D-422.

Figures



NOTES:

1. THE PRE-REMEDIAL INVESTIGATION PROJECTED EDGE OF LANDFILLED MATERIALS ON THIS FIGURE IS APPROXIMATE AS DRAWN AND IS BASED ON VISUAL OBSERVATIONS OF THE GROUND SURFACE MADE DURING SITE VISITS CONDUCTED JUNE 20, 2006 THROUGH JULY 14, 2006.
2. THE EDGE OF LANDFILLED WASTES OBSERVED DURING TEST PIT ACTIVITIES IS DRAWN BASED ON OBSERVATIONS OF MATERIALS EXCAVATED DURING TEST PIT ACTIVITIES CONDUCTED FROM JULY 26, 2007 TO SEPTEMBER 6, 2007 AND MARCH 26, 2008.
3. THE PORTION OF THE GREAT SWAMP NATIONAL WILDLIFE REFUGE (GSNWR) PROPERTY BOUNDARY ON THIS FIGURE WITHIN CHATHAM TOWNSHIP, NJ WAS OBTAINED FROM CHATHAM TOWNSHIP TAX PARCEL DATA PROVIDED BY CIVIL SOLUTIONS. THE PORTION OF THE GSNWR PROPERTY BOUNDARY ON THIS FIGURE OUTSIDE OF CHATHAM TOWNSHIP IS APPROXIMATE AND WAS OBTAINED FROM THE UNITED STATES FISH AND WILDLIFE SERVICE (GEOGRAPHIC INFORMATION SYSTEMS AND SPATIAL DATA).
4. BLOCK 48.20, LOTS 184 AND 189 ARE OWNED BY ROBERT J. MIELE AS TRUSTEE FOR THE TRUST CREATED BY THE LAST WILL AND TESTAMENT OF ANGELO J. MIELE. BLOCK 48.20, LOT 189.01 IS OWNED BY THE GREEN VILLAGE FIRE DEPARTMENT.

LEGEND:

- OPEN WATER
- EDGE OF LANDFILLED WASTES OBSERVED DURING TEST PIT ACTIVITIES (DASHED WHERE APPROXIMATE)
- GREAT SWAMP NATIONAL WILDLIFE REFUGE PROPERTY BOUNDARY (DASHED WHERE APPROXIMATE)
- TAX PARCELS
- WASTE AND DEBRIS OBSERVED ON GROUND SURFACE BUT NOT OBSERVED OR ANTICIPATED TO BE BELOW GROUND SURFACE
- POTENTIAL BOG TURTLE HABITAT AREA A (35.31 ACRES)
- POTENTIAL BOG TURTLE HABITAT AREA B (10.89 ACRES)

SOURCES:

1. BASEMAP FROM JAMES M. STEWART INC., LAND SURVEYORS, PHILADELPHIA, PA., (ELECTRONIC FILE: 292406.DWG DATED: 6/30/06)
2. TAX PARCEL DATA FOR CHATHAM TOWNSHIP WAS PROVIDED BY CIVIL SOLUTIONS.

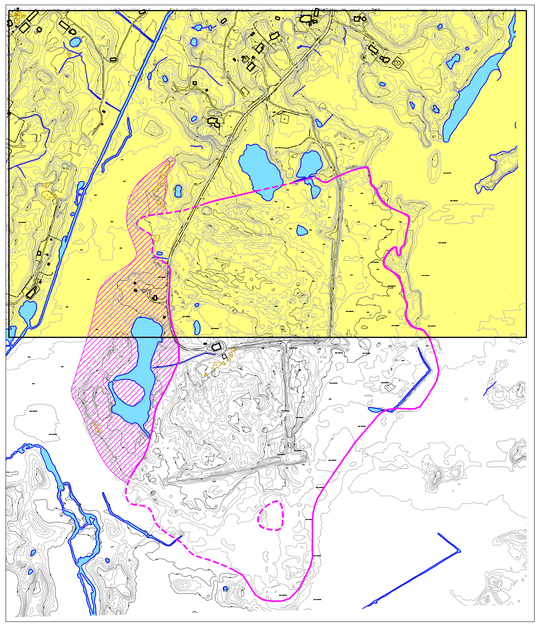
0 500' 1000'
GRAPHIC SCALE

ROLLING KNOLLS LANDFILL SUPERFUND SITE
CHATHAM, NEW JERSEY
QUALITY ASSURANCE PROJECT PLAN

SITE PLAN

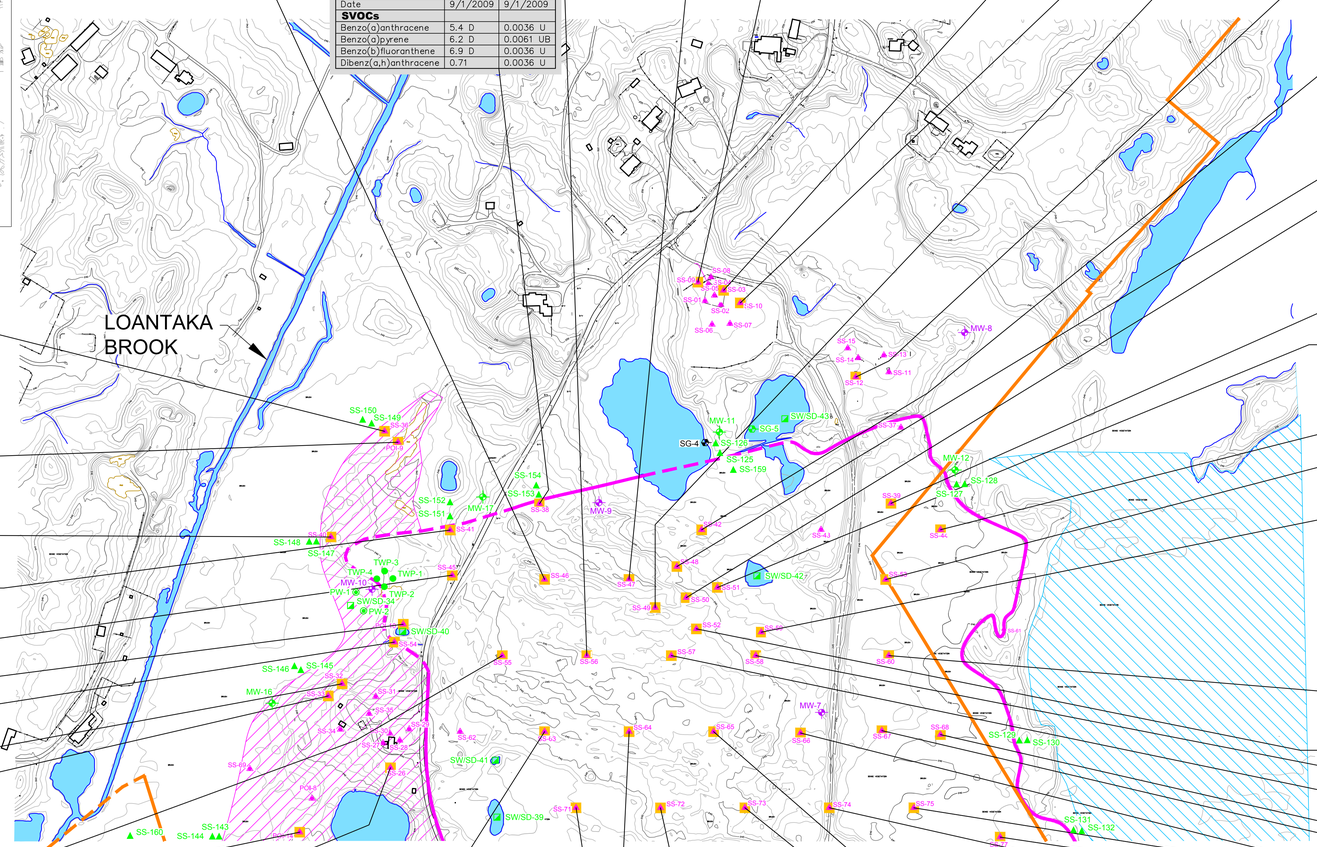
ARCADIS

FIGURE
1



SITE MAP

0 500' 1000'
GRAPHIC SCALE



SS-46		
Depth(Feet)	(0 – 1)	(6 – 7)
Date	9/1/2009	9/1/2009
SVOCs		
Benzo(a)pyrene	0.54 J	0.25 EJ
PCBs (Aroclors)		
Aroclor–1242	16 DJ	0.054 U
Aroclor–1254	12 DJ	1.2 D
Aroclor–1260	1.2 J	0.14
Aroclor–1268	2.8 J	0.067
Total PCBs (Aroclors)	32 J	2.03
PCBs (Congeners)		
Total PCBs (Congeners)	95 J	NA
Metals		
Arsenic	7 J	24.5 J
Lead	665	1,460

SS-56		
Depth(Feet)	(0 – 1)	(2 – 3)
Date	8/26/2009	8/26/2009
PCBs (Aroclors)		
Aroclor–1242	3 D	4.1 D
Aroclor–1254	7.2 D	4 D
Aroclor–1260	1.2	0.97
Total PCBs (Aroclors)	11.4	9.07
Pesticides		
Dieldrin	0.3 D	0.041 J
Metals		
Arsenic	14.6 J	20.6 J
Lead	2,060 J	1,120 J

SS-38		
Depth(Feet)	(0 – 1)	(9 – 10)
Date	9/1/2009	9/1/2009
SVOCs		
Benzo(a)anthracene	5.4 D	0.0036 U
Benzo(a)pyrene	6.2 D	0.0061 UB
Benzo(b)fluoranthene	6.9 D	0.0036 U
Dibenz(a,h)anthracene	0.71	0.0036 U

SS-47		
Depth(Feet)	(0 – 1)	(8 – 9)
Date	8/31/2009	8/31/2009
SVOCs		
Benzo(a)pyrene	0.2 J	0.21 J
PCBs (Aroclors)		
Aroclor–1254	3 D	0.61
Aroclor–1260	1.5 D	0.13
Total PCBs (Aroclors)	5.35	1.47 J
Metals		
Arsenic	23.1	5.5 J
Lead	7,140	835

SS-03	
Depth(Feet)	(0 – 1)
Date	9/19/2007
SVOCs	
Benzo(a)pyrene	0.92

SS-10	
Depth(Feet)	(0 – 1)
Date	9/20/2007
SVOCs	
Benzo(a)pyrene	0.74 D

SS-09	
Depth(Feet)	(0 – 1)
Date	9/20/2007
SVOCs	
Benzo(a)pyrene	1

SS-49	
Depth(Feet)	(0 – 1)
Date	8/31/2009
SVOCs	
Benzo(a)pyrene	1.7
Benzo(b)fluoranthene	2.4
Dibenz(a,h)anthracene	0.25 EJ
PCBs (Aroclors)	
Aroclor–1248	1.6 D
Aroclor–1254	2.7 D
Aroclor–1260	1.3 D
Total PCBs (Aroclors)	5.6
Metals	
Arsenic	21.1
Lead	1,010

SS-12	
Depth(Feet)	(0 – 1)
Date	9/20/2007
SVOCs	
Benzo(a)pyrene	0.77 D

SS-42	
Depth(Feet)	(0 – 1)
Date	8/28/2009
PCBs (Aroclors)	
Aroclor–1254	1.3 D
Total PCBs (Aroclors)	1.84

SS-48	
Depth(Feet)	(0 – 1)
Date	8/28/2009
SVOCs	
Benzo(a)pyrene	0.27 EJ
PCBs (Aroclors)	
Aroclor–1248	1.4 D
Aroclor–1254	2.4 D
Total PCBs (Aroclors)	4.4
Metals	
Lead	1,300

SS-50	
Depth(Feet)	(0 – 1)
Date	8/28/2009
PCBs (Aroclors)	
Aroclor–1254	2.3 D
Aroclor–1260	1.1
Total PCBs (Aroclors)	3.4
Metals	
Arsenic	19.1 J

SS-39	
Depth(Feet)	(0 – 1)
Date	9/16/2009
SVOCs	
Benzo(a)pyrene	0.41
PCBs (Aroclors)	
Aroclor–1242	6.1
Aroclor–1254	6.2
Total PCBs (Aroclors)	12.3
PCBs (Congeners)	
Total PCBs (Congeners)	100 J
Metals	
Lead	1,050

SS-51	
Depth(Feet)	(0 – 1)
Date	8/28/2009
SVOCs	
Benzo(a)pyrene	0.44
PCBs (Aroclors)	
Aroclor–1248	1.6 D
Aroclor–1254	3 D
Total PCBs (Aroclors)	5.45
Metals	
Lead	2,200

SS-44	
Depth(Feet)	(0 – 1)
Date	9/1/2009
PCBs (Aroclors)	
Aroclor–1254	1.1 D
Total PCBs (Aroclors)	1.83
Metals	
Lead	1,580

SS-53	
Depth(Feet)	(0 – 1)
Date	9/17/2009
SVOCs	
Benzo(a)pyrene	0.57
PCBs (Aroclors)	
Aroclor–1242	4.1
Aroclor–1254	5.6
Aroclor–1260	1.2
Total PCBs (Aroclors)	10.9
Metals	
Lead	1,110 J

SS-59	
Depth(Feet)	(0 – 1)
Date	8/27/2009
PCBs (Aroclors)	
Aroclor–1242	6.5 D
Aroclor–1254	2.7 D
Total PCBs (Aroclors)	10
Metals	
Lead	1,250 J

SS-60	
Depth(Feet)	(0 – 1)
Date	9/18/2009
PCBs (Aroclors)	
Aroclor–1248	1.2 J
Aroclor–1254	3.6 J
Aroclor–1260	1.2 J
Total PCBs (Aroclors)	6 J
Pesticides	
Dieldrin	0.29 DJ
Metals	
Lead	974

SS-52	
Depth(Feet)	(0 – 1)
Date	8/31/2009
SVOCs	
Benzo(a)anthracene	2.7
Benzo(a)pyrene	3.2 J
Benzo(b)fluoranthene	4.2 J
Dibenz(a,h)anthracene	0.58 EJ
PCBs (Aroclors)	
Aroclor–1242	9.4 D
Aroclor–1254	5.3 D
Total PCBs (Aroclors)	15.4
PCBs (Congeners)	
Total PCBs (Congeners)	12.4 J
Metals	
Lead	2,850

SS-58	
Depth(Feet)	(0 – 1)
Date	8/28/2009
PCBs (Aroclors)	
Aroclor–1248	67 D
Aroclor–1254	57 D
Aroclor–1260	1.7
Total PCBs (Aroclors)	126
PCBs (Congeners)	
Total PCBs (Congeners)	157 J
Pesticides	
Aldrin	0.27 DJN
Metals	
Lead	927

SS-36	
Depth(Feet)	(0 – 1)
Date	8/31/2009
SVOCs	
Benzo(a)anthracene	2.2
Benzo(a)pyrene	2.3
Benzo(b)fluoranthene	3.1
Dibenz(a,h)anthracene	0.51 EJ
PCBs (Aroclors)	
Aroclor–1254	1.5 DJ
Total PCBs (Aroclors)	2.06 J
Metals	
Lead	2,910

SS-40	
Depth(Feet)	(0 – 1)
Date	8/31/2009
SVOCs	
Benzo(a)pyrene	0.25 J
PCBs (Aroclors)	
Aroclor–1254	1.3 D
Total PCBs (Aroclors)	1.56
Pesticides	
alpha–Chlordane	2.5 D
gamma–Chlordane	2.3 D
Metals	
Lead	825

POI-10	
Depth(Feet)	(0 – 1)
Date	8/26/2009
PCBs (Aroclors)	
Aroclor–1254	3.6 JN
Aroclor–1260	88 D
Total PCBs (Aroclors)	91.6 J
PCBs (Congeners)	
Total PCBs (Congeners)	2.05 J
Metals	
Copper	49,900 J
Lead	1,510 J

SS-32	
Depth(Feet)	(0 – 1)
Date	11/6/2007
SVOCs	
Benzo(a)pyrene	1 J

SS-55		
Depth(Feet)	(0 – 1)	(2 – 3)
Date	9/1/2009	9/1/2009
SVOCs		
Benzo(a)pyrene	0.3 J	0.17 J
PCBs (Aroclors)		
Aroclor–1248	1.5 DJ	0.049 U
Aroclor–1254	1.4 D	0.73
Total PCBs (Aroclors)	3.54 J	1.81
Metals		
Antimony	1,960 J	2.8 J
Arsenic	529 J	8.4 J
Lead	16,500	934

POI-9	
Depth(Feet)	(0 – 1)
Date	8/27/2009
SVOCs	
Benzo(a)anthracene	30 DJ
Benzo(a)pyrene	33 DJ
Benzo(b)fluoranthene	42 DJ
Benzo(k)fluoranthene	24 DJ
Dibenz(a,h)anthracene	5 J
Indeno(1,2,3–cd)pyrene	13 J
PCBs (Aroclors)	
Total PCBs (Aroclors)	1.97 J
Metals	
Lead	7,900 J

SS-41	
Depth(Feet)	(0 – 1)
Date	8/27/2009
SVOCs	
Benzo(a)pyrene	0.26

SS-45		
Depth(Feet)	(0 – 1)	(9 – 10)
Date	8/31/2009	8/31/2009
SVOCs		
Benzo(a)pyrene	0.77	0.006

SS-54	
Depth(Feet)	(0 – 1)
Date	8/31/2009
SVOCs	
Benzo(a)pyrene	0.22 [0.24]

SS-33	
Depth(Feet)	(0 – 1)
Date	11/6/2007
SVOCs	
Benzo(a)pyrene	0.39

POI-14	
Depth(Feet)	(0 – 1)
Date	8/24/2009
Metals	
Arsenic	31.7 J
Lead	9,210 J

SS-26	
Depth(Feet)	(0 – 1)
Date	11/5/2007
SVOCs	
Benzo(a)pyrene	0.23 J

SS-63		
Depth(Feet)	(0 – 1)	(3.5 – 4.5)
Date	8/26/2009	8/26/2009
SVOCs		
Benzo(a)pyrene	0.26	0.19 EJ
PCBs (Aroclors)		
Aroclor–1242	0.24 U	2.8 D
Aroclor–1248	7.7 DJ	0.074 U
Aroclor–1254	5.3 DJ	4 D
Total PCBs (Aroclors)	13.9 J	7.44
PCBs (Congeners)		
Total PCBs (Congeners)	44.1 J	NA
Metals		
Arsenic	19.3 J	24.3 J
Lead	2,020 J	2,520 J

SS-71	
Depth(Feet)	(0 – 1)
Date	8/26/2009
PCBs (Aroclors)	
Total PCBs (Aroclors)	1.1 J
Metals	
Lead	1,070 J
Vanadium	6,140

SS-72		
Depth(Feet)	(0 – 1)	(9 – 10)
Date	8/25/2009	8/25/2009
PCBs (Aroclors)		
Aroclor–1242	0.11 U	1.8
Aroclor–1248	2.5 D	0.11 U
Aroclor–1254	3.3 D	3.9 D
Total PCBs (Aroclors)	7.07 J	6.09
PCBs (Congeners)		
Total PCBs (Congeners)	8.65 J	NA
Metals		
Arsenic	26 J	12.6 J
Lead	1,750 J	950 J

SS-65		
Depth(Feet)	(0 – 1)	(5 – 6)
Date	8/27/2009	8/27/2009
SVOCs		
Acetophenone	18 D	0.05 J
Benzo(a)anthracene	66 D	0.86
Benzo(a)pyrene	51 D	0.88
Benzo(b)fluoranthene	49 D	1.2
Benzo(k)fluoranthene	51 D	1.3
Dibenz(a,h)anthracene	4.8 J	0.44 EJ
Indeno(1,2,3–cd)pyrene	12 J	0.15 J
PCBs (Aroclors)		
Aroclor–1242	0.065 U	4.2 DJ
Aroclor–1248	1.8 D	0.15 U
Aroclor–1254	1.5 DJ	3 D
Total PCBs (Aroclors)	3.68 J	7.73 J
Metals		
Lead	1,560 J	3,380 J

SS-75	
Depth(Feet)	(0 – 1)
Date	9/15/2009
PCBs (Aroclors)	
Aroclor–1248	1.3
Aroclor–1254	2.3
Total PCBs (Aroclors)	4.17
Metals	
Arsenic	32.3
Lead	1,360

SS-77	
Depth(Feet)	(0 – 1)
Date	9/17/2009
PCBs (Aroclors)	
Aroclor–1248	1.7
Total PCBs (Aroclors)	2.16 J

SS-66	
Depth(Feet)	(0 – 1)
Date	8/28/2009
SVOCs	
Benzo(a)pyrene	0.28
PCBs (Aroclors)	
Aroclor–1248	15
Aroclor–1254	55 D
Aroclor–1260	8.1
Total PCBs (Aroclors)	78.1
PCBs (Congeners)	
Total PCBs (Congeners)	9.66 J
Metals	
Arsenic	21.9
Lead	2,100

SS-57		
Depth(Feet)	(0 – 1)	(4 – 5)
Date	8/27/2009	8/27/2009
SVOCs		
Benzo(a)pyrene	2.3	0.38 J
Benzo(b)fluoranthene	3.6	0.58 J
Dibenz(a,h)anthracene	0.17 J	0.69 EJ
PCBs (Aroclors)		
Aroclor–1248	2.8 D	4.2 D
Aroclor–1254	2.7 DJN	4.6 D
Aroclor–1260	7 D	3.3 D
Total PCBs (Aroclors)	12.5 J	12.1
Pesticides		
Heptachlor epoxide	RX	0.33 DJN
Metals		
Lead	795 J	1,060 J

SS-64		
Depth(Feet)	(0 – 1)	(5 – 6)
Date	8/27/2009	8/27/2009
SVOCs		
Dibenz(a,h)anthracene	0.21 EJ	0.49 EJ [0.36 EJ]
PCBs (Aroclors)		
Aroclor–1242	0.061 U	0.061 U [2.6 D]
Aroclor–1248	2.1 D	3.2 DJ [0.11 U]
Aroclor–1254	1.5 D	2.3 DJ [4.9 D]
Total PCBs (Aroclors)	3.99	6.32 J [8.24]
Metals		
Lead	1,930 J	1,020 J [1,130 J]

SS-73		
Depth(Feet)	(0 – 1)	(6 – 7)
Date	8/25/2009	8/25/2009
SVOCs		
Benzo(a)pyrene	0.12 EJ	0.24 J
PCBs (Aroclors)		
Aroclor–1242	0.11 U	1.7
Aroclor–1248	1.3	0.19 U
Aroclor–1254	2.5 D	1.3 J
Total PCBs (Aroclors)	4.49	3.16 J
Metals		
Lead	1,880 J	3,020 J

SS-74		
Depth(Feet)	(0 – 1)	(6 – 7)
Date	8/24/2009	8/24/2009
SVOCs		
Benzo(a)anthracene	1	2.2
Benzo(a)pyrene	1.1	2.7
Benzo(b)fluoranthene	1.2	3.8 D
Dibenz(a,h)anthracene	0.3 EJ	0.76 EJ
PCBs (Aroclors)		
Aroclor–1254	0.039 U	1.3 D
Total PCBs (Aroclors)	0.211 J	2.17

SS-67	
Depth(Feet)	(0 – 1)
Date	9/3/2009
SVOCs	
Benzo(a)pyrene	0.49
PCBs (Aroclors)	
Total PCBs (Aroclors)	1.32 J
Metals	
Lead	1,580

SS-68	
Depth(Feet)	(0 – 1)
Date	9/2/2009
SVOCs	
Benzo(a)pyrene	0.32 [0.18 EJ]
PCBs (Aroclors)	
Aroclor–1248	1.2 DJ [1.3 DJ]
Aroclor–1254	3.2 D [2.6 D]
Total PCBs (Aroclors)	4.99 J [4.41 J]
PCBs (Congeners)	
Total PCBs (Congeners)	4.91 J [9.46 J]
Metals	
Lead	1,320 [1,150]

Nonresidential Soil Remediation Standards	
Constituent	Value
VOCs	
Carbon Tetrachloride	2
Chloroform	2
SVOCs	
Acetophenone	5
Benzo(a)anthracene	2
Benzo(a)pyrene	0.2
Benzo(b)fluoranthene	2
Benzo(k)fluoranthene	23
Dibenz(a,h)anthracene	0.2
Indeno(1,2,3–cd)pyrene	2
PCBs	
Aroclor–1242	1
Aroclor–1248	1
Aroclor–1254	1
Aroclor–1260	1
Aroclor–1262	1
Aroclor–1268	1
Total PCBs (Aroclors)	1
PCBs (Congeners)	
Total PCBs (Congeners)	1
Pesticides	
Aldrin	0.2
alpha–Chlordane	1
Dieldrin	0.2
gamma–Chlordane	1
Heptachlor	0.7
Heptachlor epoxide	0.3
Metals	
Antimony	450
Arsenic	19
Cadmium	78
Copper	45,000
Lead	800
Manganese	5,900
Mercury	65
Vanadium	1,100

LEGEND:

- OPEN WATER
- EDGE OF LANDFILLED WASTES OBSERVED DURING TEST PIT ACTIVITIES (DASHED WHERE APPROXIMATE)
- GREAT SWAMP NATIONAL WILDLIFE REFUGE PROPERTY BOUNDARY (DASHED WHERE APPROXIMATE)
- WASTE AND DEBRIS OBSERVED ON GROUND SURFACE BUT NOT OBSERVED OR ANTICIPATED TO BE BELOW GROUND SURFACE
- AREAS WHERE SURFACE WATER FLOW DOES NOT EXHIBIT TYPICAL BED AND BANK MORPHOLOGY
- SOIL SAMPLING LOCATION
- SOIL SAMPLING LOCATION WITH DETECTED CONCENTRATIONS GREATER THAN NJDEP NONRESIDENTIAL SOIL REMEDIATION STANDARDS
- PROPOSED MONITORING WELL
- EXISTING MONITORING WELL
- PROPOSED TEMPORARY WELL POINT
- PROPOSED SOIL SAMPLE
- PROPOSED SURFACE WATER AND SEDIMENT SAMPLE
- PROPOSED POREWATER SAMPLE
- EXISTING STREAM GAUGE
- PROPOSED STREAM GAUGE

DATA NOTES:

UNITS = MILLIGRAMS PER KILOGRAM

[] = DUPLICATE SAMPLE

PCBS = POLYCHLORINATED BIPHENYLS

SVOCS = SEMIVOLATILE ORGANIC COMPOUNDS

VOCS = VOLATILE ORGANIC COMPOUNDS

NA = NOT ANALYZED

D = CONCENTRATIONS IDENTIFIED FROM ANALYSIS OF THE SAMPLE AT A SECONDARY DILUTION.

E = THE COMPOUND WAS QUANTITATED ABOVE THE CALIBRATION RANGE.

J = THE COMPOUND WAS POSITIVELY IDENTIFIED; HOWEVER, THE ASSOCIATED NUMERICAL VALUE IS AN ESTIMATED CONCENTRATION ONLY.

JN = THE ANALYSIS INDICATES THE PRESENCE OF A COMPOUND FOR WHICH THERE IS PRESUMPTIVE EVIDENCE TO MAKE A TENTATIVE IDENTIFICATION. THE ASSOCIATED NUMERICAL VALUE IS AN ESTIMATED CONCENTRATION ONLY.

U = THE COMPOUND WAS ANALYZED FOR BUT NOT DETECTED. THE ASSOCIATED VALUE IS THE COMPOUND QUANTITATION LIMIT.

RX = THE SAMPLE RESULTS ARE REJECTD DUE TO MATRIX INTERFERENCE.

NOTES:

1. ANALYTICAL RESULTS GIVEN IN MILLIGRAMS PER KILOGRAM FOR SOIL SAMPLES WITH DETECTED CONCENTRATIONS GREATER NEW JERSEY NONRESIDENTIAL SOIL REMEDIATION STANDARDS (DATED OCTOBER 2011).
2. THE EDGE OF LANDFILLED WASTES OBSERVED DURING TEST PIT ACTIVITIES IS DRAWN BASED ON OBSERVATIONS OF MATERIALS EXCAVATED DURING TEST PIT ACTIVITIES CONDUCTED FROM JULY 26, 2007 TO SEPTEMBER 6, 2007 AND MARCH 26, 2008.
3. THE PORTION OF THE GREAT SWAMP NATIONAL WILDLIFE REFUGE (GSNWR) PROPERTY BOUNDARY ON THIS FIGURE WITHIN CHATHAM TOWNSHIP, NJ WAS OBTAINED FROM CHATHAM TOWNSHIP TAX PARCEL DATA PROVIDED BY CIVIL SOLUTIONS. THE PORTION OF THE GSNWR PROPERTY BOUNDARY ON THIS FIGURE OUTSIDE OF CHATHAM TOWNSHIP IS APPROXIMATE AND WAS OBTAINED FROM THE UNITED STATES FISH AND WILDLIFE SERVICE (GEOGRAPHIC INFORMATION SYSTEMS AND SPATIAL DATA).
4. BLOCK 48.20, LOTS 184 AND 189 ARE OWNED BY ROBERT J. MIELE AS TRUSTEE FOR THE TRUST CREATED BY THE LAST WILL AND TESTAMENT OF ANGELO J. MIELE. BLOCK 48.20, LOT 189.01 IS OWNED BY THE GREEN VILLAGE FIRE DEPARTMENT.
5. THE EXTENT OF AREAS WHERE SURFACE WATER FLOW DOES NOT EXHIBIT TYPICAL BED AND BANK MORPHOLOGY IS BASED ON FIELD OBSERVATIONS MADE THROUGHOUT THE PERIOD OF INVESTIGATION ACTIVITIES. THE EXTENT OF THE AREA SHOWN IS APPROXIMATE.
6. ONLY SOIL ANALYTICAL RESULTS GREATER THAN NEW JERSEY NON–RESIDENTIAL SOIL REMEDIATION STANDARDS ARE POSTED.

SOURCES:

1. BASEMAP FROM JAMES M. STEWART INC., LAND SURVEYORS, PHILADELPHIA, PA., (ELECTRONIC FILE: 292406.DWG DATED: 6/30/06)
2. TAX PARCEL DATA FOR CHATHAM TOWNSHIP WAS PROVIDED BY CIVIL SOLUTIONS.

0 200' 400'
GRAPHIC SCALE

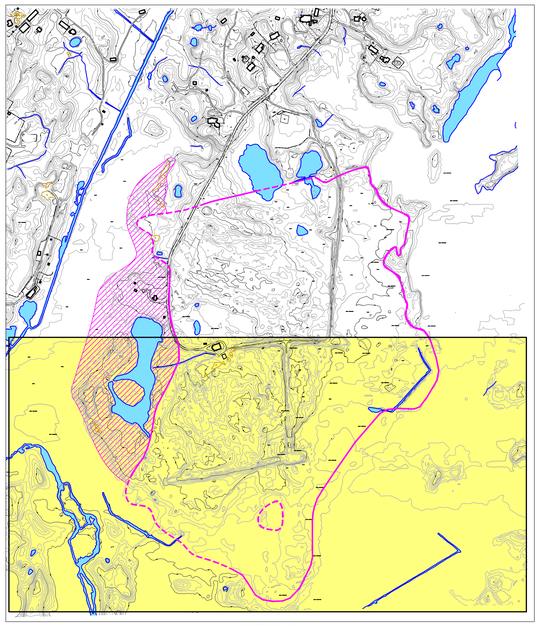
ROLLING KNOLLS LANDFILL SUPERFUND SITE
CHATHAM, NEW JERSEY
QUALITY ASSURANCE PROJECT PLAN

PROPOSED SAMPLE LOCATIONS - NORTH

ARCADIS

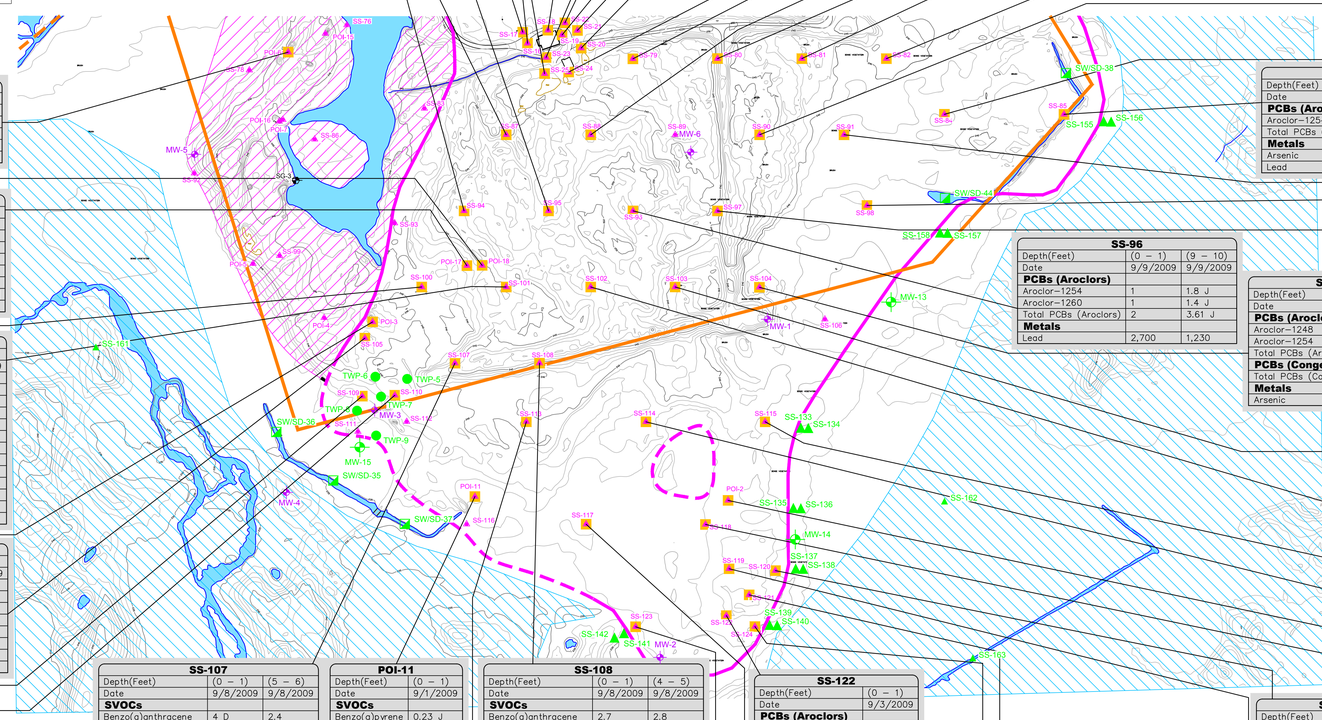
FIGURE **2a**

CITY: CRANBURY-NJ DIVGROUP: ENVCAD DB: T.FATTO LD: T.FATTO PIC:(OH) PM: K.ROMAINE TM: LHYATT LYR: ON*;OFF=*REF* PAGESETUP: ---- PLOTSTYLETABLE: PLTFULL.CTB PLOTTED: 9/19/2014 12:10 PM BY: MEYER, JULIE
G:\ENVCAD\CRANBURY\ACT\B0033203\0003\00119\0APPB\B0033203P01.DWG LAYOUT: 2A SAVED: 9/11/2014 9:35 AM ACADVER: 18.1S (LMS TECH)
XREFS: 33203X01 33203X03 IMAGES: PROJECTNAME: ----



SITE MAP

0 500' 1000'
GRAPHIC SCALE



SS-17	
Depth(Feet)	(0 – 1)
Date	11/2/2007
SVOCs	
Benzo(a)pyrene	1.2
Metals	
Lead	901 DJ

SS-16	
Depth(Feet)	(0 – 1)
Date	11/1/2007
SVOCs	
Benzo(a)pyrene	1.1 EJ

SS-25	
Depth(Feet)	(0 – 0.85)
Date	11/5/2007
SVOCs	
Benzo(a)pyrene	0.21

SS-18	
Depth(Feet)	(0 – 1)
Date	11/1/2007
SVOCs	
Benzo(a)pyrene	0.77 J

SS-23	
Depth(Feet)	(0 – 1)
Date	11/2/2007
SVOCs	
Benzo(a)pyrene	0.75

SS-22	
Depth(Feet)	(0 – 1)
Date	6/21/2007
SVOCs	
Benzo(a)anthracene	2.3 [3.3]
Benzo(a)pyrene	2.3 J [3.1]
Benzo(b)fluoranthene	3.3 J [4.5]

SS-19	
Depth(Feet)	(0 – 0.8)
Date	11/2/2007
SVOCs	
Benzo(a)anthracene	2.9
Benzo(a)pyrene	2.9
Benzo(b)fluoranthene	4.4
PCBs (Aroclors)	
Aroclor–1254	2.8 D
Total PCBs (Aroclors)	2.8
PCBs (Congeners)	
Total PCBs (Congeners)	6.41 J
Metals	
Lead	1,090 DJ

SS-24	
Depth(Feet)	(0 – 1)
Date	11/5/2007
SVOCs	
Benzo(a)pyrene	0.65 J
PCBs (Aroclors)	
Aroclor–1248	2.6 D
Aroclor–1260	2.1 D
Total PCBs (Aroclors)	4.7
PCBs (Congeners)	
Total PCBs (Congeners)	6.89 J
Metals	
Lead	1,080 DJ

SS-95		
Depth(Feet)	(0 – 1)	(6 – 7)
Date	9/10/2009	9/10/2009
PCBs (Aroclors)		
Aroclor–1254	1.7 J	2.1
Total PCBs (Aroclors)	2.46 J	3.73 J
Metals		
Lead	1,550	1,110

SS-87		
Depth(Feet)	(0 – 1)	(6 – 7)
Date	9/10/2009	9/10/2009
SVOCs		
Benzo(a)pyrene	0.28	0.36
PCBs (Aroclors)		
Aroclor–1254	7.3 J	0.52 J
Aroclor–1260	1.4 J	0.23 J
Aroclor–1268	0.92 U	2.3 J
Total PCBs (Aroclors)	8.7 J	3.26 J
Metals		
Arsenic	22.6	28.2
Lead	1,640	886

SS-94		
Depth(Feet)	(0 – 1)	(9 – 10)
Date	9/9/2009	9/9/2009
SVOCs		
Benzo(a)pyrene	0.077 EJ	0.22 EJ
PCBs (Aroclors)		
Aroclor–1248	1.3 J	0.16 J
Aroclor–1254	2.9 J	0.38
Total PCBs (Aroclors)	5.03 J	0.67 J
Metals		
Arsenic	16.9	22.7
Lead	1,400	1,040

SS-21	
Depth(Feet)	(0 – 1)
Date	6/21/2007
SVOCs	
Benzo(a)anthracene	4.3
Benzo(a)pyrene	4.3 J
Benzo(b)fluoranthene	6.2 J
Indeno(1,2,3–cd)pyrene	2.6 J

SS-20	
Depth(Feet)	(0 – 1)
Date	11/2/2007
SVOCs	
Benzo(a)anthracene	2.7
Benzo(a)pyrene	2.4
Benzo(b)fluoranthene	3.4

SS-79	
Depth(Feet)	(0 – 1)
Date	9/3/2009
PCBs (Aroclors)	
Aroclor–1254	2.7 J
Total PCBs (Aroclors)	4 J
Metals	
Lead	1,900

SS-88		
Depth(Feet)	(0 – 1)	(7 – 8)
Date	9/9/2009	9/9/2009
SVOCs		
Benzo(a)pyrene	0.51 J [0.72 J]	0.88 J
Dibenz(a,h)anthracene	0.21 EJ [0.54 EJ]	0.23 EJ
PCBs (Aroclors)		
Aroclor–1248	1.1 J [0.42 JN]	0.26 U
Aroclor–1254	4.8 J [2.4]	1.6
Total PCBs (Aroclors)	7.29 J [3.39 J]	2.01
Metals		
Arsenic	17.7 [19.8]	17.1
Lead	1,630 [2,370]	1,440

SS-80		
Depth(Feet)	(0 – 1)	(9 – 10)
Date	9/2/2009	9/2/2009
SVOCs		
Benzo(a)anthracene	11 D	5.1 D
Benzo(a)pyrene	11 D	5.8 D
Benzo(b)fluoranthene	13 DJ	6 D
Dibenz(a,h)anthracene	1.1 J	0.48 J
Indeno(1,2,3–cd)pyrene	2.5 J	1.5 J
PCBs (Aroclors)		
Aroclor–1254	0.32	1.5
Total PCBs (Aroclors)	0.407	3.18
Metals		
Lead	2,490	1,010

SS-81	
Depth(Feet)	(0 – 1)
Date	9/3/2009
PCBs (Aroclors)	
Aroclor–1242	0.6 U [3.1]
Aroclor–1248	1.7 J [0.6 U]
Aroclor–1254	5 [3.8]
Aroclor–1260	1.1 [0.87]
Total PCBs (Aroclors)	7.8 J [7.77]
Metals	
Lead	2,290 [3,190]

SS-90		
Depth(Feet)	(0 – 1)	(6 – 7)
Date	9/8/2009	9/8/2009
SVOCs		
Benzo(a)pyrene	0.082 J	0.49
PCBs (Aroclors)		
Aroclor–1242	2.4 U	1.3
Aroclor–1248	17 J	0.6 U
Aroclor–1254	12 J	2.3
Aroclor–1262	2.4 U	3.9
Total PCBs (Aroclors)	29 J	7.5
Metals		
Lead	1,540	1,620 J

SS-82	
Depth(Feet)	(0 – 1)
Date	9/3/2009
PCBs (Aroclors)	
Aroclor–1254	2.3
Total PCBs (Aroclors)	3.1 J
Metals	
Arsenic	22.4 J
Lead	4,010

SS-84	
Depth(Feet)	(0 – 1)
Date	9/2/2009
SVOCs	
Benzo(a)pyrene	0.47 J
PCBs (Aroclors)	
Aroclor–1254	9.4 D
Aroclor–1260	1.2
Total PCBs (Aroclors)	10.6
PCBs (Congeners)	
Total PCBs (Congeners)	125 J
Metals	
Lead	4,510

SS-85	
Depth(Feet)	(0 – 1)
Date	9/2/2009
PCBs (Aroclors)	
Aroclor–1254	2.2
Total PCBs (Aroclors)	3.74
Metals	
Arsenic	22.8 J
Lead	2,360

SS-91	
Depth(Feet)	(0 – 1)
Date	9/17/2009
SVOCs	
Benzo(a)pyrene	0.59
PCBs (Aroclors)	
Aroclor–1254	3.1
Total PCBs (Aroclors)	4.58 J

SS-98	
Depth(Feet)	(0 – 1)
Date	9/18/2009
PCBs (Aroclors)	
Aroclor–1248	2.4 J
Aroclor–1254	4.6
Total PCBs (Aroclors)	7.51 J
Metals	
Arsenic	25.7
Lead	2,710

POI-6	
Depth(Feet)	(0 – 1)
Date	8/25/2009
SVOCs	
Benzo(a)pyrene	0.28 J
Metals	
Lead	2,570 J

POI-18	
Depth(Feet)	(5 – 6)
Date	1/14/2010
PCBs (Aroclors)	
Aroclor–1248	1.1 DJ
Aroclor–1254	2.5 D
Total PCBs (Aroclors)	4.07 J
Metals	
Arsenic	21.2 J
Lead	1,540

POI-17	
Depth(Feet)	(5 – 6)
Date	1/13/2010
PCBs (Aroclors)	
Aroclor–1254	2.1 D [3.1 D]
Aroclor–1260	3.2 D [0.86 J]
Total PCBs (Aroclors)	5.67 [5.15 J]
Metals	
Arsenic	41.9 J [57.7 J]
Lead	1,900 [1,940]

SS-100	
Depth(Feet)	(0 – 1)
Date	9/10/2009
PCBs (Aroclors)	
Aroclor–1254	2.6
Total PCBs (Aroclors)	4.06 J
Metals	
Lead	2,650

SS-101		
Depth(Feet)	(0 – 1)	(4 – 5)
Date	9/9/2009	9/9/2009
SVOCs		
Benzo(a)pyrene	0.21 EJ	0.16 J
PCBs (Aroclors)		
Aroclor–1242	1.4	0.63 U
Aroclor–1248	0.61 U	1.9 J
Aroclor–1254	4.4	3.4 J
Aroclor–1260	1.5	2.7 J
Total PCBs (Aroclors)	7.3	8 J
PCBs (Congeners)		
Total PCBs (Congeners)	10.6 J	NA
Metals		
Arsenic	19.5	13
Lead	1,380	3,010

POI-3		
Depth(Feet)	(0 – 1)	(0.5 – 1)
Date	8/25/2009	8/25/2009
VOCs		
Carbon Tetrachloride	NA	4.4
Chloroform	NA	4.5 D
SVOCs		
Benzo(a)pyrene	0.22 J	NA
Metals		
Arsenic	29.3 J	NA
Lead	1,720 J	NA
Manganese	13,600 J	NA
Mercury	85.1	NA

SS-105	
Depth(Feet)	(0 – 1)
Date	8/26/2009
PCBs (Aroclors)	
Aroclor–1248	4.6 D
Aroclor–1254	4.4 D
Total PCBs (Aroclors)	9.31
PCBs (Congeners)	
Total PCBs (Congeners)	22.7 J
Metals	
Lead	1,070 J

SS-96		
Depth(Feet)	(0 – 1)	(9 – 10)
Date	9/9/2009	9/9/2009
PCBs (Aroclors)		
Aroclor–1254	1	1.8 J
Aroclor–1260	1	1.4 J
Total PCBs (Aroclors)	2	3.61 J
Metals		
Lead	2,700	1,230

SS-104	
Depth(Feet)	(0 – 1)
Date	9/2/2009
PCBs (Aroclors)	
Aroclor–1248	3.3 D
Aroclor–1254	1.9 D
Total PCBs (Aroclors)	5.57 J
PCBs (Congeners)	
Total PCBs (Congeners)	5.83 J
Metals	
Arsenic	22 J

SS-97		
Depth(Feet)	(0 – 1)	(6 – 7)
Date	9/4/2009	9/4/2009
SVOCs		
Benzo(a)pyrene	0.31 D	0.042 D
PCBs (Aroclors)		
Aroclor–1242	5.7	20 J
Aroclor–1254	10	4.8
Total PCBs (Aroclors)	15.7	24.8 J
PCBs (Congeners)		
Total PCBs (Congeners)	50.2 J	NA
Metals		
Arsenic	8.4 J	28.4 J
Lead	1,430	648

SS-103		
Depth(Feet)	(0 – 1)	(4 – 5)
Date	9/2/2009	9/2/2009
PCBs (Aroclors)		
Aroclor–1248	1.9 DJ	2.3 D
Aroclor–1254	3.1 D	4.1 D
Total PCBs (Aroclors)	5.55 J	7.01
Metals		
Arsenic	20.4 J	15 J
Cadmium	38.1 J	22,500 J
Lead	13,800	951

SS-102		
Depth(Feet)	(0 – 1)	(9 – 10)
Date	9/10/2009	9/10/2009
PCBs (Aroclors)		
Aroclor–1254	2.5	2.1
Total PCBs (Aroclors)	4.22 J	3.75
Metals		
Lead	1,870	4,700

SS-115	
Depth(Feet)	(0 – 1)
Date	9/14/2009
SVOCs	
Benzo(a)pyrene	1.5
Dibenz(a,h)anthracene	0.29 EJ
Metals	
Arsenic	33
Lead	6,170

SS-114	
Depth(Feet)	(0 – 1)
Date	9/14/2009
PCBs (Aroclors)	
Total PCBs (Aroclors)	1.17
Metals	
Lead	2,540

SS-110	
Depth(Feet)	(0 – 1)
Date	9/1/2009
SVOCs	
Benzo(a)pyrene	0.83
PCBs (Aroclors)	
Total PCBs (Aroclors)	1.28 J

SS-109	
Depth(Feet)	(0.5 – 1)
Date	8/31/2009
VOCs	
Chloroform	1,900 DJ

SS-107		
Depth(Feet)	(0 – 1)	(5 – 6)
Date	9/8/2009	9/8/2009
SVOCs		
Benzo(a)anthracene	4 D	2.4
Benzo(a)pyrene	3.6 D	2.7
Benzo(b)fluoranthene	4.2 D	3.1 D
Dibenz(a,h)anthracene	0.69 EJ	0.16 J
Metals		
Lead	792	1,070

POI-11	
Depth(Feet)	(0 – 1)
Date	9/1/2009
SVOCs	
Benzo(a)pyrene	0.23 J

SS-108		
Depth(Feet)	(0 – 1)	(4 – 5)
Date	9/8/2009	9/8/2009
SVOCs		
Benzo(a)anthracene	2.7	2.8
Benzo(a)pyrene	3.1	2.9
Benzo(b)fluoranthene	4.5 DJ	3.4 DJ
Dibenz(a,h)anthracene	0.27 J	0.24 J
PCBs (Aroclors)		
Aroclor–1254	0.29	2.5 DJ
Aroclor–1260	0.12	4.8 D
Total PCBs (Aroclors)	0.481	7.81 J
Metals		
Arsenic	9.8 J	28.3 J
Lead	6,270	3,340

SS-113	
Depth(Feet)	(0 – 1)
Date	9/16/2009
PCBs (Aroclors)	
Aroclor–1254	1.4
Total PCBs (Aroclors)	2.29 J
PCBs (Congeners)	
Total PCBs (Congeners)	3.55
Metals	
Antimony	881 J
Arsenic	33.9
Lead	2,280

SS-122	
Depth(Feet)	(0 – 1)
Date	9/3/2009
PCBs (Aroclors)	
Total PCBs (Aroclors)	1.28
Metals	
Lead	1,270

SS-117	
Depth(Feet)	(0 – 1)
Date	9/17/2009
PCBs (Aroclors)	
Aroclor–1254	1.8 J
Total PCBs (Aroclors)	2.66 J
Metals	
Arsenic	28.5
Lead	1,420 J

SS-123	
Depth(Feet)	(0 – 1)
Date	9/15/2009
PCBs (Aroclors)	
Aroclor–1254	1.3
Aroclor–1260	1.2
Total PCBs (Aroclors)	3.15
Metals	
Lead	1,370

SS-121	
Depth(Feet)	(0 – 1)
Date	9/3/2009
PCBs (Aroclors)	
Aroclor–1254	1.7 J
Aroclor–1260	6.9 J
Total PCBs (Aroclors)	8.6 J
PCBs (Congeners)	
Total PCBs (Congeners)	12.3 J
Metals	
Arsenic	30.2 J
Lead	1,340

SS-124	
Depth(Feet)	(0 – 1)
Date	9/15/2009
PCBs (Aroclors)	
Total PCBs (Aroclors)	1.48 J

SS-120	
Depth(Feet)	(0 – 1)
Date	9/3/2009
PCBs (Aroclors)	
Aroclor–1254	1.8
Aroclor–1260	1.6
Total PCBs (Aroclors)	3.4
Metals	
Arsenic	25.3 J
Lead	1,310

SS-119	
Depth(Feet)	(0 – 1)
Date	9/3/2009
SVOCs	
Benzo(a)pyrene	1.5
Benzo(b)fluoranthene	3.2
Dibenz(a,h)anthracene	0.33 EJ
PCBs (Aroclors)	
Aroclor–1254	1.3
Total PCBs (Aroclors)	2.3
Pesticides	
Heptachlor	1.1 D
Metals	
Lead	1,070

POI-2	
Depth(Feet)	(0 – 1)
Date	9/3/2009
PCBs (Aroclors)	
Total PCBs (Aroclors)	2.18
Metals	
Lead	1,490

SS-118	
Depth(Feet)	(0 – 1)
Date	9/15/2009
SVOCs	
Benzo(a)pyrene	0.4 D
PCBs (Aroclors)	
Aroclor–1242	11 J
Aroclor–1254	7.7 J
Aroclor–1260	4.3 J
Total PCBs (Aroclors)	23 J
Metals	
Lead	2,560

Nonresidential Soil Remediation Standards	
Constituent	Value
VOCs	
Carbon Tetrachloride	2
Chloroform	2
SVOCs	
Acetophenone	5
Benzo(a)anthracene	2
Benzo(a)pyrene	0.2
Benzo(b)fluoranthene	2
Benzo(k)fluoranthene	23
Dibenz(a,h)anthracene	0.2
Indeno(1,2,3–cd)pyrene	2
PCBs	
Aroclor–1242	1
Aroclor–1248	1
Aroclor–1254	1
Aroclor–1260	1
Aroclor–1262	1
Aroclor–1268	1
Total PCBs (Aroclors)	1
PCBs (Congeners)	
Total PCBs (Congeners)	1
Pesticides	
Aldrin	0.2
alpha–Chlordane	1
Dieldrin	0.2
gamma–Chlordane	1
Heptachlor	0.7
Heptachlor epoxide	0.3
Metals	
Antimony	450
Arsenic	19
Cadmium	78
Copper	45,000
Lead	800
Manganese	5,900
Mercury	65
Vanadium	1,100

LEGEND:

- OPEN WATER
- EDGE OF LANDFILLED WASTES OBSERVED DURING TEST PIT ACTIVITIES (DASHED WHERE APPROXIMATE)
- GREAT SWAMP NATIONAL WILDLIFE REFUGE PROPERTY BOUNDARY (DASHED WHERE APPROXIMATE)
- WASTE AND DEBRIS OBSERVED ON GROUND SURFACE BUT NOT OBSERVED OR ANTICIPATED TO BE BELOW GROUND SURFACE
- AREAS WHERE SURFACE WATER FLOW DOES NOT EXHIBIT TYPICAL BED AND BANK MORPHOLOGY
- SOIL SAMPLING LOCATION
- SOIL SAMPLING LOCATION WITH DETECTED CONCENTRATIONS GREATER THAN NJDEP NONRESIDENTIAL SOIL REMEDIATION STANDARDS
- PROPOSED MONITORING WELL
- EXISTING MONITORING WELL
- PROPOSED TEMPORARY WELL POINT
- PROPOSED SOIL SAMPLE
- PROPOSED SURFACE WATER AND SEDIMENT SAMPLE
- EXISTING STREAM GAUGE

DATA NOTES:

UNITS = MILLIGRAMS PER KILOGRAM

[] = DUPLICATE SAMPLE

PCBS = POLYCHLORINATED BIPHENYLS

SVOCS = SEMIVOLATILE ORGANIC COMPOUNDS

VOCS = VOLATILE ORGANIC COMPOUNDS

NA = NOT ANALYZED

D = CONCENTRATIONS IDENTIFIED FROM ANALYSIS OF THE SAMPLE AT A SECONDARY DILUTION.

E = THE COMPOUND WAS QUANTITATED ABOVE THE CALIBRATION RANGE.

J = THE COMPOUND WAS POSITIVELY IDENTIFIED; HOWEVER, THE ASSOCIATED NUMERICAL VALUE IS AN ESTIMATED CONCENTRATION ONLY.

JN = THE ANALYSIS INDICATES THE PRESENCE OF A COMPOUND FOR WHICH THERE IS PRESUMPTIVE EVIDENCE TO MAKE A TENTATIVE IDENTIFICATION. THE ASSOCIATED NUMERICAL VALUE IS AN ESTIMATED CONCENTRATION ONLY.

U = THE COMPOUND WAS ANALYZED FOR BUT NOT DETECTED. THE ASSOCIATED VALUE IS THE COMPOUND QUANTITATION LIMIT.

RX = THE SAMPLE RESULTS ARE REJECTD DUE TO MATRIX INTERFERENCE.

NOTES:

1. ANALYTICAL RESULTS GIVEN IN MILLIGRAMS PER KILOGRAM FOR SOIL SAMPLES WITH DETECTED CONCENTRATIONS GREATER NEW JERSEY NONRESIDENTIAL SOIL REMEDIATION STANDARDS (DATED OCTOBER 2011).
2. THE EDGE OF LANDFILLED WASTES OBSERVED DURING TEST PIT ACTIVITIES IS DRAWN BASED ON OBSERVATIONS OF MATERIALS EXCAVATED DURING TEST PIT ACTIVITIES CONDUCTED FROM JULY 26, 2007 TO SEPTEMBER 6, 2007 AND MARCH 26, 2008.
3. THE PORTION OF THE GREAT SWAMP NATIONAL WILDLIFE REFUGE (GSNWR) PROPERTY BOUNDARY ON THIS FIGURE WITHIN CHATHAM TOWNSHIP, NJ WAS OBTAINED FROM CHATHAM TOWNSHIP TAX PARCEL DATA PROVIDED BY CIVIL SOLUTIONS. THE PORTION OF THE GSNWR PROPERTY BOUNDARY ON THIS FIGURE OUTSIDE OF CHATHAM TOWNSHIP IS APPROXIMATE AND WAS OBTAINED FROM THE UNITED STATES FISH AND WILDLIFE SERVICE (GEOGRAPHIC INFORMATION SYSTEMS AND SPATIAL DATA).
4. BLOCK 48.20, LOTS 184 AND 189 ARE OWNED BY ROBERT J. MIELE AS TRUSTEE FOR THE TRUST CREATED BY THE LAST WILL AND TESTAMENT OF ANGELO J. MIELE. BLOCK 48.20, LOT 189.01 IS OWNED BY THE GREEN VILLAGE FIRE DEPARTMENT.
5. THE EXTENT OF AREAS WHERE SURFACE WATER FLOW DOES NOT EXHIBIT TYPICAL BED AND BANK MORPHOLOGY IS BASED ON FIELD OBSERVATIONS MADE THROUGHOUT THE PERIOD OF INVESTIGATION ACTIVITIES. THE EXTENT OF THE AREA SHOWN IS APPROXIMATE.
6. ONLY SOIL ANALYTICAL RESULTS GREATER THAN NEW JERSEY NON–RESIDENTIAL SOIL REMEDIATION STANDARDS ARE POSTED.

SOURCES:

1. BASEMAP FROM JAMES M. STEWART INC., LAND SURVEYORS, PHILADELPHIA, PA., (ELECTRONIC FILE: 292406.DWG DATED: 6/30/06)
2. TAX PARCEL DATA FOR CHATHAM TOWNSHIP WAS PROVIDED BY CIVIL SOLUTIONS.

0 200' 400'
GRAPHIC SCALE

ROLLING KNOLLS LANDFILL SUPERFUND SITE
CHATHAM, NEW JERSEY
QUALITY ASSURANCE PROJECT PLAN

PROPOSED SAMPLE LOCATIONS - SOUTH

ARCADIS

FIGURE
2b

CITY: CRANBURY,NJ DIV/GROUP: ENV/CAD DB: T.FATTO LD: T.FATTO PIC(Opt): PM: K.ROMANIE TM: L.HYATT LYR: ON*;OFF*;REF*
G:\ENVCAD\CRANBURY\ACT\B0033203\00\00110\QAPP\B0033203F02.DWG LAYOUT: 2B SAVED: 9/11/2014 9:38 AM ACADVER: 18.1S (LMS TECH) PAGESETUP: ---- PLOTSTYLETABLE: PLTFULL.CTB PLOTTED: 9/18/2014 12:10 PM BY: MEYER, JULIE
XREFS: 33203X01 33203X03 IMAGES: PROJECTNAME: ----

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Standard Operating Procedure: Porewater sampling using an *in-situ* dialysis membrane sampling apparatus

Rev. #: 0

Rev Date: February 8, 2013

Approval Signatures

Prepared by: _____ Date: 13 February 2013

Prepared by: _____ Date: 13 February 2013

Reviewed by: _____ Date: 13 February 2013
(Technical Expert)

I. Scope and Application

Porewater sampling will occur to assess concentrations of dissolved-phase constituents in sediment of Operable Unit E (OU-E) ponds at the Former Georgia Pacific Wood Products Facility in Fort Bragg, CA. Field personnel will install diffusion controlled *in-situ* dialysis membrane porewater samplers (DMPS) to collect data. De-oxygenated, de-ionized (DI) water will be placed inside of the dialysis membrane and the sampler will be installed in the 0-0.5 ft. below sediment surface (bss) depth interval of the surficial sediment. The sampler will be left in the sediment for a minimum of 12 days to allow for the constituent concentrations in the sampler to reach equilibrium with surrounding porewater and no more than 14 days to reduce potential for degradation of the dialysis membrane. DMPS allow for the analysis of *in-situ* conditions and reduce the influence of sampling artifacts (e.g., oxidation and temperature) on data collection.

II. Personnel Qualifications

ARCADIS field personnel will have current health and safety training, including 40-hour HAZWOPER training, site supervision training, and site-specific health and safety training. In addition, personnel overseeing, directing, or supervising sediment collection will be versed in the applicable Standard Operating Procedures (SOPs) to successfully complete the sampling activities and be experienced with general sampling methods used in aquatic environments (e.g., sediment, surface water, an/or porewater).

III. Equipment List

The following equipment will be required during *in-situ* pore water sampling activities:

- Personal protective equipment (PPE) and safety equipment as required by the site health and safety plan (HASP) and Job Safety Analysis (JSA).
- *In-situ* DMPS:
    - 5 inch (in.) x 1 in. (Length (L) x inner diameter (ID)) slotted PVC pipe;
    - Acetate cellulose tubular dialysis membrane (ACDM; 8,000 dalton nominal molecular weight cutoff) cut into 15 in. strips with stainless steel or ceramic scissors;
    - 2 in. outer diameter closed pipe nipples;
    - Rubber stop corks;
    - 8 in. x 2.0 in. (L X ID) protective slotted PVC sheath;

- Manufactured DMPS sampling apparatus (top and bottom push-rod/anchor made out of slotted PVC and plexiglass “snowshoe”);
- Stainless steel or ceramic scissors;
- 50 milliliter (mL) pipette and pipette bulb;
- 5 gallon buckets with lid and air lock;
- Laboratory grade helium or nitrogen tank (including regulator and necessary hoses);
- Air stone;
- GPS equipment with sub-meter accuracy and sample locations entered;
- Chest waders;
- Boat (aluminum Jon boat and lightweight inflatable);
- Field probe with capabilities to measure oxidation-reduction potential (ORP), dissolved oxygen (DO), temperature and pH;
- Slide hammer;
- Hand auger with 1.5 in. screw head;
- Laminated site location map (with sample locations marked);
- Laboratory supplied sample containers;
- Indelible ink pen and ball point pen;
- Transport cooler(s) with ice;
- Laboratory supplied DI water;
- Field log book;
- Digital camera;
- Sample labels;
- Canopy and stakes/weights;
- Decontamination supplies (see Field Sampling Equipment Decontamination Procedures SOP, No. 1213199) and;
- Sample packaging and shipping supplies (see Field Sample Packing, Handling and Shipping SOP, No 1223199)

IV. Cautions

Helium/nitrogen tanks must be delivered to the site by an appropriate agent complying with Materials of Trade, Department of Transportation, and/or International Air Transport Association regulations, as necessary. Helium/nitrogen tanks must be stored and transported on-site in compliance with appropriate Materials of Trade and health and safety regulations.

If inclement weather occurs, then sampling must be conducted under cover to prevent potential contamination of porewater samples by rainwater.

To prevent oxidation of the porewater samples, the deployment and retrieval procedures must take place as quickly as possible, and agitation of the sampler should be minimized during deployment and retrieval.

If DMPS are to be used to sample for VOCs, then packing tape must be avoided on the sample containers to prevent contamination. If DMPS are to be used to sample for metals, then stainless steel or ceramic tools should be used to prevent contamination.

If a slide hammer must be used to insert the DMPS into the sediment, use caution as to not damage the sampling device. Use the hammer as gently as possible and position as best as possible in areas clear of debris and rocks.

To the extent possible, store and/or stage empty and full sample containers and coolers out of direct sunlight and under ice.

Be careful not to spill laboratory-prepared containers that may contain preservatives. Reduction of the preservative in the container may impact the integrity of the sample and analytical results and is a health and safety concern.

Shipping determinations must be made for samples to be collected prior to mobilization for the field event, and appropriate measure must be taken to ship the samples in accordance with Department of Transportation, and/or International Air Transport Association regulations.

V. Health and Safety Considerations

Always review and follow site specific SOPs and consult the site-specific HASP and JSAs.

Wear appropriate PPE and have safety equipment specified by the site HASP and JSAs. Use caution when transporting boats and working over water.

Follow appropriate health and safety standards and regulations for storing and transporting compressed gas cylinders.

VI. Procedure

Sampling devices will be custom manufactured and are modified based on methods described by Vrobleski et al., (2002).

Probe assembly:

1. Don PPE as specified by the HASP and JSA.

2. Decontaminate DMPS pieces and 5 gallon buckets to be used to hold DMPS during deoxygenation.

3. Place laboratory supplied DI water into the previously decontaminated 5 gallon buckets.

4. Assemble helium tank with regulator, hoses and air stone at end of discharge hose. Slowly turn on gas release valve to gauge appropriate pressure (i.e., seals and hoses maintain integrity) and evaluate potential leaks. If pressure is too high or if leaks are present, then turn off regulator and adjust tubing. Repeat this step as necessary to achieve appropriate pressure and stop leaks.

5. Bubble helium gas into a sufficient number of the DI filled buckets to hold all DMPS for the event until the dissolved oxygen (DO) concentration falls below 0.5 mg/L as measured by a calibrated field probe (see Measuring Basic Water Quality Parameters In-Situ SOP, No 1343199). Keep remaining DI filled buckets for the following step.

6. Label two buckets filled with DI water “1st rinse” and “2nd rinse”.

7. Cut strips of ACDM to lengths of approximately 15 in. using scissors and dip the strip twice into the bucket labeled “1st rinse” and twice into the bucket labeled “2nd rinse” to remove any residual packing solution.

8. Insert the 5 in. x 1 in. (L x ID) slotted PVC pipe into ACDM and tie an overhand knot at one end of the ACDM.

9. Submerge the ACDM into the de-oxygenated, DI water, making sure that the bag is completely filled. Tie an overhand knot on the loose end of the sampler

to seal the bag. Turn the ACDM upside down to make sure that it is completely sealed.

10. Place the ACDM inside of its protective sheath (to create the DMPS); making sure that the sampler remains submerged in the de-oxygenated DI water. Screw on PVC nipples, with rubber stop cork previously inserted, to both ends of the DMPS. Keep the DMPS in the de-oxygenated, DI water with continuous helium bubbling until deployment.

Sampler deployment:

1. Don PPE, as required by the HASP and JSAs. If necessary, deploy the boat into the water body where sampler will be installed. Follow the boat deployment, trailering, and transport JSA when handling the boat.

2. Use GPS survey equipment to locate the proposed sample location. If sample location must be relocated from the pre-determined locations, then field staff must contact the Task Manager and/or Project Manger to discuss potential relocation of the location. Survey and document field modifications to sample locations, when necessary, and note reasons for the modification in the field notebook.

3. Identify the proposed sample location in the field notebook, along with other appropriate information collected during sediment sampling activities (i.e., texture, color, presence of debris, presence of oily sheen, and presence of organic matter, and odor; see Sediment Sampling with Dewatering SOP, No 1383199a).

4. Record the sampling location and station position with the GPS.

5. Submerge calibrated field probe (with push-rod if necessary) into the surficial sediment and record ORP, DO, temperature, and pH. Be careful not to force the probe, which may result in breakage of the sampling equipment. Record measurements in field notebook.

6. If sediment collection activities are proposed at the sample location, sediment samples will be collected directly adjacent to the area of porewater collection prior to porewater sampler deployment to prevent disturbance of the surface sediment that may occur during the porewater sampler deployment/retrieval process.

7. On shore (or onboard the boat if used), remove the DMPS from the de-oxygenated, DI water and attach to the spike and push-rod pieces of the sampling apparatus by screwing the pieces together.

8. Lower the sampling apparatus through the water column until it reaches the sediment surface (as judged by field staff using a sediment probe with a flat head).

9. Once the sediment surface is encountered, mark the distance on the sampling apparatus with permanent marker above the water surface that is equal to the distance between the bottom of the sampling apparatus and 1 in. above the top of the DMPS.

10. Insert the sampling apparatus perpendicular into the sediment until the mark made in step 8 is level with the water surface of the water.

11. If the sediment is too compact to direct push the sampling apparatus, then gently use a slide hammer to install the sampler to its appropriate depth. If the sampling apparatus will not install gently using a slide hammer, then dig a pilot hole using a 1.5 in. diameter screw head hand auger before perform the sampling apparatus final installation.

12. After the sampler has been inserted to its appropriate depth, place the weighted plexiglass “snow-shoe” on top of the DMPS by sliding in onto the push-rod and making sure that it encounters the sediment surface by probing with a piece of PVC.

13. Repeat steps 6 through 11 to deploy DMPS with sufficient volume to meet analytical needs.

Sampler retrieval:

1. Don PPE, as required by the HASP and JSAs. Identify the sample location in the field notebook.

2. Use GPS survey equipment, as well as visual inspection of the push-rod, to accurately locate the original sample location.

3. Record changes of the sampler location from the initial placement, as necessary, with the GPS.

4. Submerge calibrated field probe (with push-rod if necessary) into the surficial sediment and record DO, pH, oxidation-reduction potential (ORP) and temperature. Record measurements in field notebook.

5. Remove the sampling apparatus by slowly pulling the push-rod. Disassemble the DMPS from the sampling apparatus and pour as much residual sediment inside the spike and/or push-core back into the pond, directly above the location from which it was removed.

6. Bring the sampling apparatus to a stable platform (e.g., boat deck or shore), taking care not to agitate the device to prevent oxidation of the porewater samples. Sampling location should be under a canopy or cover, if necessary, dependent on weather (see Section IV of this SOP).

7. Un-screw the segments of the DMPS and remove the ACDM as soon as possible following retrieval; sampling of the DMPS should begin within 20 minutes of retrieval to prevent oxidation of the sample and precipitation of metals from solution. Dip the ACDM into a bucket of DI water to remove gross adsorption of sediment particles. Cut the knot off of the ACDM and pipette sample into laboratory supplied sampling containers, making sure not to place any residual sediment into the sample container.

8. Place push-core and spike into appropriate location for decontamination procedure.

VII. Waste Management

Materials generated during the sediment sampling and decontamination activities along with disposable equipment will be transported for off-site disposal in accordance with project requirements and applicable State regulations.

VIII. Data Recording and Management

Daily sampling activities will be recorded in the field notebook. Photographs of sampling apparatuses and field activities will be taken as appropriate, and photographs taken will be recorded (e.g., subject matter, photograph location, and photograph facing) in the field notebook. Copies of the field notebook will be forwarded to the Project Manager or designee, as requested. Upon completion of the field activities, field notebooks will be maintained in the project files.

IX. Quality Assurance

Field-derived quality assurance blanks will be collected as specified in the Work Plan, depending on the project quality objectives. There will be one method blank carried out on a DMPS apparatus for the de-oxygenated, DI water procedure. There will be another method blank carried out each day of the retrieval process on the scissors used to cut the ACDM.

X. References

Vrobleski DA, Petkewich MD, and Campbell TR. 2002. Field Tests of Diffusion Samplers for Inorganic Constituents in Wells and at a Groundwater-Discharge Zone. United States Geological Survey. Water Resources Investigations Report 02-4031.

ARCADIS
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Field Log Book Entries

Rev. #: 0

Rev Date: 11 August 2009

Approval Signatures

Prepared by: Andrew Kanik Date: 8/11/09

Reviewed by: Michael J. Heffell Date: 8/11/09
(Technical Expert)

I. Scope and Application

This ARCADIS Standard Operating Procedure covers the entries needed in a field log book for environmental investigations.

This SOP does not address all of the entries that may be needed for a specific project, and does not address health and safety, equipment decontamination, field parameter measurements, sample preservation, chain-of-custody, or laboratory analysis. For direction on requirements in these areas, refer to other ARCADIS SOPs, the project work plans including the quality assurance project plan, sampling plan, and health and safety plan, as appropriate.

II. Personnel Qualifications

ARCADIS personnel participating in fieldwork and making entries into the field log book should have a minimum of one (1) year of field experience (or be under the supervision and accompanied in the field by someone who does) and current health and safety training including 40-hour HAZWOPER training, site supervisor training, site-specific training, first aid, and CPR, as needed. Field personnel will also be compliant with client-specific training requirements. In addition, ARCADIS field sampling personnel will be versed in the relevant SOPs and posses the required skills and experience necessary to successfully complete the desired field work.

III. Equipment List

- Field Log Book
- Ball point (medium point) pen with blue or black ink (black preferred). A fine point Sharpie pen may be used if the ink does not bleed through the page and become visible on back side of the page. If weather conditions prevent the use of a pen, indicate so in the log and use an alternate writing instrument .
- Zip-lock baggie or other weather-proof container to protect the field log book from the elements.

IV. Cautions

All entries in the field log must be legible and archivable. Do not leave the field log book exposed to the elements or other conditions that might moisten the pages and smear/dissolve the entries. When not in the field, the log book should be stored in a location that is easily accessible to field crews.

V. Health and Safety Considerations

ARCADIS field personnel will be familiar and compliant with Client-specific health and safety requirements.

VI. Procedure

- Print legibly. Do not use cursive writing.
- The name of the project, project number and project location should be written in indelible ink on the outside of the field log book.
- On the inside of the front cover, write "If Found, Please Return to ARCADIS" and include the appropriate address and phone number, the name of the person to which the book is assigned, and the name of the project manager.
- Reserve the first page of the book for a Table of Contents.
- Reserve the last five (5) pages of the book for important contacts, notes, reminders, etc.
- Each day of field work, the following should be recorded in the field log book as applicable:

    a) Project Name

    b) Date and time arrived

    c) Work Site Location

    d) Names of people on-site related to the project including ARCADIS employees, visitors, subcontractor employees, agency personnel, client representative, etc.

    e) Describe the work to be performed briefly, and list the equipment on-site

    f) Indicate the health and safety (H&S) level to be used

    g) Record instrument calibrations and checks

    h) Record time and general content of H&S briefing

    i) Describe the weather conditions, including temperature, precipitation, and wind speed and direction

    j) List periodic time entries in the far left hand column of each page

    k) Minimize unused space on each page

- The tailgate meeting must be recorded in the log book and the tailgate form completed. If H&S monitoring is performed, record the time and results of initial and followup monitoring.

- Note factual observations including collection of QA/QC samples, delays, well damage, accidents, work plan deviations, instrument problems, and problem resolutions.

- Describe work performed and how documented such as photographs, sample core logs, water sampling logs, etc.

- Describe bases for field decisions including pertinent conversations with visitors, regulators, or project personnel.

- Note final instrument calibrations and checks.

- Sign the log book at the end of each day at a minimum. Draw a line to the end of the page to indicate no further entries on that page. Sign the bottom of each page if possible.

- If an entry to the log book is changed, strike out the deleted text or item with a single line such that the entry remains legible, and initial and date the change. Such changes should only be made by the same person that made the initial entry.

- Field log book entries must be made in the field at the site, not at a later time at a different location. Supplemental entries to the log book may be made at a later date. The supplemental entry must be clearly identified as such and the entry must be signed and dated as described in this SOP.

- Problems noted in the field log book must be brought to the attention of the project manager and task manager in a timely fashion. Problems may be reported in person, on the telephone, or in a written daily log form. If daily logs are prepared and you will not be able to personally give the daily log to the project manager, send the daily log via FAX or overnight courier to the project manager and task manager.

VII. Waste Management

Investigation-derived waste will be managed as described in the Investigation-Derived Waste Handling and Storage SOP. A drum/waste inventory should be maintained on a pre-designated page in the field log book.

VIII. Data Recording and Management

Each page of the field log book should be scanned for electronic/digital archiving at periodic intervals. This will ensure that copies of the field notes are available in the event the field book is lost or damaged, and that field data can be easily disseminated to others without the risk of physically sending the field log book. Field log books that are full should be archived with the project files, and readily retrievable.

IX. Quality Assurance

Be mindful that the field log book may be produced in court. All entries should be legible (as discussed above). Entries should also be in English, unless working in a country where English is not the predominant language or you are directed otherwise by the project manager.

X. References

Not Applicable

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Soil Drilling and Sample Collection

Rev. #: 2

Rev Date: March 8, 2011

Approval Signatures

Prepared by: _____ Date: 03/08/2011

Reviewed by: _____ Date: 03/08/2011
(Technical Expert)

I. Scope and Application

Overburden drilling is commonly performed using the hollow-stem auger drilling method. Other drilling methods suitable for overburden drilling, which are sometimes necessary due to site-specific geologic conditions, include: drive-and-wash, spun casing, Rotasonic, dual-rotary (Barber Rig), and fluid/mud rotary. Direct-push techniques (e.g., Geoprobe or cone penetrometer) may also be used. The drilling method to be used at a given site will be selected based on site-specific consideration of anticipated drilling depths, site or regional geologic knowledge, types of sampling to be conducted, required sample quality and volume, and cost.

No oils or grease will be used on equipment introduced into the boring (e.g., drill rod, casing, or sampling tools).

II. Personnel Qualifications

The Project Manager (a qualified geologist, environmental scientist, or engineer) will identify the appropriate soil boring locations, depth and soil sample intervals in a written plan.

Personnel responsible for overseeing drilling operations must have at least 16 hours of prior training overseeing drilling activities with an experienced geologist, environmental scientist, or engineer with at least 2 years of prior experience.

III. Equipment List

The following materials will be available during soil boring and sampling activities, as required:

- Site Plan with proposed soil boring/well locations;
- Work Plan or Field Sampling Plan (FSP), and site Health and Safety Plan (HASP);
- personal protective equipment (PPE), as required by the HASP;
- drilling equipment required by the American Society for Testing and Materials (ASTM) D 1586, when performing split-spoon sampling;
- disposable plastic liners, when drilling with direct-push equipment;
- appropriate soil sampling equipment (e.g., stainless steel spatulas, knife);

- equipment cleaning materials;
- appropriate sample containers and labels;
- chain-of-custody forms;
- insulated coolers with ice, when collecting samples requiring preservation by chilling;
- photoionization detector (PID) or flame ionization detector (FID); and
- field notebook and/or personal digital assistant (PDA).

IV. Cautions

Prior to beginning field work, underground utilities in the vicinity of the drilling areas will be identified by one of the following three actions (lines of evidence):

- Contact the State One Call
- Obtain a detailed site utility plan drawn to scale, preferably an “as-built” plan
- Conduct a detailed visual site inspection

In the event that one or more of the above lines of evidence cannot be conducted, or if the accuracy of utility location is questionable, a minimum of one additional line of evidence will be utilized as appropriate or suitable to the conditions. Examples of additional lines of evidence include but are not limited to:

- Private utility locating service
- Research of state, county or municipal utility records and maps including computer drawn maps or geographical information systems (GIS)
- Contact with the utility provider to obtain their utility location records
- Hand augering or digging
- Hydro-knife
- Air-knife
- Radio Frequency Detector (RFD)

- Ground Penetrating Radar (GPR)
- Any other method that may give ample evidence of the presence or location of subgrade utilities.

Overhead power lines also present risks and the following safe clearance must be maintained from them.

Power Line Voltage Phase to Phase (kV)	Minimum Safe Clearance (feet)
50 or below	10
Above 50 to 200	15
Above 200 to 350	20
Above 350 to 500	25
Above 500 to 750	35
Above 750 to 1,000	35

ANSI Standard B30.5-1994, 5-3.4.5

Avoid using drilling fluids or materials that could impact groundwater or soil quality, or could be incompatible with the subsurface conditions.

Water used for drilling and sampling of soil or bedrock, decontamination of drilling/sampling equipment, or grouting boreholes upon completion will be of a quality acceptable for project objectives. Testing of water supply should be considered.

Specifications of materials used for backfilling borehole will be obtained, reviewed and approved to meet project quality objectives.

V. Health and Safety Considerations

Field activities associated with overburden drilling and soil sampling will be performed in accordance with a site-specific HASP, a copy of which will be present on site during such activities.

VI. Procedure

Drilling Procedures

The drilling contractor will be responsible for obtaining accurate and representative samples; informing the supervising geologist of changes in drilling pressure; and

keeping a separate general log of soils encountered, including blow counts (i.e., the number of blows from a soil sampling drive weight [140 pounds] required to drive the split-barrel sampler in 6-inch increments). The term "samples" means soil materials from particular depth intervals, whether or not portions of these materials are submitted for laboratory analysis. Records will also be kept of occurrences of premature refusal due to boulders or construction materials that may have been used as fill. Where a boring cannot be advanced to the desired depth, the boring will be abandoned and an additional boring will be advanced at an adjacent location to obtain the required sample. Where it is desirable to avoid leaving vertical connections between depth intervals, the borehole will be sealed using cement and/or bentonite. Multiple refusals may lead to a decision by the supervising geologist to abandon that sampling location.

Soil Characterization Procedures

Soils encountered while drilling soil borings will be collected using one of the following methods:

- 2-inch split-barrel (split-spoon) sampler, if using the ASTM D 1586 - Standard Test Method for Penetration Test and Split-Barrel Sampling of Soils

- Plastic internal soil sample sleeves if using direct-push drilling.

Soils are typically field screened with an FID or PID at sites where volatile organic compounds are present in the subsurface. Field screening is performed using one of the following methods:

- Upon opening the sampler, the soil is split open and the PID or FID probe is placed in the opening and covered with a gloved hand. Such readings should be obtained at several locations along the length of the sample

- A portion of the collected soil is placed in a jar, which is covered with aluminum foil, sealed, and allowed to warm to room temperature. After warming, the cover is removed, the foil is pieced with the FID or PID probe, and a reading is obtained.

Samples selected for laboratory analysis will be handled, packed, and shipped in accordance with the procedures outlined in the Work Plan, FSP, or Chain-of-Custody, Handling, Packing, and Shipping SOP.

A geologist will be onsite during drilling and sampling operations to describe each soil interval on the soil boring log, including:

- percent recovery;
- structure and degree of sample disturbance;
- soil type;
- color;
- moisture condition;
- density;
- grain-size;
- consistency; and
- other observations, particularly relating to the presence of waste materials

Further details regarding geologic description of soils are presented in the Soil Description SOP.

Particular care will be taken to fully describe any sheens observed, oil saturation, staining, discoloration, evidence of chemical impacts, or unnatural materials.

VII. Waste Management

Water generated during cleaning procedures will be collected and contained onsite in appropriate containers for future analysis and appropriate disposal.

PPE (such as gloves, disposable clothing, and other disposable equipment) resulting from personnel cleaning procedures and soil sampling/handling activities will be placed in plastic bags. These bags will be transferred into appropriately labeled 55-gallon drums or a covered roll-off box for appropriate disposal.

Soil materials will be placed in sealed 55-gallon steel drums or covered roll-off boxes and stored in a secured area. Once full, the material will be analyzed to determine the appropriate disposal method.

VIII. Data Recording and Management

The supervising geologist or scientist will be responsible for documenting drilling events using a bound field notebook and/or PDA to record all relevant information in a clear and concise format. The record of drilling events will include:

- start and finish dates of drilling;
- name and location of project;
- project number, client, and site location;
- sample number and depths;
- blow counts and recovery;
- depth to water;
- type of drilling method;
- drilling equipment specifications, including the diameter of drilling tools;
- documentation of any elevated organic vapor readings;
- names of drillers, inspectors, or other people onsite; and
- weather conditions.

IX. Quality Assurance

Equipment will be cleaned prior to use onsite, between each drilling location, and prior to leaving the site. Drilling equipment and associated tools, including augers, drill rods, sampling equipment, wrenches, and other equipment or tools that may have come in contact with soils and/or waste materials will be cleaned with high-pressure steam-cleaning equipment using a potable water source. The drilling equipment will be cleaned in an area designated by the supervising engineer or geologist that is located outside of the work zone. More elaborate cleaning procedures may be required for reusable soil samplers (split-spoons) when soil samples are obtained for laboratory analysis of chemical constituents.

X. References

American Society of Testing and Materials (ASTM) D 1586 - *Standard Test Method for Penetration Test and Split-Barrel Sampling of Soils*.

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Surface and Subsurface Soil Sampling Using Manual Methods

Rev. #: 1

Rev Date: March 6, 2009

Approval Signatures

Prepared by: _____ Date: 3/6/09

Reviewed by: _____ Date: 3/6/09
(Technical Expert)

I. Scope and Application

This document describes procedures for surface and subsurface soil sampling using hand tools.

II. Personnel Qualifications

ARCADIS personnel directing, supervising, or leading soil sampling activities should have a minimum of 2 years of previous environmental soil sampling experience. ARCADIS personnel providing assistance to soil sample collection and associated activities should have a minimum of 6 months of related experience or an advanced degree in environmental sciences.

III. Equipment List

The following materials will be available, as required, during soil sampling activities:

- personal protective equipment (PPE), as specified by the site Health and Safety Plan (HASP);
- stainless steel bowls;
- stainless steel spoons;
- stainless steel spades;
- stainless steel hand augers;
- indelible ink pens;
- engineer's ruler or survey rod;
- sealable plastic bags (e.g., Ziploc®);
- equipment decontamination materials
- sample bottles and preservatives appropriate for the parameters to be sampled for laboratory analysis, if any;
- transport container with ice (if sampling for laboratory analysis);
- appropriate sample containers and forms; and

- field notebook and/or personal digital assistant (PDA).

Documentation forms and notebooks to have on hand include: soil sample log forms, chain-of-custody forms, sample labels and seals, field logbook/PDA.

IV. Cautions / Hazards

Task specific Job Safety Analysis (JSAs) must be developed to identify site hazards associated with the investigation and reviewed by all field crew members prior to the start of work. Safe Performance Self-Assessment (SPSA) to be performed by employees before performing a new task. Underground utilities will be cleared per the ARCADIS Utility Location Policy and Procedure.

V. Health and Safety Considerations

Soil sample collection will be performed in accordance with a site-specific Health and Safety Plan (HASP) and task specific JSA forms, copies of which will be present on site during such activities.

VI. Procedure

Soil samples may be collected at intervals from the ground surface to various depths. Sample locations will be identified using stakes, flagging, or other appropriate means, and will be noted in a field logbook, PDA, and/or soil sampling logs. Sample points will be located by surveying, use of a global positioning system (GPS), and/or measurements from other surveyed site features.

1. Equipment that will come in contact with the soil sample should be cleaned in accordance with the appropriate equipment decontamination SOP(s), or else new, disposable equipment should be used. Collect equipment blanks in accordance with the project Quality Assurance Project Plan (QAPP).

2. Clear the ground surface of brush, root mat, grass, leaves, or other debris.

3. Use a spade, spoon, scoop, or hand auger to collect a sample of the required depth interval.

4. Use an engineer's ruler to verify that the sample is collected to the correct depth and record the top and bottom depths from the ground surface.

5. To collect samples below the surface interval, remove the surface interval first; then collect the deeper interval. To prevent the hole from collapsing, it may be

necessary to remove a wider section from the surface or use cut polyvinyl chloride (PVC) tubing or pipe to maintain the opening.

6. Collect samples for volatile organic compounds (VOCs) as discrete samples using Encore® samplers or cut syringes (see Extraction/Preservation of Soil/Sediment Samples for VOCs SOP).

7. Homogenize samples for other analyses across the required interval or mix them with other discrete grab samples to form a composite sample (see Compositing or Homogenizing Samples SOP).

8. Place sample in clean sample container; label with sample identification number, date, and time of collection; and place on ice (if obtained for laboratory analysis). Prepare samples for packaging and shipping to the laboratory in accordance with the Chain-of-Custody Handling, Packing, and Shipping SOP.

9. Backfill sample holes to grade with native material or with clean builder's sand or other suitable material.

VII. Waste Management

Waste soils will be managed as specified in the FSP or Work Plan, and according to state and /or federal requirements. Personal Protective Equipment (PPE) and decontamination fluids will be contained separately and staged at the project site for appropriate disposal. Waste containers must be a sealed and labeled at the time of generation. Labels will indicate date, sample locations, site name, city, state, and description of the matrix (e.g., soil, PPE).

VIII. Data Recording and Management

Field documentation such as log book entries and chain-of –custody records will be transmitted to the ARCADIS PM or Task Manager each day unless otherwise directed. The field team leader will retain all site documentation while in the field and add to project files when the field mobilization is complete.

IX. Quality Assurance

Quality assurance samples (rinse blanks, duplicates, and MS/MSDs) will be collected at the frequency specified in the FSP and/or QAPP and depending on the project quality objectives. Reusable soil sampling equipment will be cleaned prior to use following equipment cleaning SOP. Field rinse blanks will be used to confirm that decontamination procedures are sufficient and samples are representative of site

conditions. Any deviations from the SOP will be discussed with the project manager prior to changing any field procedures.

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Compositing or Homogenizing Samples

Rev. #: 01

Rev Date: March 11, 2009

Approval Signatures

Prepared by: Andrew Korik Date: 3/11/09

Reviewed by: Michael Gefell (Technical Expert) Date: 3/11/09

I. Scope and Application

The general procedures to be used in composting/homogenizing solid and semisolid samples are outlined below.

II. Personnel Qualifications

ARCADIS personnel directing, supervising, or leading compositing and/or homogenizing of samples should have a minimum of 2 years of previous field experience and current health and safety training including 40-hour HAZWOPER training, site supervisor training, site-specific training, first aid, and CPR, as needed. Field personnel will also be compliant with client-specific training requirements. In addition, ARCADIS field sampling personnel will be versed in the relevant SOPs and posses the required skills and experience necessary to successfully complete the desired field work

III. Equipment List

The following materials will be available, as required, when compositing or homogenizing samples.

- personal protective equipment (PPE), as specified by the site Health and Safety Plan (HASP)
- stainless steel, plastic, glass or ceramic spoon (or disposable equivalent)
- stainless steel, plastic, glass or ceramic bowl (or disposable equivalent)
- stainless steel, plastic, glass or ceramic jar/bottle (or disposable equivalent)
- shovel or trowel
- plastic sheeting
- decontamination supplies
- digital camera (if allowed by facility policy)
- appropriate sample containers and forms
- field notebook and/or personal digital assistant (PDA)

IV. Cautions

The field crew must be aware of the potential chemicals of concern (COCs), and equipped with a variety of sample homogenizing equipment. The field crew must take care not to use equipment that may react with suspected COCs. For example, stainless steel implements should not be used to homogenize strongly acidic materials.

Soil, sediment, sludge and other solid/semisolid materials that are easily mixed should be thoroughly homogenized. Excessive, vigorous mixing should be avoided as COCs can be mobilized/liberated posing a health and safety risk and diminishing the representativeness of the sample.

Implements used for compositing/homogenizing should be thoroughly decontaminated between samples. Field blanks and rinse blanks should be obtained.

A Shipping Determination must be performed, by DOT-trained personnel, for all environmental and geotechnical samples that are to be shipped, as well as some types of equipment/supplies that are to be shipped.

V. Health and Safety Considerations

- Sample compositing/homogenizing will be performed using procedures consistent with the project Health and Safety Plan.
- Appropriate personal protective equipment (PPE) must be worn by all field personnel within the designated work area.
- Air monitoring may be required during certain field activities as required in the Site Health and Safety Plan.

ARCADIS field personnel will be familiar and compliant with Client-specific health and safety requirements.

VI. Procedure

Samples may require homogenization across a given depth interval, or several discrete grabs (usually five) may be combined into a composite sample. Samples for volatile organic compound (VOC) analysis will not be homogenized or composited. The procedure for mixing samples is provided below.

1. Mix the materials in a stainless steel (or appropriate non-reactive material) bowl using a stainless steel spoon (or disposable equivalents). When dealing with large sample quantities, use disposable plastic sheeting and a shovel or trowel. Note: When preparing samples for metals analyses, do not use disposable aluminum (or metal tools or trays other than stainless steel), as it may influence the analytical results.

2. Flatten the pile by pressing the top without further mixing.

3. Divide the circular pile by into equal quarters by dividing out two diameters at right angles.

4. Mix each quarter individually using appropriate non-reactive bowls, spoons and/or sheeting.

5. Mix two quarters (as described above) to form halves, then mix the two halves to form a composite or homogenous sample.

6. Place composite or homogenized sample into specified containers. Remaining material will be disposed of in accordance with project requirements and applicable regulations.

VII. Waste Management

Investigation-derived waste will be managed as described in the Investigation-Derived Waste Handling and Storage SOP.

VIII. Data Recording and Management

Sample identification, interval depth (if appropriate), sample date and time will be recorded in the field notebook, the boring log, and/or the PDA. The sample will also be identified on an appropriate chain of custody form, for submittal to an analytical laboratory for analysis. Consider digital photography to record unusual field conditions or to document compliance (i.e. proper labeling and storage of drums/IDW containers).

IX. Quality Assurance

All materials to be re-used for sample compositing/homogenizing will be decontaminated as appropriate. Field blanks and rinse blanks will be collected to evaluate decontamination procedures and to provide an indication as to whether external contamination has potentially been introduced.

X. References

Not Applicable.

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Extraction/Preservation of Soil/Sediment for VOCs

Rev. #: 1

Rev Date: April 9, 2008

Approval Signatures

Prepared by: Caron Koll Date: 4/9/08

Reviewed by: Dennis K. Cyprio Date: 4/9/08
(Technical Expert)

I. Scope and Application

Soil or sediment samples collected for volatile organic compound (VOC) analysis must be handled in a manner which will minimize the loss of contaminants due to volatilization and biodegradation. Based on experience and open literature, it has been concluded that field extraction and preservation must be conducted in a manner to ensure that contaminants do not degrade or volatilize during sample handling and transport. The following equipment and procedures summarize the method of field preservation of soil samples.

II. Personnel Qualifications

ARCADIS field personnel will have current health and safety training, including 40-hour HAZWOPER training, site supervision training, and site-specific health and safety training. At least one person on the sampling team must be trained per Department of Transportation (DOT) and (International Air Transportation Administration (IATA) requirements to prepare and offer shipments of samples by a commercial carrier and training in Materials of Trade when transporting this material in ARCADIS or private vehicles for work-related purposes. Trained personnel will use the following shipping guides:

- ARCADIS Hazardous Materials (aka Dangerous Goods) using Shipping Guide No. US-002 - Environmental Samples-Solids Known or Suspected of Being Hazardous per DOT Definition

- ARCADIS Hazardous Materials (aka Dangerous Goods) using Shipping Guide No. US-012 – Environmental Samples solid containing Methanol and or Sodium Bisulfate Preservative (collected using TeraCore® Encore®, EazyDraw® Syringe Samplers).

In addition, ARCADIS personnel overseeing, directing, or supervising soil collection will be versed in the applicable standard operating procedures (SOPs) to successfully complete the sample activities.

III. Equipment List

- portable balance, small electronic or manual scale calibrated with an appropriate certified weight;

- analyte-free water;

- Site specific Health and Safety Plan (HASP);

- personal protective equipment (PPE), per the HASP;
- 1¾ cm inside-diameter disposable soil coring device syringes (supplied by laboratory);
- coolers or transport containers with contained ice;
- large soil sampling device (e.g., split-spoon sampler);
- indelible ink pens;
- field logbook;
- duct tape;
- 1-gallon freezer bags;
- appropriate forms;
- preservative-free empty sample containers;
- Encore™ (or equivalent, e.g. TeraCore®, EazyDraw®) samplers and cut plastic syringes; and/or
- sampling containers provided by the laboratory (dependent on the type of purge and trap unit that will be used to analyze the samples):
  - low-concentration containers with a magnetic stir bar and a solution of 1 gram of sodium bisulfate dissolved in 5 milliliter (mL) of organic-free water. Tare weight of container and contents should be recorded on the label.
  - high-concentration [greater than 200 micrograms per kilogram (ug/kg)] containers will contain 10 mL of methanol and also have the tare weight recorded on the label. Tare weight of the container and contents should be recorded on the label.

IV. Cautions

Once the proper weight has been contained within the syringe, the piston of the syringe is used to push the soil into the 40-mL sample vial. Care must be taken so as not to spill or splash the preservative already in the vials. Caution must also be used when recapping the vial, as even a small amount of soil on the rim of the vial may

cause improper sealing and subsequently lead to loss of the preservative and surrogates. The samples must be placed in coolers and maintained at approximately 4°C. The soil sample vials will be weighed by the laboratory before extractions are completed. For this reason, extra labels or tape are not to be added to the vials. Containers or syringes that differ from the tare weight by more than 0.01 gram should not be used.

Avoid over tightening sample vials lids. Over tightened lids may damage the Teflon seal and integrity of the sample.

Samples unpreserved at 4°C have a holding time of 48-hours, from the time of collection and analysis or preservation. If samples are to be shipped unpreserved, plan to express mail via air and to shipment on the same day as collection, unless performance data can be provided to support longer holding times. The 40 mL vials are unacceptable as unpreserved sample containers due to VOC loss via volatilization and biodegradation.

Freezing unpreserved samples in proper containers may be considered to extend holding times to 5 days.

Soils are to be collected and contained in the least amount of time possible to minimize the loss of VOCs. Trimming of outer layer of the exposed the soil sample should be considered, if the sample has been exposed to the atmosphere for more than a couple of minutes,

V. Health and Safety Considerations

Care must be taken so as not to spill or splash the preservative already in the vials, when applicable. Sodium bisulfate is a strong acid and can cause severe burns. If the preservative makes contact, immediately flush with potable water. Immediately consult with a medical professional if any burning, pain, or irritation persists.

The 40-mL sample vials can shatter while tightening. Amber vials are more prone to breakage. Use appropriate cut resistant gloves to avoid possible laceration while tightening vials.

Refer to the site specific health and safety plan (HASP) for further health and safety considerations.

VI. Procedure

Container Preparation

Container preservation may be done either in the field or in the laboratory. Procedures for both methods are provided in this SOP. Standard sample containers for laboratory preservation will include either TeraCore® Encore®, EazyDraw®.

Field preservation will depend on the soil concentration, if known.

For high concentration soils (greater than 200 ug/kg), laboratory-prepared 40-mL VOA vials filled with 5 mL to 10 mL of analyte-free purge and trap grade methanol (at a minimum of 5 mL methanol) to 5 gram soil/sediment. The sample container size may be dependent on the type of purge and trap unit that will be used to analyze the samples.

Containers for low VOC concentrations will include 1 gram of sodium bisulfate dissolved in 5 mL of organic-free water.

The analytical laboratory also adds the appropriate surrogate compounds to the methanol based on the analytical method quality assurance [e.g. 8015, 8021, 8260b, Massachusetts Compendium of Analytical Methods for Volatile Petroleum Hydrocarbons (VPH), or 8260b, USEPA, 2002; DEQE, 2000; MADEP, 2003]. The laboratory records the weight of each vial to the nearest 0.1 gram after both methanol and surrogates have been added. These containers must be stored in coolers and maintained at approximately $4^{o}C \pm 2^{o}$.

Sampling

Selection of a soil/sediment sampling interval will be determined based on a site-specific sampling plan and collected either via TeraCore® Encore®, EazyDraw® or by preservation in the field with methanol and/or sodium bisulfate in containers pre-measured by the laboratory.

<u>Preservation in the Field (laboratory pre-filled sample containers)</u>

Soil/sediment is collected in-situ or from a larger sampling device (e.g., split-spoon, auger, or other sampling device) with a disposable coring device (syringe), also supplied by the laboratory, as soon as possible upon sample retrieval to avoid exposure to air and VOC loss. A coring device that may be used of amendable to soil/sediment type consists of a plastic syringe with the tip removed. It is essential that

the diameter be suitable for injection into the sample container. A small electronic or manual balance is needed for weighing the syringe and soil.

1. Once the tare weight of the syringe is determined and a sample interval is selected, soil sample collection is accomplished by manually pushing a syringe into the soil/sediment with the piston withdrawn or collection with a stainless steel spoon.

2. The soil sample weight is determined by subtracting the tared weight from the total weight of the soil and syringe.

3. Acceptable soil sample weight is 5 grams for a 40-mL vial sample container. However, the laboratory may supply larger sized sample containers and require a laboratory-specific weight of soil/sediment.

   - If a syringe is used and the sample weight is less than 5 grams, the syringe may be pushed into the soil again, with the piston withdrawn to gather additional soil.

   - If the sample weight is greater than 5 grams, a portion of soil may be extruded and removed from the syringe.

4. Weigh the containers in the field. Record the weight of each sample. Subtract the tare weight of the container and preservative to obtain the weight of sample. Record the weights on the sample labels and in the field notebook.

5. If the volatile concentrations of the sample are not known, two low-concentration vials and one high-concentration vial should be prepared, as discussed in Section III. Additional vials are needed for samples to be used for laboratory quality control purposes. Note: Samples that contain carbonate minerals may effervesce upon contact with the acidic low-concentration preservative. If the effervescence is small, the loss of volatiles will be limited by quickly capping the vial. If large amounts of gas are generated, target analytes may be lost and the vials may shatter. If this occurs, document the issue in the field notebook and collect another sample using a fresh container prepared with 5 mL (1 mL of water is equivalent to 1 gram of water) of analyte-free water and no preservative.

6. (Place samples on ice immediately after collection and ship or deliver to the laboratory as soon as possible.

7. An additional sample fraction should be placed in a clean glass jar with no preservative for laboratory use to determine percent solids. Moisture content determination is required to report the sample results on a dry weight basis. Moisture content determination is required to report the sample results on a dry weight basis. If soil samples will be analyzed for other parameters, the moisture content can usually be taken from the other sample containers. However, when sampling for VOCs only, a small separate laboratory-supplied container must be filled.

Laboratory Preservation (Encore™ or equivalent)

1. Collect an approximate 5-gram sample using an Encore™ sampler or cut plastic syringe.

2. Place samples on ice immediately after collection and ship or deliver to the laboratory as soon as possible. Samples in capped Encore™ samplers should be delivered within 24 hours of collection to allow the sample to be persevered within 48 hours from collection and meet holding time.

3. In addition to the soil sample collected for VOC analysis, soil must be collected and placed into an empty container for moisture content analysis. Moisture content determination is required to report the sample results on a dry weight basis. If soil samples will be analyzed for other parameters, the moisture content can usually be taken from the other sample containers. However, when sampling for VOCs only, a small separate laboratory-supplied container must be filled.

Shipping Container Preparation

Use ARCADIS Hazardous Materials (aka Dangerous Goods) using Shipping Guide No. US-012 – Environmental Samples solid containing Methanol and or Sodium Bisulfate Preservative (collected using TeraCore® Encore®, EazyDraw® Syringe Samplers) for sample container preparation. Among other requirements depending on whether the samples are shipped by air verse by ground shipping containers must be marked with **"This package conforms to 49 CFR 173.4."** Note: in order to comply with 49 CFR 173.4, the total volume of methanol mixture per shipping container must be less than 30 grams. In addition, other pertinent requirements of this reference are as follows:

- Each inner receptacle is securely packed in an inside packaging with cushioning and absorbent material. The inside packaging cannot react chemically with the

material and needs to be capable of absorbing the entire contents of the receptacle. (Note: a foam container for the vials meets these requirements.)

- The inside packaging is securely packed in a strong outside packaging. (Note: a cooler meets this requirement.)
- The gross mass of the completed package does not exceed 64 pounds.

Consult ARCADIS Hazardous Materials (aka Dangerous Goods) using Shipping Guide No. US-012 – Environmental Samples, Solid Containing Methanol and/or Sodium Bisulfate Preservative (collected using TeraCore® Encore®, EazyDraw® Syringe Samplers) for appropriate packing and labeling for shipments via air and ground. In addition, consult the Chain-of-Custody SOP.

VII. Waste Management

Used methanol or sodium bisulfate, if any, will be contained in an airtight drum or container. Containers will be labeled with the project name, date, and contents. Appropriate client specified personnel will be notified for the transport of container to the appropriate on-site storage area for disposal at an appropriate facility. Any unused sample containers with methanol or sodium bisulfate will be shipped back to the laboratory using original packaging material per DOT or IATA procedures.

VIII. Data Recording and Management

Sampling activities, (i.e. location, depth, soil/sediment type, sample identification, sample container tare weight, sample weights, effervescence) will be recorded in the field logbook. Chain of custody (COC) will be prepared per the approved SOP and copies of the COC will be transmitted to the project manager and maintained in project files.

IX. Quality Assurance

Quality assurance activities will be completed to comply with the site specific sampling plan and/or quality assurance project plan.

A methanol trip blank should accompany the sample containers at all times in the field and during transport. This consists of a sample container prepared in a similar manner as the soil sample containers. One trip blank should accompany each sample delivery group.

Field blanks and ambient air blanks are optional when sampling via the methanol preservation method.

Discrete blind duplicate samples may be collected in separate soil/sediment sample containers. Compositing or homogenizing multiple soil/sediment samples into one sample container is not acceptable.

Site-specific matrix spike and matrix spike duplicate (MS/MSD) analyses, if required, may be collected from a single soil/sediment sample container; no additional sample volume is required.

X. References

Arizona Department of Environmental Quality (ADEQ), 2000. Implementation of EPA Method 5035-Soil Preparation of EPA Method 8015B, 8121B and 8260B, Arizona Revised Statues (A.R.S.) 49-104 (A). April 19, 2000.

Massachusetts Department of Environmental Protection (MADEP), 2003. Method for the Determination of Volatile Petroleum Hydrocarbons, MADEP-VPH-03-1.1, Revision 1.1. December 2003.

USEPA, 2002. *Test Methods for Evaluating Solid Waste*, SW-846, Third Edition, Method 5035A – Closed System Purge and Trap for Volatile Organics in Soils and Waste Samples. July 2002.

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Sediment Sampling

Rev. #: 0

Rev Date: July 29, 2003

Approval Signatures

Prepared by: _____ Date: _____

Reviewed by: _____ Date: _____
(Technical Expert)

Reviewed by: _____ Date: _____
(Project Manager)

I. Scope and Application

This Standard Operating Procedure (SOP) sets forth the field procedures for collection of sediment via Lexan tubing and grab samples using a hand-held dredge.

II. Personnel Qualifications

To be completed by Preparer and reviewed by Technical Expert.

III. Equipment List

The following materials will be available, as required, during sediment sampling:

- health and safety equipment (as required by the site Health and Safety Plan [HASP]);
- cleaning equipment;
- disposable aluminum pans;
- disposable spatulas;
- appropriate sample containers and forms;
- coolers with ice;
- field notebook;
- anchor;
- boat and motor;
- rope;
- survey's rod;
- duct tape;
- Lexan tubing with end caps;
- push rod;

- hacksaw;
- steel core driver;
- vacuum pump;
- piston sampler/check valve push core device; and
- 6-foot rule.

IV. Cautions

To be completed by Preparer and reviewed by Technical Expert.

V. Health and Safety Considerations

To be completed by Preparer and reviewed by Technical Expert.

VI. Procedures

The following procedures will be used to collect sediment samples:

1. Don health and safety equipment (as required in the HASP).
2. Clean reusable sampling equipment as follows: non-phosphate detergent and distilled water wash; distilled water rinse; rinse equipment with solvent (hexane); distilled water rinse; allow to air dry and wrap in aluminum foil.
3. Use GPS surveying techniques to locate the proposed sample location and position the boat with anchors.
4. Identify the proposed sample location in the field notebook, along with other appropriate information collected during sediment sampling activities.
5. Measure the total depth of the water using a surveyor's rod to the nearest 0.1 foot.
6. At each sample location, lower a section of Lexan tube until it just reaches the top of the sediment (sections of Lexan tube may need to be spliced together or the Lexan tube may be attached to a check valve core device).

7. Push the Lexan tube with a straight vertical entry into the sediment so as to secure a reliably representative core sample. Measure the depth of sediment.

8. Drive the tube several inches more using a steel core drive and measure the additional distance. (This procedure is performed to obtain a “plug” at the bottom of the core and prevent the loose sediment from escaping.)

9. Place a vacuum pump on the top end of the Lexan tube and create a vacuum to prevent the sediment from escaping (note this is not needed if using a check valve core device).

10. Slowly pull the tube from the sediment, twisting it slightly as it is removed (if necessary).

11. Before the tube is fully removed from the water, place a cap on the bottom end of the tube while it is still submerged.

12. Keeping the tube upright, wipe the bottom end dry and seal the end with duct tape and label. Measure the length of sediment recovered and evaluate the integrity of the core. If additional cores are necessary to obtain a sufficient sample, repeat the coring procedure at the location adjacent to the previous one sampled.

13. While keeping the core upright, use a hacksaw to make a horizontal cut in the tube approximately 1 inch above the sediment.

14. Recap the cut end of the tube, seal the cap with duct tape, and mark this end as “top.”

15. Wipe the tube dry.

16. If sample sectioning is required, slice tube open or push sediment from tube and slice according to appropriate segmenting scheme (i.e., every 2 inches in cap material and 0 to 3 inches in native sediment).

17. Homogenize samples in a disposable aluminum pan.

18. Place homogenized sample in appropriate sample containers and cap.

19. Label all sample containers.

20. Place filled sample containers on ice in a cooler.

21. Follow procedures for packing, handling, and shipping with associated chain-of-custody procedures.

22. Record required information on the appropriate forms and/or field notebook.

23. Field duplicate and matrix spike/matrix spike duplicate (MS/MSD) samples will be obtained for every 20 sediment samples collected.

24. As an alternative sampling method, Steps 6 through 15 may be replaced with Steps a through g, as follows:

    a. At each sample location, drop open dredge from side of boat making sure that the end of the rope is maintained at all times.

    b. Once the dredge has been allowed to settle into the bottom sediment, a hard pull on the rope will close the sediment inside the dredge.

    c. Retrieve the dredge into the boat.

    d. Open the dredge to allow the sediment to empty onto a stainless steel tray or bowl.

    e. Multiple casts will be made and composited at each location until sufficient sample volume is obtained.

    f. Observe the sample and record descriptions in the field notebook.

    g. If chemical laboratory analyses are being performed, rinse blanks will be obtained by pouring deionized water through a cleaned stainless steel dredge onto a cleaned stainless steel tray. From the tray, the appropriate sample containers will be filled. Rinse blanks should be collected at the start and finish of sampling activities.

VII. Data Recording and Project Management

To be completed by Preparer and reviewed by Technical Expert.

VIII. Quality Assurance

To be completed by Preparer and reviewed by Technical Expert.

IX. References

To be completed by Preparer and reviewed by Technical Expert.

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Sediment Core Collection

Rev. #: 0

Rev Date: July 28, 2003

Approval Signatures

Prepared by: _____ Date: _____

Reviewed by: _____ Date: _____
(Technical Expert)

Reviewed by: _____ Date: _____
(Project Manager)

I. Scope and Application

This Standard Operating Procedure (SOP) describes the procedures to collect sediment core samples.

II. Personnel Qualifications

To be completed by Preparer and reviewed by Technical Expert.

III. Equipment List

Sediment Sampling Equipment

The following materials will be needed during sediment sampling activities:

- aluminum boat with outboard motor;
- health and safety equipment, as required by the site Health and Safety Plan (HASP);
- cleaning equipment;
- aluminum or stainless steel tray;
- duct tape;
- Lexan tubing with end caps;
- brass push rod;
- hacksaw;
- stainless steel core driver;
- vacuum pump;
- piston sampler;
- photoionization detector (PID);
- 6-foot rule or survey rod;

- transport container with ice;
- appropriate sample containers and forms; and
- field notebook.

Field Cleaning Equipment

The following equipment will be needed for field cleaning after sediment sampling is completed:

- health and safety equipment (as required in the HASP);
- distilled water (laboratory-supplied);
- non-phosphate soap (Alconox or equivalent);
- distilled water;
- appropriate cleaning solvent (e.g., hexane);
- rinse collection plastic containers;
- brushes;
- aluminum foil;
- garbage bags;
- spray bottles for solvent; and
- Ziploc-type bags.

IV. Cautions

To be completed by Preparer and reviewed by Technical Expert.

V. Health and Safety Considerations

To be completed by Preparer and reviewed by Technical Expert.

VI. Procedure

Sediment Sampling Procedure

1. Identify the proposed sample location in the field notebook along with other appropriate information collected during the sediment probing activities.

2. Don personal protective equipment (PPE), as required by the HASP.

3. At each sample location, lower a section of Lexan tube until it just reaches the top of sediment. Measure the depth of water. (Sections of Lexan tube may need to be spliced together in deep water locations.)

4. Push the Lexan tube into the sediment by hand until refusal. Measure the depth of sediment.

5. Drive the tube several more inches using a stainless steel core driver block and measure the distance. This procedure is performed to obtain a “plug” at the bottom of the core and prevent the loose sediment from escaping;

6. Pump the water out from inside the Lexan tubing.

7. Place a vacuum pump on the top end of the Lexan tube and create a vacuum to prevent the sediments/plug from escaping.

8. Slowly pull the tube from the sediment, twisting it slightly as it is removed (if necessary).

9. Before the tube is fully removed from the water, place a cap on the bottom end of the tube while it is still submerged.

10. Keeping the tube upright, wipe the bottom end dry and seal the cap with duct tape and label. Measure the length of sediment recovered and evaluate the integrity of the core. If the core is not suitably intact, repeat coring procedure within 5 to 10 feet of the first location attempted.

11. While still keeping the core upright, use a hacksaw to make a horizontal cut in the tube approximately 1 inch above the sediment.

12. Re-cap the cut end of the tube, seal the cap with duct tape, and mark this end as “top.”

13. Wipe the tube dry.

14. Place a completed sample label on the tube.

15. Record the following information on both the tube and on the cap: 1) sample number; 2) sampling date; and 3) sampling time.

16. Place the core sample upright in a container with ice.

17. Repeat the above procedures until the appropriate number of core samples are collected (for the sampling event or the sampling day).

18. Extrude the sediment cores from the Lexan tubing onto an aluminum or stainless steel tray. Describe and record sample description, including depths at which sediment characteristics change and visual characteristics.

19. Section the sediment cores into the intervals determined for the project. Use a decontaminated hacksaw or knife to section the sediment cores. Characterize each sediment sample for color, texture, and visual staining/odors. Place each sediment sample into the appropriate laboratory-supplied sample containers.

20. Label all sample containers according to the appropriate procedures.

21. Handle, pack, and ship samples using the chain-of-custody procedures in accordance with the appropriate SOP.

Field Cleaning Procedure

1. Follow health and safety procedures specified in the HASP.

2. Cleaning of reusable sampling equipment (e.g., trays, spatulas, scoops, and core driver) will follow the decontamination procedures presented in the equipment cleaning SOP.

3. Cleaning will be conducted in plastic containers to collect all decontamination rinsate.

VII. Waste Management

Materials generated during the sediment sampling activities and disposable equipment will be transported for offsite disposal in accordance with applicable rules and regulations.

VIII. Data Recording and Management

To be completed by Preparer and reviewed by Technical Expert.

IX. Quality Assurance

To be completed by Preparer and reviewed by Technical Expert.

X. References

To be completed by Preparer and reviewed by Technical Expert.

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Field Equipment Decontamination

Rev. #: 3

Rev Date: April 26, 2010

Approval Signatures

Prepared by: _____ Date: 4/26/2010
Keith Shepherd

Reviewed by: _____ Date: 4/26/2010
Richard Murphy (Technical Expert)

I. Scope and Application

Equipment decontamination is performed to ensure that sampling equipment that contacts a sample, or monitoring equipment that is brought into contact with environmental media to be sampled, is free from analytes of interest and/or constituents that would interfere with laboratory analysis for analytes of interest. Equipment must be cleaned prior to use for sampling or contact with environmental media to be sampled, and prior to shipment or storage. The effectiveness of the decontamination procedure should be verified by collecting and analyzing equipment blank samples.

The equipment cleaning procedures described herein includes pre-field, in the field, and post-field cleaning of sampling tools which will be conducted at an established equipment decontamination area (EDA) on site (as appropriate). Equipment that may require decontamination at a given site includes: soil sampling tools; groundwater, sediment, and surface-water sampling devices; water testing instruments; down-hole instruments; and other activity-specific sampling equipment. Non-disposable equipment will be cleaned before collecting each sample, between sampling events, and prior to leaving the site. Cleaning procedures for sampling equipment will be monitored by collecting equipment blank samples as specified in the applicable work plan or field sampling plan. Dedicated and/or disposable (not to be re-used) sampling equipment will not require decontamination.

II. Personnel Qualifications

ARCADIS field sampling personnel will have current health and safety training, including 40-hour HAZWOPER training, site supervisor training, and site-specific training, as needed. In addition, ARCADIS field sampling personnel will be versed in the relevant SOPs and possess the skills and experience necessary to successfully complete the desired fieldwork. The project HASP and other documents will identify any other training requirements such as site specific safety training or access control requirements.

III. Equipment List

- health and safety equipment, as required in the site Health and Safety Plan (HASP)
- distilled water

- Non-phosphate detergent such as Alconox or, if sampling for phosphorus phosphorus-containing compounds, Luminox (or equivalent).
- tap water
- rinsate collection plastic containers
- DOT-approved waste shipping container(s), as specified in the work plan or field sampling plan (if decontamination waste is to be shipped for disposal)
- brushes
- large heavy-duty garbage bags
- spray bottles
- (Optional) – Isoprophyl alcohol (free of ketones) or methanol
- Ziploc-type bags
- plastic sheeting

IV. Cautions

Rinse equipment thoroughly and allow the equipment to dry before re-use or storage to prevent introducing solvent into sample medium. If manual drying of equipment is required, use clean lint-free material to wipe the equipment dry.

Store decontaminated equipment in a clean, dry environment. Do not store near combustion engine exhausts.

If equipment is damaged to the extent that decontamination is uncertain due to cracks or dents, the equipment should not be used and should be discarded or submitted for repair prior to use for sample collection.

A proper shipping determination will be performed by a DOT-trained individual for cleaning materials shipped by ARCADIS.

V. Health and Safety Considerations

Review the material safety data sheets (MSDS) for the cleaning materials used in decontamination. If solvent is used during decontamination, work in a well-ventilated area and stand upwind while applying solvent to equipment. Apply solvent in a manner that minimizes potential for exposure to workers. Follow health and safety procedures outlined in the HASP.

VI. Procedure

A designated area will be established to clean sampling equipment in the field prior to sample collection. Equipment cleaning areas will be set up within or adjacent to the specific work area, but not at a location exposed to combustion engine exhaust. Detergent solutions will be prepared in clean containers for use in equipment decontamination.

Cleaning Sampling Equipment

1. Wash the equipment/pump with potable water.

2. Wash with detergent solution (Alconox, Liquinox or equivalent) to remove all visible particulate matter and any residual oils or grease.

3. If equipment is very dirty, precleaning with a brush and tap water may be necessary.

4. (Optional) – Flush with isopropyl alcohol (free of ketones) or with methanol. This step is optional but should be considered when sampling in highly impacted media such as non-aqueous phase liquids or if equipment blanks from previous sampling events showed the potential for cross contamination of organics.

5. Rinse with distilled/deionized water.

Decontaminating Submersible Pumps

Submersible pumps may be used during well development, groundwater sampling, or other investigative activities. The pumps will be cleaned and flushed before and between uses. This cleaning process will consist of an external detergent solution wash and tap water rinse, a flush of detergent solution through the pump, followed

by a flush of potable water through the pump. Flushing will be accomplished by using an appropriate container filled with detergent solution and another contained filled with potable water. The pump will run long enough to effectively flush the pump housing and hose (unless new, disposable hose is used). Caution should be exercised to avoid contact with the pump casing and water in the container while the pump is running (do not use metal drums or garbage cans) to avoid electric shock. Disconnect the pump from the power source before handling. The pump and hose should be placed on or in clean polyethylene sheeting to avoid contact with the ground surface.

VII. Waste Management

Equipment decontamination rinsate will be managed in conjunction with all other waste produced during the field sampling effort. Waste management procedures are outlined in the work plan or Waste Management Plan (WMP).

VIII. Data Recording and Management

Equipment cleaning and decontamination will be noted in the field notebook. Information will include the type of equipment cleaned, the decontamination location and any deviations from this SOP. Specific factors that should be noted include solvent used (if any), and source of water.

Any unusual field conditions should be noted if there is potential to impact the efficiency of the decontamination or subsequent sample collection.

An inventory of the solvents brought on site and used and removed from the site will be maintained in the files. Records will be maintained for any solvents used in decontamination, including lot number and expiration date.

Containers with decontamination fluids will be labeled.

IX. Quality Assurance

Equipment blanks should be collected to verify that the decontamination procedures are effective in minimizing potential for cross contamination. The equipment blank is prepared by pouring deionized water over the clean and dry tools and collecting the deionized water into appropriate sample containers. Equipment blanks should be analyzed for the same set of parameters that are performed on the field samples collected with the equipment that was cleaned. Equipment blanks are collected per equipment set, which represents all of the tools needed to collect a specific sample.

X. References

USEPA Region 9, Field Sampling Guidance #1230, Sampling Equipment Decontamination.

USEPA Region 1, Low Stress (low flow) Purging and Sampling Procedure for the Collection of Groundwater Samples from Monitoring Wells.

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Investigation-Derived Waste Handling and Storage

Rev. #: 2

Rev Date: March 6, 2009

Approval Signatures

Prepared by: Andrew Kamik Date: 3/6/09

Reviewed by: Liz Marsh Date: 3/6/09
(Technical Expert)

I. Scope and Application

The objective of this Standard Operating Procedure (SOP) is to describe the procedures to manage investigation-derived wastes (IDW), both hazardous and non-hazardous, generated during site activities, which may include, but are not limited to - drilling, trenching/excavation, construction, demolition, monitoring well sampling, soil sampling, decontamination and remediation. Please note that this SOP is intended for materials that have been deemed a solid waste as defined by 40 CFR § 261.2 (which may includes liquids, solids, and sludges). In some cases, field determinations will be made based on field screening or previous data that materials are not considered a solid waste. IDW may include soil, groundwater, drilling fluids, decontamination liquids, personal protective equipment (PPE), sorbent materials, construction and demolition debris, and disposable sampling materials that may have come in contact with potentially impacted materials. IDW will be collected and staged at the point of generation. Quantities small enough to be containerized in 55-gallon drums will be taken to a designated temporary storage area (discussed in further detail under Drum Storage) onsite pending characterization and disposal. Waste materials will be analyzed for constituents of concern to evaluate proper disposal methods. PPE and disposable sampling equipment will be placed in DOT-approved drums prior to disposal and typically does not require laboratory analysis. This SOP describes the necessary equipment, field procedures, materials, regulatory references, and documentation procedures necessary for proper handling and storage of IDW up to the time it is properly disposed. The procedures for handling IDW are based on the United States Environmental Protection Agency's Guide to Management of Investigation Derived Wastes (USEPA, 1992). IDW is assumed to be contaminated with the site constituents of concern (COCs) until analytical evidence indicates otherwise. IDW will be managed to ensure the protection of human health and the environment and will comply with all applicable or relevant and appropriate requirements (ARAR). The following Laws and Regulations on Hazardous Waste Management are potential ARAR for this site.

State Laws and Regulations

- To Be Determined Based on Location of Site and Location of Treatment, Storage, and/or Disposal Facility (TSDF) to be utilized

Federal Laws and Regulations

- Resource Conservation and Recovery Act (RCRA) 42 USC § 6901-6987
- Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) 42 USC § 9601-9675

- Superfund Amendments and Reauthorization Act (SARA)
- Department of Transportation (DOT) Hazardous Materials Transportation

Pending characterization, IDW will be stored appropriately within each area of contamination (AOC). Under RCRA, "storage" is defined as the holding of hazardous waste for a temporary period, at the end of which the hazardous waste is treated, disposed of, or stored elsewhere" (40 CFR § 260.10). The onsite waste staging area will be in a secure and controlled area. Waste characterization can either be based on generator knowledge, such as using materials safety data sheets (MSDS'), or can be based upon analytical results. The laboratory used for waste characterization analysis must have the appropriate state and federal certifications and be approved by ARCADIS and Client. IDW will be classified as RCRA hazardous or non-regulated under RCRA based on the waste characterization.

If IDW is characterized as RCRA hazardous waste, RCRA and DOT requirements must be followed for packaging, labeling, transporting, storing, and record keeping as described in 40 CFR § 262 and 49 CFR § 171-178. Wastes judged to potentially meet the criteria for hazardous wastes shall be stored in DOT approved packaging. Waste material classified as RCRA non-hazardous may be handled and disposed of as an industrial waste.

Liquid wastes judged to potentially meet the criteria for hazardous wastes shall be stored in DOT approved 55 gallon drums or other approved containers that are compatible with the type of material stored therein. Solid materials deemed to potentially meet hazardous criteria will be drummed where practicable. Large quantities of potentially hazardous solid materials must be containerized (such as in a roll-off box) for up to a maximum of 90 or 180 days as described in the Excavated Solids Section. Waste material classified as non-hazardous may be handled and disposed of as an industrial waste and is not subject to the 90-day or 180-day on-site storage limitation.

This is a standard (i.e., typically applicable) operating procedure which may be varied or changed as required, dependent upon site conditions, equipment limitations, or limitations imposed by the procedure. The ultimate procedure employed will be documented in the project work plans or reports. If changes to the sampling procedures are required due to unanticipated field conditions, the changes will be discussed with the Project Manager and Client as soon as practicable and documented in the report.

II. Personnel Qualifications

ARCADIS field sampling personnel will have current health and safety training including 40-hour HAZWOPER training, site supervisor training, site-specific training, first aid, and CPR, as needed. ARCADIS personnel may sign manifests on a case-to-case basis for clients, provided the appropriate agreement is in place between ARCADIS and the client documenting that ARCADIS is not the generator, but is acting as authorized representative for the generator. ARCADIS personnel who sign hazardous waste manifests will have the current DOT hazardous materials transportation training according to 49 CFR § 172.704. ARCADIS field personnel will also comply with client-specific training such as LPS. In addition, ARCADIS field sampling personnel will be versed in the relevant SOPs and posses the required skills and experience necessary to successfully complete the desired field work.

III. Equipment List

The following materials, as required, shall be available for IDW handling and storage:

Appropriate personal protective equipment as specified in the Site Health and Safety Plan

- 55-gallon steel drums, DOT 1A2 or equivalent
- ¾ -inch socket wrench
- Hammer
- Leather gloves
- Drum dolly
- Appropriate drum labels (outdoor waterproof self adhesive)
- Polyethylene storage tank
- Appropriate labeling, packing, chain-of-custody forms, and shipping materials as specified in the *Chain-of-Custody* SOP and *Field Sampling Handling, Packing, and Shipping* SOP.
- Indelible ink and/or permanent marking pens
- Plastic sheeting

- Appropriate sample containers, labels, and forms
- Stainless-steel bucket auger
- Stainless steel spatula or knife
- Stainless steel hand spade
- Stainless steel scoop
- Digital camera
- Field logbook.

IV. Cautions

- Filled drums can be very heavy, always use appropriate moving techniques and equipment.
- Similar media will be stored in the same drums to aid in sample analysis and disposal.
- Drum lids must be secured to prevent rainwater from entering the drums.
- Drums containing solid material may not contain any free liquids.
- Waste containers stored for extended periods of time may be subject to deterioration. Drum over packs may be used as secondary containment.
- All drums must be in good condition to prevent potential leakage and facilitate subsequent disposal. Inspect the drums for dents and rust, and verify the drum has a secure lid prior to use.

V. Health and Safety Considerations

- Appropriate personal protective equipment must be worn by all field personnel within the designated work area.
- Air monitoring may be required during certain field activities as required in the Site Health and Safety Plan.

- If excavating in potentially hazardous areas is possible, contingency plans should be developed to address the potential for encountering gross contamination or non-aqueous phase liquids.

- ARCADIS field personnel will be familiar and compliant with Client-specific health and safety requirements such as Chevron's hand safety policy including the prohibition of fixed and/or folding blade knives.

VI. Procedure

Waste storage and handling procedures to be used depend upon the type of generated waste. For this reason, IDW should be stored in a secure location onsite in separate 55-gallon storage drums, solids can be stockpiled onsite (if non-hazardous), and purge water may be stored in polyethylene tanks. Waste materials such as broken sample bottles or equipment containers and wrappings will be stored in 55-gallon drums unless they were not in contact with sample media.

Management of IDW

Minimization of IDW should be considered by the Project Manager during all phases of the project. Site managers may want to consider techniques such as replacing solvent-based cleaners with aqueous-based cleaners for decontamination of equipment, reuse of equipment (where it can be decontaminated), limitation of traffic between exclusion and support zones, and drilling methods and sampling techniques that generate little waste. Alternative drilling and subsurface sampling methods may include the use of small diameter boreholes, as well as borehole testing methods such as a core penetrometer or direct push technique instead of coring (EPA, 1993).

Drum Storage

Drums containing hazardous waste shall be stored in accordance with the requirements of 40 CFR 265 Subpart I (for containers) and 265 Subpart DD (for containment buildings). All 55-gallon drums will be stored at a secure, centralized on-site location that is readily accessible for vehicular pick-up. Drums confirmed as, or believed to contain hazardous waste will be stored over an impervious surface provided with secondary containment. The storage location will, for drums containing liquid, have a containment system that can contain at least the larger of 10% of the aggregate volume of staged materials or 100% of the volume of the largest container. Drums will be closed during storage and be in good condition in accordance with the Guide to Management of Investigation-Derived Wastes (USEPA, 1992).

Hazardous Waste Determination

Waste material must be characterized to determine if it meets any of the federal definitions of hazardous waste as required by 40 CFR § 262.11. If the waste does not meet any of the federal definitions, it must then be established if any state-specific hazardous waste criteria exist/apply.

Generator Status

Once hazardous waste determination has been made, the generator status will be determined. Large quantity generators (LQG) are generators who generate more than 1,000 kilograms of hazardous waste in a calendar month. Small quantity generators (SQG) of hazardous waste are generators who generate greater than 100 kilograms but less than 1,000 kilograms of hazardous waste in a calendar month. Conditionally exempt small quantity generators (CESQG) are generators who generate less than 100 kilograms of hazardous waste per month. Please note that a generator status may change from month to month and that a notice of this change is usually required by the generator's state agency.

Accumulation Time for Hazardous Waste

A LQG may accumulate hazardous waste on site for 90 days or less without a permit and without having interim status provided that such accumulation is in compliance with specifications in 40 CFR § 262.34. A SQG may accumulate hazardous waste on site for 180 days or less without a permit or without having interim status subject to the requirements of 40 CFR § 262.34(d). CESQG requirements are found in 40 CFR § 261.5. **NOTE**: The CESQG and SQG provisions of 40 CFR § 261.5, 262.20(e), 262.42(b) and 262.44 may not be recognized by some states (e.g. Rhode Island). **State-specific regulations must be reviewed and understood prior to the generation of hazardous waste.**

<u>Satellite Accumulation of Hazardous Waste</u>

Satellite accumulation (SAA) shall mean the accumulation of as much as fifty-five (55) gallons of hazardous waste, or the accumulation of as much as one quart of acutely hazardous waste, in containers at or near any point of generation where the waste initially accumulates, which is under the control of the operator of the process generating the waste, without a permit or interim status and without complying with the requirements of 40 CFR § 262.34(a) and without any storage time limit, provided that the generator complies with 40 CFR § 262.34(c)(1)(i).

Once more than 55 gallons of hazardous waste accumulates in SAA, the generator has three days to move this waste into storage.

Storage recommendations for hazardous waste include:

- Ignitable Hazardous wastes must be >50 feet from the property line per 40 CFR § 265.176 (LQG generators only).
- Hazardous waste must be stored on a concrete slab (asphalt is acceptable if there are no free liquids in the waste) per 40 CFR § 265.176.
- Drainage must be directed away from the accumulation area.
- Area must be properly vented.
- Area must be secure.

Drum/Container Labeling

Drums will be labeled on both the side and lid of the drum using a permanent marking pen. Old drum labels must be removed to the extent possible, descriptions crossed out should any information remain, and new labels affixed on top of the old labels. Other containers used to store various types of waste (polyethylene tanks, roll-off boxes, end-dump trailers, etc.) will be labeled with an appropriate "Waste Container" or “Testing in Progress” label pending characterization. Drums and containers will be labeled as follows:

- Appropriate waste characterization label (Testing In Progress, Hazardous, or Non-Hazardous)
- Waste generator's name (e.g., client name)
- Project name
- Name and telephone number of ARCADIS project manager
- Composition of contents (e.g., used oil, acetone 40%, toluene 60%)
- Media (e.g., solid, liquid)
- Accumulation start date

- Drum number of total drums as reconciled with the Drum Inventory maintained in the field log book.

IDW containers will remain closed except when adding or removing waste. Immediately upon beginning to place waste into the drum/container, a “Waste Container” or “Testing in Progress” label will be filled out to include the information specified above, and affixed to the container. Once the contents of the container are identified as either non-hazardous or hazardous, the following additional labels will be applied. Containers with waste determined to be non-hazardous will be labeled with a green and white "Non-Hazardous Waste" label over the "Waste Container" label. Containers with waste determined to be hazardous will be stored in an onsite storage area and will be labeled with the "Hazardous Waste" label and affixed over the "Waste Container" label. The ACCUMULATION DATE for the hazardous waste is the date the waste is first placed in the container and is the same date as the date on the "Waste Container" label. DOT hazardous class labels must be applied to all hazardous waste containers for shipment offsite to an approved disposal or recycling facility. In addition a DOT proper shipping name shall be included on the hazardous waste label. The transporter should be equipped with the appropriate DOT placards. However, placarding or offering placards to the initial transporter is the responsibility of the generator per 40 CFR § 262.33.

Inspections and Documentation

All IDW will be documented as generated on a Drum Inventory Log maintained in the field log book. The Drum Inventory will record the generation date, type, quantity, matrix and origin (e.g. Boring-1, Test Pit 3, etc) of materials in every drum, as well as a unique identification number for each drum. The drum inventory will be used during drum pickup to assist with labeling of drums. The drum storage area and any other areas of temporarily staged waste, such as soil/debris piles, will be inspected weekly. The weekly inspections will be recorded in the field notebook or on a Weekly Inspection Log. Digital photographs will be taken upon the initial generation and drumming/staging of waste, and final labeling after characterization to document compliance with labeling and storage protocols, and condition of the container. Evidence of damage, tampering or other discrepancy should be documented photographically.

Emergency Response and Notifications

Specific procedures for responding to site emergencies will be detailed in the HASP. If the generator is designated as a LQG, a Contingency Plan will need to be prepared to include emergency response and notification procedures per 40 CFR § 265 Subpart D. In the event of a fire, explosion, or other release which could threaten human health

outside of the site or when Client or ARCADIS has knowledge of a spill that has reached surface water, Client or ARCADIS must immediately notify the National Response Center (800-424-8802) in accordance with 40 CFR § 262.34. Other notifications to state agencies may also be necessary.

Drilling Soil Cuttings and Muds

Soil cuttings are solid to semi-solid soils generated during trenching activities, subsurface soil sampling, or installation of monitoring wells. Depending on the drilling method, drilling fluids known as "muds" may be used to remove soil cuttings. Drilling fluids flushed from the borehole must be directed into a settling section of a mud pit. This allows reuse of the decanted fluids after removal of the settled sediments. Soil cuttings will be labeled and stored in 55-gallon drums with bolt-sealed lids.

Excavated Solids

Excavated solids may include, but are not limited to soil, fill and construction and demolition debris. Excavated solids may be temporarily stockpiled onsite as long as the material is a RCRA non-hazardous waste and the solids will be treated onsite pursuant to a certified, authorized, or permitted treatment method, or properly disposed off-site. Stockpiled materials characterized as hazardous must be immediately containerized and removed from the site within 90 days of generation (except for soils using satellite accumulation). Excavated solids should be stockpiled and maintained in a secure area onsite. At a minimum, the floor of the stockpile area will be covered with a 20-mil high density polyethylene liner that is supported by a foundation or at least a 60-mil high density polyethylene liner that is not supported by a foundation. The excavated material will not contain free liquids. The owner/operator will provide controls for windblown dispersion, run-on control, and precipitation runoff. The run-on control system will prevent flow onto the active portion of the pile during peak discharge from at least a 25-year storm and the run-off management system will collect and control at least the water volume resulting from a 24-hour, 25-year storm (EPA, 1992). Additionally, the stockpile area will be inspected on a weekly basis and after storm events. Individual states may require that the stockpile be inspected/certified by a licensed professional engineer. Stockpiled material will be covered with a 6-mil polyvinyl chloride (PVC) liner. The stockpile cover will be secured in place with appropriate material (concrete blocks, weights, etc.) to prevent the movement of the cover. Excavated solids may also be placed in roll off containers and covered with a 6-mil PVC liner pending results for waste characterization.

Decontamination Solutions

Decontamination solutions are generated during the decontamination of personal protective equipment and sampling equipment. Decontamination solutions may range from detergents, organic solvents and acids used to decontaminate small field sampling equipment to steam cleaning rinsate used to wash heavy field equipment. These solutions are to be labeled and stored in 55-gallon drums with bolt-sealed lids.

Disposable Equipment

Disposable equipment includes personal protective equipment (tyvek coveralls, gloves, booties and APR cartridges) and disposable sampling equipment such as trowels or disposable bailers. If the media sampled exhibits hazardous characteristics per results of waste characterization sampling, disposable equipment will also be disposed of as a hazardous waste. These materials will be stored onsite in labeled 55-gallon drums pending analytical results for waste characterization.

Purge Water

Purge water includes groundwater generated during well development, groundwater sampling, or aquifer testing. The volume of groundwater generated will dictate the appropriate storage procedure. Monitoring well development and groundwater sampling may generate three well volumes of groundwater or more. This volume will be stored in labeled 55-gallon drums. Aquifer tests may generate significantly greater volumes of groundwater depending on the well yield and the duration of the test. Therefore, large-volume portable polyethylene tanks will be considered for temporary storage pending groundwater-waste characterization.

Purged Water Storage Tank Decontamination and Removal

The following procedures will be used for inspection, cleaning, and offsite removal of storage tanks used for temporary storage of purge water. These procedures are intended to be used for rented portable tanks such as Baker Tanks or Rain for Rent containers. Storage tanks will be made of inert polyethylene materials.

The major steps for preparing a rented tank for return to a vendor include characterizing the purge water, disposing of the purge water, decontaminating the tank, final tank inspection, and mobilization. Decontamination and inspection procedures are describe in further detail below.

- Tank Cleaning: Most vendors require that tanks be free of any sediment and water before returning, a professional cleaning service may be required. Each

specific vendor should be consulted concerning specific requirements for returning tanks.

- Tank Inspection: After emptying the tank, purged water storage tanks should be inspected for debris, chemical staining, and physical damage. The vendors require that tanks be returned in the original condition (i.e., free of sediment, staining and no physical damage).

VII. Waste Characterization Sampling and Shipping

Soil/Solids Characterization

Waste characterization will be conducted in accordance with waste hauler, waste handling facility, and state/federal requirements. In general, RCRA hazardous wastes are those solid wastes determined by a Toxicity Characteristic Leaching Procedure (TCLP) test or to contain levels of certain toxic metals, pesticides, or other organic chemicals above specific federally regulated thresholds. If the one or more of 40 toxic compounds listed in Table I of 40 CFR § 261.24 are detected in the sample at levels above the maximum unregulated concentrations, the waste must be characterized as a toxic hazardous waste. Wastes can also be considered “listed” hazardous waste depending on site-specific processes.

Composite soil samples will be collected at a frequency of one sample per 10 cubic yard basis for stockpiled soil or one per 55-gallon drum for containerized. A four point composite sample will be collected per 10 cubic yards of stockpiled material and for each drum. Sample and composite frequencies may be adjusted in accordance with the waste handling facility’s requirements. Waste characterization samples may be analyzed for the TCLP volatile organic compounds (VOCs), TCLP semi-volatile organic compounds (SVOCs), TCLP RCRA metals, and polychlorinated biphenyls, as well as corrosivity (pH), reactivity and flammability (flashpoint). Additional samples may be collected and analyzed by the laboratory on a contingency basis.

Wastewater Characterization

Waste characterization will be conducted in accordance with the requirements of the waste hauler, waste handling facility, and state/federal governments. In general, purge water should be analyzed by methods appropriate for the known contaminants, if any, that have been historically detected in the monitoring wells. Samples will be collected and analyzed in accordance with the requirements of the waste disposal facility.

Wastewater characterization samples may be analyzed for TCLP volatile organic compounds (VOCs), TCLP semi-volatile organic compounds (SVOCs), TCLP RCRA

metals, and polychlorinated biphenyls, as well as corrosivity (pH), reactivity and flammability (flashpoint). Additional samples may be collected and analyzed by the laboratory on a contingency basis.

Sample Handling and Shipping

All samples will be appropriately labeled, packed, and shipped, and the chain-of-custody will be filled out in accordance with the Chain-of-Custody SOP and Field Sampling Handling, Packing, and Shipping SOP and Hazardous Materials Packaging and Shipping SOP.

It should be noted that additional training is required for packaging and shipping of hazardous and/or dangerous materials. Please reference the following ARCADIS intranet team page for more information: http://team/sites/hazmat/default.aspx.

Preparing Waste Shipment Documentation (Hazardous and Non-Hazardous)

Waste profiles will be prepared by the ARCADIS PM and forwarded, along with laboratory analytical data to the Client PM for approval/signature. The Client PM will then return the profile to ARCADIS who will then forward to the waste removal contractor for preparation of a manifest. The manifest will be reviewed by ARCADIS prior to forwarding to the Client PM for approval. Upon approval of the manifest, the Client PM will return the original signed manifest directly to the waste contractor or to the ARCADIS PM for forwarding to the waste contractor.

Final drum labeling and pickup will be supervised by an ARCADIS representative who is experienced with waste labeling procedures. The ARCADIS representative will have a copy of the drum inventory maintained in the field book and will reconcile the drum inventory with the profile numbers on the labels and on the manifest. Different profile numbers will be generated for different matrices or materials in the drums. For example, the profile number for drill cuttings will be different than the profile number for purge water. **When there are multiple profiles it is critical that the proper label, with the profile number appropriate to a specific material be affixed to the proper drums.** A copy of the ARCADIS drum inventory will be provided to the waste transporter during drum pickup and to the facility receiving the waste.

VIII. Data Recording and Management

Waste characterization sample handling, packing, and shipping procedures will be documented in accordance with the *Quality Assurance Project Plan*, if one exists. Copies of the chains-of-custody forms will be maintained in the project file.

Following waste characterization, IDW containers will be re-labeled with the appropriate waste hazardous or non-hazardous waste labels and the client will initiate disposal at the appropriate waste disposal facility.

IX. Quality Assurance

The chain-of-custody and sample labels for waste characterization samples will be filled out in accordance with the *Quality Assurance Project Plan*.

X. References

United States Environmental Protection Agency (USEPA). 1992. Guide to Management of Investigation-Derived Wastes. Office of Remedial and Emergency Response. Hazardous Site Control Division. January 1992.

USEPA. 1991. *Guide to Discharging CERCLA Aqueous Wastes to Publicly Owned Treatment Works (POTWs)*. Office of Remedial and Emergency Response. Hazardous Site Control Division 0S-220W. March 1991.

ARCADIS
Infrastructure · Water · Environment · Buildings

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Chain-of-Custody, Handling, Packing and Shipping

Rev. #: 2

Rev Date: March 6, 2009

Approval Signatures

Prepared by: _____ Date: 3/6/09
Caron Koll

Reviewed by: _____ Date: 3/6/09
Jane Kennedy(Technical Expert)

I. Scope and Application

This Standard Operating Procedure (SOP) describes the chain-of-custody, handling, packing, and shipping procedures for the management of samples to decrease the potential for cross-contamination, tampering, mis-identification, and breakage, and to insure that samples are maintained in a controlled environment from the time of collection until receipt by the analytical laboratory.

II. Personnel Qualifications

ARCADIS field sampling personnel will have current health and safety training, including 40-hour HAZWOPER training, Department of Transportation (DOT) training, site supervisor training, and site-specific training, as needed. In addition, ARCADIS field sampling personnel will be versed in the relevant SOPs and possess the skills and experience necessary to successfully complete the desired field work.

III. Equipment List

The following list provides materials that may be required for each project. Project documents and sample collection requirements should be reviewed prior to initiating field operations:

- indelible ink pens (black or blue);
- polyethylene bags (resealable-type);
- clear packing tape, strapping tape, duct tape;
- chain of custody
- DOT shipping forms, as applicable
- custody seals or tape;
- appropriate sample containers and labels,;
- insulated coolers of adequate size for samples and sufficient ice to maintain 4°C during collection and transfer of samples;
- wet ice;
- cushioning and absorbent material (i.e., bubble wrap or bags);

- temperature blank
- sample return shipping papers and addresses; and
- field notebook.

IV. Cautions

Review project requirements and select appropriate supplies prior to field mobilization.

Insure that appropriate sample containers with applicable preservatives, coolers, and packing material have been supplied by the laboratory.

Understand the offsite transfer requirements for the facility at which samples are collected.

If overnight courier service is required schedule pick-up or know where the drop-off service center is located and the hours of operation. Prior to using air transportation, confirm air shipment is acceptable under DOT and International Air Transport Association (IATA) regulation

Schedule pick-up time for laboratory courier or know location of laboratory/service center and hours of operation.

Understand DOT and IATA shipping requirements and evaluate dangerous goods shipping regulations relative to the samples being collected (i.e. complete an ARCADIS shipping determination). Review the ARCADIS SOPs for shipping, packaging and labeling of dangerous goods. Potential samples requiring compliance with this DOT regulation include:

- Methanol preservation for Volatile Organic Compounds in soil samples
- Non-aqueous phase liquids (NAPL)

V. Health and Safety Considerations

Follow health and safety procedures outlined in the project/site Health and Safety Plan (HASP).

Use caution and appropriate cut resistant gloves when tightening lids to 40 mL vials. These vials can break while tightening and can lacerate hand. Amber vials (thinner glass) are more prone to breakage.

Some sample containers contain preservatives.

- The preservatives must be retained in the sample container and should in no instance be rinsed out.
- Preservatives may be corrosive and standard care should be exercised to reduce potential contact to personnel skin or clothing. Follow project safety procedures if spillage is observed.
- If sample container caps are broken discard the bottle. Do not use for sample collection.

VI. Procedure

Chain-of-Custody Procedures

1. Prior to collecting samples, complete the chain-of-custody record header information by filling in the project number, project name, and the name(s) of the sampling technician(s) and other relevant project information. Attachment 1 provides an example chain-o- custody record

2. Chain-of-custody information MUST be printed legibly using indelible ink (black or blue).

3. After sample collection, enter the individual sample information on the chain-of-custody:

    a. Sample Identification indicates the well number or soil location that the sample was collected from. Appropriate values for this field include well locations, grid points, or soil boring identification numbers (e.g., MW-3, X-20, SB-30). When the depth interval is included, the complete sample ID would be “SB-30 (0.5-1.0) where the depth interval is in feet. Please note it is very important that the use of hyphens in sample names and depth units (i.e., feet or inches) remain consistent for all samples entered on the chain-of-custody form. DO NOT use the apostrophe or quotes in the sample ID. Sample names may also use the abbreviations “FB,” “TB,” and “DUP” as prefixes or suffixes to indicate that the sample is a field blank, trip blank, or field duplicate, respectively. NOTE: The sample

nomenclature may be dictated by the project database and require unique identification for each sample collected for the project. Consult the project data management plan for additional information regarding sample identification.

b. List the date of sample collection. The date format to be followed should be mm/dd/yy (e.g., 03/07/09) or mm/dd/yyyy (e.g. 03/07/2009).

c. List the time that the sample was collected. The time value should be presented using military format. For example, 3:15 P.M. should be entered as 15:15.

d. The composite field should be checked if the sample is a composite over a period of time or from several different locations and mixed prior to placing in sample containers.

e. The “Grab”. field should be marked with an “X” if the sample was collected as an individual grab sample. (e.g. monitoring well sample or soil interval).

f. Any sample preservation should be noted.

g. The analytical parameters that the samples are being analyzed for should be written legibly on the diagonal lines. As much detail as possible should be presented to allow the analytical laboratory to properly analyze the samples. For example, polychlorinated biphenyl (PCB) analyses may be represented by entering “PCBs” or “Method 8082.” Multiple methods and/or analytical parameters may be combined for each column (e.g., PCBs/VOCs/SVOCs or 8082/8260/8270). These columns should also be used to present project-specific parameter lists (e.g., Appendix IX+3 target analyte list. Each sample that requires a particular parameter analysis will be identified by placing the number of containers in the appropriate analytical parameter column. For metals in particular, indicate which metals are required.

h. Number of containers for each method requested. This information may be included under the parameter or as a total for the sample based on the chain of custody form used.

i. Note which samples should be used for site specific matrix spikes.

j. Indicate any special project requirements.

k. Indicate turnaround time required.

l. Provide contact name and phone number in the event that problems are encountered when samples are received at the laboratory.

m. If available attach the Laboratory Task Order or Work Authorization forms

n. The remarks field should be used to communicate special analytical requirements to the laboratory. These requirements may be on a per sample basis such as “extract and hold sample until notified,” or may be used to inform the laboratory of special reporting requirements for the entire sample delivery group (SDG). Reporting requirements that should be specified in the remarks column include: 1) turnaround time; 2) contact and address where data reports should be sent; 3) name of laboratory project manager; and 4) type of sample preservation used.

o. The “Relinquished By” field should contain the signature of the sampling technician who relinquished custody of the samples to the shipping courier or the analytical laboratory.

p. The “Date” field following the signature block indicates the date the samples were relinquished. The date format should be mm/dd/yyyy (e.g., 03/07/2005).

q. The “Time” field following the signature block indicates the time that the samples were relinquished. The time value should be presented using military format. For example, 3:15 P.M. should be entered as 15:15.

r. The “Received By” section is signed by sample courier or laboratory representative who received the samples from the sampling technician or it is signed upon laboratory receipt from the overnight courier service.

3. Complete as many chain-of-custody forms as necessary to properly document the collection and transfer of the samples to the analytical laboratory.

4. Upon completing the chain-of-custody forms, forward two copies to the analytical laboratory and retain one copy for the field records.

5. If electronic chain-of-custody forms are utilized, sign the form and make 1 copy for ARCADIS internal records and forward the original with the samples to the laboratory.

Handling Procedures

1. After completing the sample collection procedures, record the following information in the field notebook with indelible ink:

   - project number and site name;
   - sample identification code and other sample identification information, if appropriate;
   - sampling method;
   - date;
   - name of sampler(s);
   - time;
   - location (project reference);
   - location of field duplicates and both sample identifications;
   - locations that field QC samples were collected including equipment blanks, field blanks and additional sample volume for matrix spikes; and
   - any comments.

2. Complete the sample label with the following information in indelible ink:

   - sample type (e.g., surface water);
   - sample identification code and other sample identification information, if applicable;
   - analysis required;
   - date;
   - time sampled; and
   - initials of sampling personnel;

- sample matrix; and
- preservative added, if applicable.

3. Cover the label with clear packing tape to secure the label onto the container and to protect the label from liquid.

4. Confirm that all caps on the sample containers are secure and tightly closed.

5. In some instances it may be necessary to wrap the sample container cap with clear packing tape to prevent it from becoming loose.

6. For some projects individual custody seals may be required. Custody seal evidence tape may be placed on the shipping container or they may be placed on each sample container such that the cooler or cap cannot be opened without breaking the custody seal. The custody seal should be initialed and dated prior to relinquishing the samples.

Packing Procedures

Following collection, samples must be placed on wet ice to initiate cooling to 4°C immediately. Retain samples on ice until ready to pack for shipment to the laboratory.

1. Secure the outside and inside of the drain plug at the bottom of the cooler being used for sample transport with “Duct” tape.

2. Place a new large heavy duty plastic garbage bag inside each cooler

3. Place each sample bottle wrapped in bubble wrap inside the garbage bag. VOC vials may be grouped by sample in individual resealable plastic bags). If a cooler temperature blank is supplied by the laboratory, it should be packaged following the same procedures as the samples. If the laboratory did not include a temperature blank, do not add one. Place 1 to 2 inches of cushioning material (i.e., vermiculite) at the bottom of the cooler.

4. Place the sealed sample containers upright in the cooler.

5. Package ice in large resealable plastic bags and place inside the large garbage bag in the cooler. Samples placed on ice will be cooled to and maintained at a temperature of approximately 4°C.

6. Fill the remaining space in the cooler with cushioning material such as bubble wrap. The cooler must be securely packed and cushioned in an upright position and be surrounded (Note: to comply with 49 CFR 173.4, filled cooler must not exceed 64 pounds).

7. Place the completed chain-of-custody record(s) in a large resealable bag and tape the bag to the inside of the cooler lid.

8. Close the lid of the cooler and fasten with packing tape.

9. Wrap strapping tape around both ends of the cooler.

10. Mark the cooler on the outside with the following information: shipping address, return address, “Fragile, Handle with Care” labels on the top and on one side, and arrows indicating “This Side Up” on two adjacent sides.

11. Place custody seal evidence tape over front right and back left of the cooler lid, initial and date, then cover with clear plastic tape.

Note: Procedure numbers 2, 3, 5, and 6 may be modified in cases where laboratories provide customized shipping coolers. These cooler types are designed so the sample bottles and ice packs fit snugly within preformed styrofoam cushioning and insulating packing material.

Shipping Procedures

1. All samples will be delivered by an express carrier within 48 hours of sample collection. Alternatively, samples may be delivered directly to the laboratory or laboratory service center or a laboratory courier may be used for sample pickup.

2. If parameters with short holding times are required (e.g., VOCs [EnCore™ Sampler], nitrate, nitrite, ortho-phosphate and BOD), sampling personnel will take precautions to ship or deliver samples to the laboratory so that the holding times will not be exceeded.

3. Samples must be maintained at 4°C±2°C until shipment and through receipt at the laboratory

4. All shipments must be in accordance with DOT regulations and ARCADIS dangerous goods shipping SOPs.

5. When the samples are received by the laboratory, laboratory personnel will complete the chain-of-custody by recording the date and time of receipt of samples, measuring and recording the internal temperature of the shipping container, and checking the sample identification numbers on the containers to ensure they correspond with the chain-of-custody forms.

Any deviations between the chain-of-custody and the sample containers, broken containers, or temperature excursions will be communicated to ARCADIS immediately by the laboratory.

VII. Waste Management

Not applicable

VIII. Data Recording and Management

Chain-of-custody records will be transmitted to the ARCADIS PM or designee at the end of each day unless otherwise directed by the ARCADIS PM. The sampling team leader retains copies of the chain-of-custody forms for filing in . the project file. Record retention shall be in accordance with project requirements.

IX. Quality Assurance

Chain-of-custody forms will be legibly completed in accordance with the applicable project documents such as Sampling and Analysis Plan (SAP), Quality Assurance Project Plan (QAPP), Work Plan, or other project guidance documents. A copy of the completed chain-of-custody form will be sent to the ARCADIS Project Manager or designee for review.

X. References

Not Applicable

Attachment 1

ARCADIS
Infrastructure, environment, facilities

ID#:

CHAIN OF CUSTODY & LABORATORY ANALYSIS REQUEST FORM

Page ___ of ___

Lab Work Order #

Send Results to:

Contact & Company Name: | Telephone:

Address: | Fax:

City | State | Zip | E-mail Address:

Project Name/Location (City, State): | Project #:

Sampler's Printed Name: | Sampler's Signature:

Preservative							
Filtered (✓)							
# of Containers							
Container Information							

PARAMETER ANALYSIS & METHOD

Keys

Preservation Key:
A. H_2SO_4
B. HCL
C. HNO_3
D. NaOH
E. None
F. Other: _____
G. Other: _____
H. Other: _____

Container Information Key:
1. 40 ml Vial
2. 1 L Amber
3. 250 ml Plastic
4. 500 ml Plastic
5. Encore
6. 2 oz. Glass
7. 4 oz. Glass
8. 8 oz. Glass
9. Other: _____
10. Other: _____

Matrix Key:
SO - Soil | SE - Sediment | NL - NAPL/Oil
W - Water | SL - Sludge | SW - Sample Wipe
T - Tissue | A - Air | Other: _____

Sample ID	Collection Date	Collection Time	Type (✓) Comp	Type (✓) Grab	Matrix								REMARKS

Special Instructions/Comments:

☐ **Special QA/QC Instructions(✓):**

Laboratory Information and Receipt		Relinquished By	Received By	Relinquished By	Laboratory Received By
Lab Name:	Cooler Custody Seal (✓)	Printed Name:	Printed Name:	Printed Name:	Printed Name:
☐ Cooler packed with ice (✓)	☐ Intact ☐ Not Intact	Signature:	Signature:	Signature:	Signature:
Specify Turnaround Requirements:	Sample Receipt:	Firm:	Firm/Courier:	Firm/Courier:	Firm:
Shipping Tracking #:	Condition/Cooler Temp: _____	Date/Time:	Date/Time:	Date/Time:	Date/Time:

20030826 CofC AR Form 01.12.2007

Distribution: **WHITE – Laboratory returns with results** **YELLOW – Lab copy** **PINK – Retained by BBL**

Imagine the result

Surface Water Sampling
Standard Operating Procedure

Rev. #: 0

Date: June 3, 2013

Approval Signatures

Prepared by: _____ Date: June 3, 2013
Jesse Starr

Reviewed by: _____ Date: June 3, 2013
Shannon Dunn
(Technical Expert)

I. Scope and Application

This Standard Operating Procedure (SOP) describes the collection of surface water samples using a grab method, discrete depth sampler or peristaltic pump. This SOP should be followed whenever collecting surface water samples.

This SOP may change depending upon field conditions, equipment limitations, or limitations imposed by the procedure. Substantive modification to this SOP will be approved in advance by the Project Manager.

II. Personnel Qualifications

ARCADIS field personnel will have current health and safety training, including 40-hour HAZWOPER training, site supervisor training, and site-specific training, as needed. In addition, ARCADIS field personnel will be versed in the relevant SOPs and will possess the skills and experience necessary to successfully complete the desired field work. The project Health and Safety Plan (HASP) and other documents will identify any other training requirements such as site-specific safety training or access control requirements.

III. Equipment List

The following equipment list contains materials that may be needed in carrying out the procedures contained in this SOP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- personal protective equipment (PPE) and other safety equipment, as required in the project Health and Safety Plan (HASP)
- project Quality Assurance Project Plan (QAPP)
- Sampling and Analysis Plan (SAP)
- indelible ink pens
- appropriate sample containers, labels, and forms
- decontamination supplies including bucket, distilled or deionized water, cleansers appropriate for removing expected chemicals of concern.
- sample packing and shipping materials

- water-quality (temperature/pH/specific conductivity/ORP/turbidity/dissolved oxygen) meter and flow-through measurement cell. Several brands may be used, including:
  - YSI 6-Series Multi-Parameter Instrument
  - Hydrolab Series 3 or Series 4a Multiprobe and Display
  - Horiba U-10 or U-22 Water Quality Monitoring System
- for grab sampling method: pole with polyethylene and/or stainless steel dipper, if applicable
- for discrete depth sampling method: discrete depth samplers (e.g., Kemmerer or Van Dorn samplers)
- for peristaltic pump sampling method: peristaltic pump with appropriate power source, Teflon® tubing or Teflon®-lined polyethylene tubing of an appropriate size for the pump being used. For peristaltic pumps, dedicated Tygon® tubing (or other type as specified by the manufacturer) will also be used through the pump apparatus.

IV. Cautions

If heavy precipitation occurs and no cover over the sampling area can be erected, sampling must be discontinued until adequate cover is provided. Rain water could contaminate surface water samples.

Do not use permanent marker or felt-tip pens for labels on sample container or sample coolers – use indelible ink. The permanent markers could introduce volatile constituents into the samples.

It may be necessary to field-filter some parameters (e.g., metals) prior to collection, depending on preservation, analytical method, and project quality objectives.

Store and/or stage empty and full sample containers and coolers out of direct sunlight.

Be careful not to over-tighten lids with Teflon liners or septa (e.g., 40 mL vials). Over tightening can cause the glass to shatter or impair the integrity of the Teflon seal.

Use caution and appropriate cut resistant gloves when tightening lids to 40 mL vials. These vials can break while tightening and can lacerate hand. Amber vials (thinner glass) are more prone to breakage.

The ability to safely access the surface water sampling locations should be verified prior to sampling.

Field activities will be performed in accordance with a project-specific HASP, a copy of which will be present onsite during such activities.

Safety hazards associated with sampling surface water include fast-moving water, deep water, and steep slopes close to sampling sites. Extreme caution should be used when approaching sampling sites. Work will be performed in accordance with the project-specific HASP.

V. Procedure

Sampling Method

Surface water samples will be collected from sampling locations sequentially from downstream to upstream to prevent cross-contamination associated with sediment disturbance. Surface water samples will be collected prior to sediment sample collection.

Grab Sample Collection

Personnel conducting surface water sampling using grab sample collection techniques should perform the following:

1. Collect appropriate equipment, cleaned and decontaminated.

2. Obtain appropriate sampling containers.

3. Mobilize to surface water sampling location in accordance with the work plan or SAP.

4. Collect sample by directly lowering the laboratory-supplied sample container into the water and allowing the bottle to partially fill with water. The sampler will hold the bottle immediately below the water surface and allows the bottle to fill with sample. Field personnel will handle only the portions of the sample containers that do not come in contact with the sample, to avoid contamination. Additionally, care will be taken to avoid exposing samples and sample containers to atmospheric inputs such as dirt or dust.

5. Measure water quality parameters.

6. Transfer surface water samples into laboratory-supplied sample containers to complete the scope described in the SAP. Avoid overfilling sample containers to prevent preservatives, if present, in sample container from being lost.

Sample Collection Using a Discrete Depth Sampler (e.g., Kemmerer or Van Dorn)

Personnel conducting surface water sampling using grab sample collection techniques should perform the following:

1. Collect appropriate equipment, cleaned and decontaminated.

2. Obtain appropriate sampling containers.

3. Mobilize to surface water sampling location in accordance with the work plan or SAP.

4. Carefully set the sampling device so that water is allowed to pass through the tube.

5. Lower the pre-set sampling device to the predetermined depth using marked rope or line attached to the device.

6. When at desired depth; send down the messenger, closing the device. Avoid disturbing the bottom.

7. Retrieve sampler and discharge the first 10-20 mL to clear any potential cross-contamination.

8. Measure water quality parameters

9. Transfer surface water samples into laboratory-supplied sample containers to complete the scope described in the SAP. Avoid overfilling sample containers to prevent preservatives, if present, in sample container from being lost.

10. Pack and store samples appropriately for transport to laboratory.

Sample Collection Using Peristaltic Pump

Personnel conducting surface water sampling using peristaltic pump collection techniques should perform the following:

1. Surface water will be collected using a peristaltic pump if flow is slow and conventional sampling procedures are impossible without collecting excess

suspended sediment in the sample. Note any observations such as color or odors and determine the depth of water. Record the information in the field log book or field log forms.

2. Personnel should be aware that contact with peristaltic pump apparatus (e.g., control knobs) can serve as a source of metals contamination in dissolved metals analyses. Operation of pump controls should be conducted with gloves that do not come into contact with the sample or with materials that contact the sample.

3. Attach tubing to pump and configure tubing such that intake in positioned at the desired sample depth within the water column and discharge is into desired sample container.

4. Turn the pump on and adjust the flow rate as necessary to avoid splashing or overfilling.

5. Measure water quality parameters on a volume of sample that will not be shipped to the laboratory to avoid cross-contamination in the sample to be analyzed.

6. Collect surface water samples by diverting flow out of the unfiltered discharge tubing into the appropriate labeled sample container.

– If a flow-through analytical cell is being used to measure field parameters, the flow-through cell should be disconnected after stabilization of the field indicator parameters and prior to surface water sample collection. Under no circumstances should analytical samples be collected from the discharge of the flow-through cell.

– When the sample container is full, tightly screw on the cap.

– Samples should be collected in the following order: VOCs, TOC, SVOCs, metals and cyanide, and others (or other order as defined in the Sampling and Analysis Plan (SAP)).

7. Pack and store samples appropriately for transport to laboratory.

VI. Waste Management

Liquid investigation-derived wastes (IDWs), such decontamination liquids or excess surface water, will be collected into 55-gallon drums and may be transferred into large-volume polyethylene tanks with secondary containment pending treatment and/or disposal.

Non-aqueous liquid wastes, if generated (e.g., hexane, non-aqueous phase liquid [NAPL]), will be segregated and stored in appropriately sized buckets with secondary containment pending disposal.

PPE, soiled disposable items, and other trash will be stored in 55-gallon drums and stored on site pending disposal.

IDWs will be collected and stored on site in United States Department of Transportation (DOT)-compliant 55-gallon drums and/or large-volume tanks with secondary containment. Fifty-five-gallon drums and tanks will be labeled with DOT-compliant labels with the following information: drum contents, generator contact information, and date container was filled. IDWs known to be hazardous will be segregated and stored separately from non-hazardous IDWs. Solid IDWs will be segregated and stored separately from liquid IDWs.

IDWs will be sampled as needed for disposal characterization and stored on site pending treatment and/or disposal. IDWs may be managed in conjunction with remedial activities.

All IDWs will be stored in a secure onsite location pending treatment and disposal and/or discharge.

VII. Data Recording and Management

Record field data in field notebook and/or on field log sheets.

VIII. Quality Assurance

Sample quality will be achieved by complying with the procedures outlined in this SOP. Cross-contamination will be prevented by following standard decontamination protocols. Field activities will be supervised by appropriate experienced field supervisors. Additional quality assurance information is presented in the project-specific Quality Assurance Project Plan.

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Low-Flow Groundwater Purging and Sampling Procedures for Monitoring Wells

Rev. #: 4

Rev Date: February 2, 2011

Approval Signatures

Prepared by: _____ Date: 2/2/2011

Reviewed by: _____ Date: 2/2/2011
(Technical Expert)

I. Scope and Application

Groundwater samples will be collected from monitoring wells to evaluate groundwater quality. The protocol presented in this standard operating procedure (SOP) describes the procedures to be used to purge monitoring wells and collect groundwater samples. This protocol has been developed in accordance with the United States Environmental Protection Agency (USEPA) Region I Low Stress (Low Flow) Purging and Sampling Procedures for the Collection of Groundwater Samples from Monitoring Wells (USEPA SOP No. GW0001; July 30, 1996). Both filtered and unfiltered groundwater samples may be collected using this low-flow sampling method. Filtered samples will be obtained using a 0.45-micron disposable filter. No wells will be sampled until well development has been performed in accordance with the procedures presented in the SOP titled Monitoring Well Development, unless that well has been sampled or developed within the prior 1-year time period. Groundwater samples will not be collected within 1 week following well development.

II. Personnel Qualifications

ARCADIS personnel directing, supervising, or leading groundwater sample collection activities should have a minimum of 2 years of previous groundwater sampling experience. ARCADIS personnel providing assistance to groundwater sample collection and associated activities should have a minimum of 6 months of related experience or an advanced degree in environmental sciences, engineering, hydrogeology, or geology.

The supervisor of the groundwater sampling team will have at least 1 year of previous supervised groundwater sampling experience.

Prior to mobilizing to the field, the groundwater sampling team should review and be thoroughly familiar with relevant site-specific documents including but not limited to the site work plan, field sampling plan, QAPP, HASP, and historical information. Additionally, the groundwater sampling team should review and be thoroughly familiar with documentation provided by equipment manufacturers for all equipment that will be used in the field prior to mobilization.

III. Equipment List

Specific to this activity, the following materials (or equivalent) will be available:

- Health and safety equipment (as required in the site Health and Safety Plan [HASP]).

- Site Plan, well construction records, prior groundwater sampling records (if available).
- Sampling pump, which may consist of one or more of the following:
  - submersible pump (e.g., Grundfos Redi-Flo 2);
  - peristaltic pump (e.g., ISCO Model 150); and/or
  - bladder pump (e.g., Marschalk System 1, QED Well Wizard, Geotech, etc.).
- Appropriate controller and power source for pump:
  - Submersible and peristaltic pumps require electric power from either a generator or a deep cell battery.
  - Submersible pumps such as Grundfos require a pump controller to run the pump
  - Bladder pumps require a pump controller and a gas source (e.g., air compressor or compressed N_2 or CO_2 gas cylinders).
- Teflon® tubing or Teflon®-lined polyethylene tubing of an appropriate size for the pump being used. For peristaltic pumps, dedicated Tygon® tubing (or other type as specified by the manufacturer) will also be used through the pump apparatus.
- Water-level probe (e.g., Solinist Model 101).
- Water-quality (temperature/pH/specific conductivity/ORP/turbidity/dissolved oxygen) meter and flow-through measurement cell. Several brands may be used, including:
  - YSI 6-Series Multi-Parameter Instrument;
  - Hydrolab Series 3 or Series 4a Multiprobe and Display; and/or
  - Horiba U-10 or U-22 Water Quality Monitoring System.
- Supplemental turbidity meter (e.g., Horiba U-10, Hach 2100P, LaMotte 2020). Turbidity measurements collected with multi-parameter meters have been shown to sometimes be unreliable due to fouling of the optic lens of the

turbidity meter within the flow-through cell. A supplemental turbidity meter will be used to verify turbidity data during purging if such fouling is suspected. Note that industry improvements may eliminate the need for these supplemental measurements in the future.

- Appropriate water sample containers (supplied by the laboratory).
- Appropriate blanks (trip blank supplied by the laboratory).
- 0.45-micron disposable filters (if field filtering is required).
- Large glass mixing container (if sampling with a bailer).
- Teflon® stirring rod (if sampling with a bailer).
- Cleaning equipment.
- Groundwater sampling log (attached) or bound field logbook.

Note that in the future, the client may acquire different makes/models of some of this equipment if the listed makes/models are no longer available, or as a result of general upgrades or additional equipment acquisitions. In the event that the client uses a different make/model of the equipment listed, the client will use an equivalent type of equipment (e.g., pumps, flow-through analytical cells) and note the specific make/model of the equipment used during a sampling event on the groundwater sampling log. In addition, should the client desire to change to a markedly different sampling methodology (e.g., discrete interval samplers, passive diffusion bags, or a yet to be developed technique), the client will submit a proposed SOP for the new methodology for USEPA approval prior to implementing such a change.

The maintenance requirements for the above equipment generally involve decontamination or periodic cleaning, battery charging, and proper storage, as specified by the manufacturer. For operational difficulties, the equipment will be serviced by a qualified technician.

IV. Cautions

If heavy precipitation occurs and no cover over the sampling area and monitoring well can be erected, sampling must be discontinued until adequate cover is provided. Rain water could contaminate groundwater samples.

Do not use permanent marker or felt-tip pens for labels on sample container or sample coolers – use indelible ink. The permanent markers could introduce volatile constituents into the samples.

It may be necessary to field filter some parameters (e.g., metals) prior to collection, depending on preservation, analytical method, and project quality objectives.

Store and/or stage empty and full sample containers and coolers out of direct sunlight.

To mitigate potential cross-contamination, groundwater samples are to be collected in a pre-determined order from least impacted to impacted based on previous analytical data. If no analytical data are available, samples are collected in order of upgradient, then furthest downgradient to source area locations.

Be careful not to over-tighten lids with Teflon liners or septa (e.g., 40 mL vials). Over-tightening can cause the glass to shatter or impair the integrity of the Teflon seal.

V. Health and Safety Considerations

Use caution and appropriate cut resistant gloves when tightening lids to 40 mL vials. These vials can break while tightening and can lacerate hand. Amber vials (thinner glass) are more prone to breakage.

If thunder or lighting is present, discontinue sampling and take cover until 30 minutes have passed after the last occurrence of thunder or lighting.

Use caution when removing well caps as well may be under pressure, cap can dislodge forcefully and cause injury.

Use caution when opening protective casing on stickup wells as wasps frequently nest inside the tops of the covers. Also watch for fire ant mounds near well pads when sampling in the south or western U.S.

VI. Procedure

Groundwater will be purged from the wells using an appropriate pump. Peristaltic pumps will initially be used to purge and sample all wells when applicable. If the depth to water is below the sampling range of a peristaltic pump (approximately 25 feet), submersible pumps or bladder pumps will be used provided the well is constructed with a casing diameter greater than or equal to 2 inches (the minimum well diameter capable of accommodating such pumps). Bladder pumps are preferred over peristaltic and submersible pumps if sampling of VOCs is required to prevent volatilization. For smaller diameter wells where the depth to water is below the sampling range of a

peristaltic pump, alternative sampling methods (i.e., bailing or small diameter bladder pumps) will be used to purge and sample the groundwater. Purge water will be collected and containerized.

1. Calibrate field instruments according to manufacturer procedures for calibration.

2. Measure initial depth to groundwater prior to placement of pumps.

3. Prepare and install pump in well: For submersible and non-dedicated bladder pumps, decontaminate pump according to site decontamination procedures. Non-dedicated bladder pumps will require a new Teflon® bladder and attachment of an air line, sample discharge line, and safety cable prior to placement in the well. Attach the air line tubing to the air port on the top of the bladder pump. Attach the sample discharge tubing to the water port on the top of the bladder pump. Care should be taken not to reverse the air and discharge tubing lines during bladder pump set-up as this could result in bladder failure or rupture. Attach and secure a safety cable to the eyebolt on the top of bladder pump (if present, depending on pump model used). Slowly lower pump, safety cable, tubing, and electrical lines into the well to a depth corresponding to the approximate center of the saturated screen section of the well. Take care to avoid twisting and tangling of safety cable, tubing, and electrical lines while lowering pump into well; twisted and tangled lines could result in the pump becoming stuck in the well casing. Also, make sure to keep tubing and lines from touching the ground or other surfaces while introducing them into the well as this could lead to well contamination. If a peristaltic pump is being used, slowly lower the sampling tubing into the well to a depth corresponding to the approximate center of the saturated screen section of the well. The pump intake or sampling tube must be kept at least 2 feet above the bottom of the well to prevent mobilization of any sediment present in the bottom of the well.

4. If using a bladder pump, connect the air line to the pump controller output port. The pump controller should then be connected to a supply line from an air compressor or compressed gas cylinder using an appropriate regulator and air hose. Take care to tighten the regulator connector onto the gas cylinder (if used) to prevent leaks. Teflon tape may be used on the threads of the cylinder to provide a tighter seal. Once the air compressor or gas cylinder is connected to the pump controller, turn on the compressor or open the valve on the cylinder to begin the gas flow. Turn on the pump controller if an on/off switch is present and verify that all batteries are charged and fully operating before beginning to pump.

5. Connect the pump discharge water line to the bottom inlet port on the flow-through cell connected to the water quality meter.

6. Measure the water level again with the pump in the well before starting the pump. Start pumping the well at 200 to 500 milliliters (mL) per minute (or at lower site-specific rate if specified). The pump rate should be adjusted to cause little or no water level drawdown in the well (less than 0.3 feet below the initial static depth to water measurement) and the water level should stabilize. The water level should be monitored every 3 to 5 minutes (or as appropriate, lower flow rates may require longer time between readings) during pumping if the well diameter is of sufficient size to allow such monitoring. Care should be taken not to break pump suction or cause entrainment of air in the sample. Record pumping rate adjustments and depths to water. If necessary, pumping rates should be reduced to the minimum capabilities of the pump to avoid pumping the well dry and/or to stabilize indicator parameters. A steady flow rate should be maintained to the extent practicable. Groundwater sampling records from previous sampling events (if available) should be reviewed prior to mobilization to estimate the optimum pumping rate and anticipated drawdown for the well in order to more efficiently reach a stabilized pumping condition.

   If the recharge rate of the well is very low, alternative purging techniques should be used, which will vary based on the well construction and screen position. For wells screened across the water table, the well should be pumped dry and sampling should commence as soon as the volume in the well has recovered sufficiently to permit collection of samples. For wells screened entirely below the water table, the well should be pumped until a stabilized level (which may be below the maximum displacement goal of 0.3 feet) can be maintained and monitoring for stabilization of field indicator parameters can commence. If a lower stabilization level cannot be maintained, the well should be pumped until the drawdown is at a level slightly higher than the bentonite seal above the well screen. Sampling should commence after one well volume has been removed and the well has recovered sufficiently to permit collection of samples.

   During purging, monitor the field indicator parameters (e.g., turbidity, temperature, specific conductance, pH, etc.) every 3 to 5 minutes (or as appropriate). Field indicator parameters will be measured using a flow-through analytical cell or a clean container such as a glass beaker. Record field indicator parameters on the groundwater sampling log. The well is considered stabilized and ready for sample collection when turbidity values remain within 10% (or within 1 NTU if the turbidity reading is less than 10 NTU), the specific conductance and temperature values remain within 3%, ORP readings remain within ± 10 mV and pH remains within 0.1 units for three consecutive readings collected at 3- to 5-minute intervals (or other appropriate interval, alternate stabilization goals may exist in different geographic regions, consult the site-specific Work Plan for stabilization criteria). If the field indicator parameters do not stabilize within 1 hour of the start of purging, but the groundwater turbidity is

below the goal of 50 NTU and the values for all other parameters are within 10%, the well can be sampled. If the parameters have stabilized but the turbidity is not in the range of the 50 NTU goal, the pump flow rate should be decreased to a minimum rate of 100 mL/min to reduce turbidity levels as low as possible. Dissolved oxygen is extremely susceptible to various external influences (including temperature or the presence of bubbles on the DO meter); care should be taken to minimize the agitation or other disturbance of water within the flow-through cell while collecting these measurements. If air bubbles are present on the DO probe or in the discharge tubing, remove them before taking a measurement. If dissolved oxygen values are not within acceptable range for the temperature of groundwater (Attachment 1), then again check for and remove air bubbles on probe before re-measuring. If the dissolved oxygen value is 0.00 or less, then the meter should be serviced and re-calibrated. If the dissolved oxygen values are above possible results, then the meter should be serviced and re-calibrated.

During extreme weather conditions, stabilization of field indicator parameters may be difficult to obtain. Modifications to the sampling procedures to alleviate these conditions (e.g., measuring the water temperature in the well adjacent to the pump intake) will be documented in the field notes. If other field conditions exist that preclude stabilization of certain parameters, an explanation of why the parameters did not stabilize will also be documented in the field logbook.

7. Complete the sample label(s) and cover the label(s) with clear packing tape to secure the label onto the container.

8. After the indicator parameters have stabilized, collect groundwater samples by diverting flow out of the unfiltered discharge tubing into the appropriate labeled sample container. If a flow-through analytical cell is being used to measure field parameters, the flow-through cell should be disconnected after stabilization of the field indicator parameters and prior to groundwater sample collection. Under no circumstances should analytical samples be collected from the discharge of the flow-through cell. When the container is full, tightly screw on the cap. Samples should be collected in the following order: VOCs, TOC, SVOCs, metals and cyanide, and others (or other order as defined in the site-specific Work Plan).

9. If sampling for total and filtered metals and/or PCBs, a filtered and unfiltered sample will be collected. Install an in-line, disposable 0.45-micron particle filter on the discharge tubing after the appropriate unfiltered groundwater sample has been collected. Continue to run the pump until an initial volume of “flush” water has been run through the filter in accordance with the manufacturer’s directions (generally 100 to 300 mL). Collect filtered groundwater sample by diverting flow

out of the filter into the appropriately labeled sample container. When the container is full, tightly screw on the cap.

10. Secure with packing material and store at 4°C in an insulated transport container provided by the laboratory.

11. Record on the groundwater sampling log or bound field logbook the time sampling procedures were completed, any pertinent observations of the sample (e.g., physical appearance, and the presence or lack of odors or sheens), and the values of the stabilized field indicator parameters as measured during the final reading during purging (Attachment 2 – Example Sampling Log).

12. Turn off the pump and air compressor or close the gas cylinder valve if using a bladder pump set-up. Slowly remove the pump, tubing, lines, and safety cable from the well. Do not allow the tubing or lines to touch the ground or any other surfaces which could contaminate them. .

13. If tubing is to be dedicated to a well, it should be folded to a length that will allow the well to be capped and also facilitate retrieval of the tubing during later sampling events. A length of rope or string should be used to tie the tubing to the well cap. Alternatively, if tubing and safety line are to be saved and reused for sampling the well at a later date they may be coiled neatly and placed in a clean plastic bag that is clearly labeled with the well ID. Make sure the bag is tightly sealed before placing it in storage.

14. Secure the well and properly dispose of personal protective equipment (PPE) and disposable equipment.

15. Complete the procedures for packaging, shipping, and handling with associated chain-of-custody.

16. Complete decontamination procedures for flow-through analytical cell and submersible or bladder pump, as appropriate.

17. At the end of the day, perform calibration check of field instruments.

If it is not technically feasible to use the low-flow sampling method, purging and sampling of monitoring wells may be conducted using the bailer method as outlined below:

1. Don appropriate PPE (as required by the HASP).

2. Place plastic sheeting around the well.

3. Clean sampling equipment.

4. Open the well cover while standing upwind of the well. Remove well cap and place on the plastic sheeting. Insert PID probe approximately 4 to 6 inches into the casing or the well headspace and cover with gloved hand. Record the PID reading in the field log. If the well headspace reading is less than 5 PID units, proceed; if the headspace reading is greater than 5 PID units, screen the air within the breathing zone. If the breathing zone reading is less than 5 PID units, proceed. If the PID reading in the breathing zone is above 5 PID units, move upwind from well for 5 minutes to allow the volatiles to dissipate. Repeat the breathing zone test. If the reading is still above 5 PID units, don appropriate respiratory protection in accordance with the requirements of the HASP. Record all PID readings. For wells that are part of the regular weekly monitoring program and prior PID measurements have not resulted in a breathing zone reading above 5 PID units, PID measurements will be taken monthly.

5. Measure the depth to water and determine depth of well by examining drilling log data or by direct measurement. Calculate the volume of water in the well (in gallons) by using the length of the water column (in feet), multiplying by 0.163 for a 2-inch well or by 0.653 for a 4-inch well. For other well diameters, use the formula:

   Volume (in gallons) = π TIMES well radius (in feet) squared TIMES length of water column (in feet) TIMES 7.481 (gallons per cubic foot)

6. Measure a length of rope or twine at least 10 feet greater than the total depth of the well. Secure one end of the rope to the well casing and secure the other end to the bailer. Test the knots and make sure the rope will not loosen. Check bailers so that all parts are intact and will not be lost in the well.

7. Lower bailer into well and remove one well volume of water. Contain all water in appropriate containers.

8. Monitor the field indicator parameters (e.g., turbidity, temperature, specific conductance, and pH). Measure field indicator parameters using a clean container such as a glass beaker or sampling cups provided with the instrument. Record field indicator parameters on the groundwater sampling log.

9. Repeat Steps 7 and 8 until three or four well volumes have been removed. Examine the field indicator parameter data to determine if the parameters have stabilized. The well is considered stabilized and ready for sample collection when turbidity values remain within 10% (or within 1 NTU if the turbidity reading is less than 10 NTU), the specific conductance and temperature values remain

within 3%, and pH remains within □0.1 units for three consecutive readings collected once per well volume removed.

10. If the field indicator parameters have not stabilized, remove a maximum of five well volumes prior to sample collection. Alternatively, five well volumes may be removed without measuring the field indicator parameters.

11. If the recharge rate of the well is very low, wells screened across the water table may be bailed dry and sampling should commence as soon as the volume in the well has recovered sufficiently to permit collection of samples. For wells screened entirely below the water table, the well should only be bailed down to a level slightly higher than the bentonite seal above the well screen. The well should not be bailed completely dry, to maintain the integrity of the seal. Sampling should commence as soon as the well volume has recovered sufficiently to permit sample collection.

12. Following purging, allow water level in well to recharge to a sufficient level to permit sample collection.

13. Complete the sample label and cover the label with clear packing tape to secure the label onto the container.

14. Slowly lower the bailer into the screened portion of the well and carefully retrieve a filled bailer from the well causing minimal disturbance to the water and any sediment in the well.

15. The sample collection order (as appropriate) will be as follows:

    a. VOCs;

    b TOC;

    c. SVOCs;

    d. metals and cyanide; and

    e. others.

16. When sampling for volatiles, collect water samples directly from the bailer into 40-mL vials with Teflon®-lined septa.

17. For other analytical samples, remove the cap from the large glass mixing container and slowly empty the bailer into the large glass mixing container. The

sample for dissolved metals and/or filtered PCBs should either be placed directly from the bailer into a pressure filter apparatus or pumped directly from the bailer with a peristaltic pump, through an in-line filter, into the pre-preserved sample bottle.

18. Continue collecting samples until the mixing container contains a sufficient volume for all laboratory samples.

19. Mix the entire sample volume with the Teflon® stirring rod and transfer the appropriate volume into the laboratory jar(s). Secure the sample jar cap(s) tightly.

20. If sampling for total and filtered metals and/or PCBs, a filtered and unfiltered sample will be collected. Sample filtration for the filtered sample will be performed in the field using a peristaltic pump prior to preservation. Install new medical-grade silicone tubing in the pump head. Place new Teflon® tubing into the sample mixing container and attach to the intake side of pump tubing. Attach (clamp) a new 0.45-micron filter (note the filter flow direction). Turn the pump on and dispense the filtered liquid directly into the laboratory sample bottles.

21. Secure with packing material and store at 4°C in an insulated transport container provided by the laboratory.

22. After sample containers have been filled, remove one additional volume of groundwater. Measure the pH, temperature, turbidity, and conductivity. Record on the groundwater sampling log or bound field logbook the time sampling procedures were completed, any pertinent observations of the sample (e.g., physical appearance, and the presence or lack of odors or sheens), and the values of the field indicator parameters.

23. Remove bailer from well, secure well, and properly dispose of PPE and disposable equipment.

24. If a bailer is to be dedicated to a well, it should be secured inside the well above the water table, if possible. Dedicated bailers should be tied to the well cap so that inadvertent loss of the bailer will not occur when the well is opened.

25. Complete the procedures for packaging, shipping, and handling with associated chain-of-custody.

VII. Waste Management

Materials generated during groundwater sampling activities, including disposable equipment, will be placed in appropriate containers. Containerized waste will be disposed of by the client consistent with the procedures identified in the HASP.

VIII. Data Recording and Management

Initial field logs and chain-of-custody records will be transmitted to the ARCADIS PM at the end of each day unless otherwise directed by the PM. The groundwater team leader retains copies of the groundwater sampling logs.

IX. Quality Assurance

In addition to the quality control samples to be collected in accordance with this SOP, the following quality control procedures should be observed in the field:

- Collect samples from monitoring wells in order of increasing concentration, to the extent known based on review of historical site information if available.
- Equipment blanks should include the pump and tubing (if using disposable tubing) or the pump only (if using tubing dedicated to each well).
- Collect equipment blanks after wells with higher concentrations (if known) have been sampled.
- Operate all monitoring instrumentation in accordance with manufacturer's instructions and calibration procedures. Calibrate instruments at the beginning of each day and verify the calibration at the end of each day. Record all calibration activities in the field notebook.
- Clean all groundwater sampling equipment prior to use in the first well and after each subsequent well using procedures for equipment decontamination.

X. References

United States Environmental Protection Agency (USEPA). 1986. RCRA Groundwater Monitoring Technical Enforcement Guidance Document (September 1986).

USEPA Region II. 1998. *Ground Water Sampling Procedure Low Stress (Low Flow) Purging and Sampling*.

USEPA. 1991. Handbook Groundwater, Volume II Methodology, Office of Research and Development, Washington, DC. USEPN62S, /6-90/016b (July, 1991).

U.S. Geological Survey (USGS). 1977. National Handbook of Recommended Methods for Water-Data Acquisition: USGS Office of Water Data Coordination. Reston, Virginia.

Attachment 1

Groundwater Sampling Log

Attachment 2

Oxygen Solubility in Fresh Water

Temperature (degrees C)	**Dissolved Oxygen** (mg/L)
0	14.6
1	14.19
2	13.81
3	13.44
4	13.09
5	12.75
6	12.43
7	12.12
8	11.83
9	11.55
10	11.27
11	11.01
12	10.76
13	10.52
14	10.29
15	10.07
16	9.85
17	9.65
18	9.45
19	9.26
20	9.07
21	8.9
22	8.72
23	8.56
24	8.4
25	8.24
26	8.09
27	7.95
28	7.81
29	7.67
30	7.54
31	7.41
32	7.28
33	7.16
34	7.05
35	6.93

Reference: Vesilind, P.A., *Introduction to Environmental Engineering*, PWS Publishing Company, Boston, 468 pages (1996).

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Soil Description

Rev. #: 0

Rev Date: May 20, 2008

Approval Signatures

Prepared by: _____ Date: 5/22/08

Reviewed by: _____ Date: 5/22/08
(Technical Expert)

I. Scope and Application

This ARCADIS standard operating procedure (SOP) describes proper soil description procedures. This SOP should be followed for all unconsolidated material unless there is an established client-required specific SOP or regulatory-required specific SOP. In cases where there is a required specific SOP, it should be followed and should be referenced and/or provided as an appendix to reports that include soil classifications and/or boring logs. When following a required non-ARCADIS SOP, additional information required by this SOP should be included in field notes with client approval.

This SOP has been developed to emphasize field observation and documentation of details required to:

- make hydrostratigraphic interpretations guided by depositional environment/geologic settings;

- provide information needed to understand the distribution of constituents of concern; properly design wells, piezometers, and/or additional field investigations; and develop appropriate remedial strategies.

This SOP incorporates elements from various standard systems such as ASTM D2488-06, Unified Soil Classification System, Burmister and Wentworth. However, none of these standard systems focus specifically on contaminant hydrogeology and remedial design. Therefore, although each of these systems contain valuable guidance and information related to correct descriptions, strict application of these systems can omit information critical to our clients and the projects that we perform.

This SOP does not address details of health and safety; drilling method selection; boring log preparation; sample collection; or laboratory analysis. Refer to other ARCADIS SOPS, the project work plans including the quality assurance project plan, sampling plan, and health and safety plan (HASP), as appropriate.

II. Personnel Qualifications

Soil descriptions will be completed only by persons who have been trained in ARCADIS soil description procedures. Field personnel will complete training on the ARCADIS soil description SOP in the office and/or in the field under the guidance of an experienced field geologist. For sites where soil descriptions have not previously been well documented, soil descriptions should be performed only by trained persons with a degree in geology or a geology-related discipline.

III. Equipment List

The following equipment should be taken to the field to facilitate soil descriptions:

- field book, field forms or PDA to record soil descriptions;
- field book for supplemental notes;
- this SOP for Soil Descriptions and any project-specific SOP (if required);
- field card showing Wentworth scale;
- Munsell® soil color chart;
- tape measure divided into tenths of a foot;
- stainless steel knife or spatula;
- hand lens;
- water squirt bottle;
- jar with lid;
- personal protective equipment (PPE), as required by the HASP; and
- digital camera.

IV. Cautions

Drilling and drilling-related hazards including subsurface utilities are discussed in other SOPs and site-specific HASPs and are not discussed herein.

Soil samples may contain hazardous substances that can result in exposure to persons describing soils. Routes for exposure may include dermal contact, inhalation and ingestion. Refer to the project specific HASP for guidance in these situations.

V. Health and Safety Considerations

Field activities associated with soil sampling and description will be performed in accordance with a site-specific HASP, a copy of which will be present on site during such activities. Know what hazardous substances may be present in the soil and understand their hazards. Always avoid the temptation to touch soils with bare hands, detect odors by placing soils close to your nose, or tasting soils.

VI. Procedure

1. Select the appropriate sampling method to obtain representative samples in accordance with the selected sub-surface exploration method, e.g. split-spoon or Shelby sample for hollow-stem drilling, Lexan or acetate sleeves for dual-tube direct push, etc.

2. Proceed with field activities in required sequence. Although completion of soil descriptions is often not the first activity after opening sampler, identification of stratigraphic changes is often necessary to select appropriate intervals for field screening and/or selection of laboratory samples.

3. Examine all of each individual soil sample (this is different than examining each sample selected for laboratory analysis), and record the following for each stratum:

- depth interval;
- principal component with descriptors, as appropriate;
- amount and identification of minor component(s) with descriptors as appropriate;
- moisture;
- consistency/density;
- color; and
- additional description or comments (recorded as notes).

The above is described more fully below.

DEPTH

To measure and record the depth below ground level (bgl) of top and bottom of each stratum, the following information should be recorded.

1. Measured depth to the top and bottom of sampled interval. Use starting depth of sample based upon measured tool length information and the length of sample interval.

2. Length of sample recovered, not including slough (material that has fallen into hole from previous interval), expressed as fraction with length of recovered sample as numerator over length of sampled interval as denominator (e.g. 14/24 for 14 inches recovered from 24-inch sampling interval that had 2 inches of slough discarded).

3. Thickness of each stratum measured sequentially from the top of recovery to the bottom of recovery.

4. Any observations of sample condition or drilling activity that would help identify whether there was loss from the top of the sampling interval, loss from the bottom of the sampling interval, or compression of the sampling interval. Examples: 14/24, gravel in nose of spoon; or 10/18 bottom 6 inches of spoon empty.

DETERMINATION OF COMPONENTS

Obtain a representative sample of soil from a single stratum. If multiple strata are present in a single sample interval, each stratum should be described separately. More specifically, if the sample is from a 2-foot long split-spoon where strata of coarse sand, fine sand and clay are present, then the resultant description should be of the three individual strata unless a combined description can clearly describe the interbedded nature of the three strata. Example: Fine Sand with interbedded lenses of Silt and Clay, ranging between 1 and 3 inches thick.

Identify principal component and express volume estimates for minor components on logs using the following standard modifiers.

Modifier	Percent of Total Sample (by volume)
and	36 - 50
some	21 - 35
little	10 - 20
trace	<10

Determination of components is based on using the Udden-Wentworth particle size classification (see below) and measurement of the average grain size diameter. Each size grade or class differs from the next larger grade or class by a constant ratio of ½. Due to visual limitations, the finer classifications of Wentworth's scale cannot be distinguished in the field and the subgroups are not included. Visual determinations in the field should be made carefully by comparing the sample to the field gauge card that shows Udden-Wentworth scale or by measuring with a ruler. Use of field sieves s

recommended to assist in estimating percentage of coarse grain sizes. Settling test or wash method (Appendix X4 of ASTM D2488) is recommended for determining presence and estimating percentage of clay and silt.

Udden-Wenworth Scale Modified ARCADIS, 2008			
Size Class	Millimeters	Inches	Standard Sieve #
Boulder	256 – 4096	10.08+	
Large cobble	128 - 256	5.04 -10.08	
Small cobble	64 - 128	2.52 – 5.04	
Very large pebble	32 – 64	0.16 - 2.52	
Large pebble	16 – 32	0.63 – 1.26	
Medium pebble	8 – 16	0.31 – 0.63	
Small pebble	4 – 8	0.16 – 0.31	No. 5 +
Granule	2 – 4	0.08 – 0.16	No.5 – No.10
Very coarse sand	1 -2	0.04 – 0.08	No.10 – No.18
Coarse sand	½ - 1	0.02 – 0.04	No.18 - No.35
Medium sand	¼ - ½	0.01 – 0.02	No.35 - No.60
Fine sand	1/8 -¼	0.005 – 0.1	No.60 - No.120
Very fine sand	1/16 – 1/8	0.002 – 0.005	No. 120 – No. 230
Silt (subgroups not included)	1/256 – 1/16	0.0002 – 0.002	Not applicable (analyze by pipette or hydrometer)
Clay (subgroups not included	1/2048 – 1/256	.00002 – 0.0002	

Identify components as follows. Remove particles greater than very large pebbles (64-mm diameter) from the soil sample. Record the volume estimate of the greater than very large pebbles. Examine the sample fraction of very large pebbles and smaller particles and estimate the volume percentage of the pebbles, granules, sand, silt and clay. Use the jar method, visual method, and/or wash method (Appendix X4 of ASTM D2488) to estimate the volume percentages of each category.

Determination of actual dry weight of each Udden-Wentworth fraction requires laboratory grain-size analysis using sieve sizes corresponding to Udden-Wentworth fractions and is highly recommended to determine grain-size distributions for each hydrostratigraphic unit.

Lab or field sieve analysis is advisable to characterize the variability and facies trends within each hydrostratigraphic unit. Field sieve-analysis can be performed on selected samples to estimate dry weight fraction of each category using ASTM D2488 Standard Practice for Classification of Soils for Engineering Purposes as guidance, but replace required sieve sizes with the following Udden-Wentworth set: U.S. Standard sieve mesh sizes 6; 12; 20; 40; 70; 140; and 270 to retain pebbles; granules; very coarse sand; coarse sand; medium sand; fine sand; and very fine sand, respectively.

PRINCIPAL COMPONENT

The principal component is the size fraction or range of size fractions containing the majority of the volume. Examples: the principal component in a sample that contained 55% pebbles would be “Pebbles”; or the principal component in a sample that was 20% fine sand, 30% medium sand and 25% coarse sand would be “Fine to coarse Sand” or for a sample that was 40% silt and 45% clay the principal component would be “Clay and Silt”.

Include appropriate descriptors with the principal component. These descriptors vary for different particle sizes as follows.

Angularity – Describe the angularity for very coarse sand and larger particles in accordance with the table below (ASTM D-2488-06). Figures showing examples of angularity are available in ASTM D-2488-06 and the ARCADIS Soil Description Field Guide.

Description	Criteria
Angular	Particles have sharp edges and relatively plane sides with unpolished surfaces.
Subangular	Particles are similar to angular description but have rounded edges.
Subrounded	Particles have nearly plane sides but have well-rounded corners and edges.
Rounded	Particles have smoothly curved sides and no edges.

Plasticity – Describe the plasticity for silt and clay based on observations made during the following test method (ASTM D-2488-06).

- As in the dilatancy test below, select enough material to mold into a ball about ½ inch (12 mm) in diameter. Mold the material, adding water if necessary, until it has a soft, but not sticky, consistency.

- Shape the test specimen into an elongated pat and roll by hand on a smooth surface or between the palms into a thread about 1/8 inch (3 mm) in diameter. (If the sample is too wet to roll easily, it should be spread into a thin layer and allowed to lose some water by evaporation.) Fold the sample threads and reroll repeatedly until the thread crumbles at a diameter of about 1/8 inch. The thread will crumble when the soil is near the plastic limit.

Description	Criteria
Nonplastic	A $^{1}/_{8}$ inch (3 mm) thread cannot be rolled at any water content.
Low	The thread can barely be rolled and the lump cannot be formed when drier than the plastic limit.
Medium	The thread is easy to roll and not much time is required to reach the plastic limit. The thread cannot be rerolled after reaching the plastic limit. The lump crumbles when drier than the plastic limit.
High	It takes considerable time rolling and kneading to reach the plastic limit. The thread can be rolled several times after reaching the plastic limit. The lump can be formed without crumbling when drier than the plastic limit

Dilatancy – Describe the dilatancy for silt and silt-sand mixtures using the following field test method (ASTM D-2488-06).

- From the specimen select enough material to mold into a ball about ½ inch (12 mm) in diameter. Mold the material adding water if necessary, until it has a soft, but not sticky, consistency.
- Smooth the ball in the palm of one hand with a small spatula.
- Shake horizontally, striking the side of the hand vigorously with the other hand several times.
- Note the reaction of water appearing on the surface of the soil.
- Squeeze the sample by closing the hand or pinching the soil between the fingers, and not the reaction as none, slow, or rapid in accordance with the table below. The reaction is the speed with which water appears while shaking and disappears while squeezing.

Description	Criteria
None	No visible change in the specimen.
Slow	Water appears slowly on the surface of the specimen during shaking and does not disappear or disappears slowly upon squeezing.
Rapid	Water appears quickly on the surface of the specimen during shaking and disappears quickly upon squeezing.

MINOR COMPONENT(S)

The minor component(s) are the size fraction(s) containing less than 50% volume. Example: the identified components are estimated to be 60% medium sand to granules, 25 % silt and clay; 15 % pebbles – there are two identified minor components: silt and clay; and pebbles.

Include a standard modifier to indicate percentage of minor components (see Table on Page 5) and the same descriptors that would be used for a principal component. Plasticity should be provided as a descriptor for the silt and clay. Dilatancy should be provided for silt and silt-sand mixtures. Angularity should be provided as a descriptor for pebbles and coarse sand. For the example above, the minor constituents with

modifiers could be: some silt and clay, low plasticity; little medium to large pebbles, sub-round.

SORTING

Sorting is the opposite of grading, which is a commonly used term in the USCS or ASTM methods to describe the uniformity of the particle size distribution in a sample. Well-sorted samples are poorly graded and poorly sorted samples are well graded. ARCADIS prefers the use of sorting for particle size distributions and grading to describe particle size distribution trends in the vertical profile of a sample or hydrostratigraphic unit because of the relationship between sorting and the energy of the depositional process. For soils with sand-sized or larger particles, sorting should be determined as follows:

- Well sorted – the range of particle sizes is limited (e.g. the sample is comprised of predominantly one or two grain sizes)

- Poorly sorted – a wide range of particle sizes are present

You can also use sieve analysis to estimate sorting from a sedimentological perspective; sorting is the statistical equivalent of standard deviation. Smaller standard deviations correspond to higher degree of sorting (see Remediation Hydraulics, 2008).

MOISTURE

Moisture content should be described for every sample since increases or decreases in water content is critical information. Moisture should be described in accordance with the table below (percentages should not be used unless determined in the laboratory).

Description	Criteria
Dry	Absence of moisture, dry to touch, dusty.
Moist	Damp but no visible water.
Wet (Saturated)	Visible free water, soil is usually below the water table.

CONSISTENCY or DENSITY

This can be determined by standard penetration test (SPT) blow counts (ASTM D-1586) or field tests in accordance with the tables below. For SPT blow counts the N-value is used. The N-value is the blows per foot for the 6" to 18" interval. Example: for 24-inch spoon, recorded blows per 6-inch interval are: 4/6/9/22. Since the second interval is 6" to12", the third interval is 12" to 18", the N value is 6+9, or 15. Fifty blow counts for less than 6 inches is considered refusal.

Fine-grained soil – Consistency

Description	Criteria
Very soft	N-value < 2 or easily penetrated several inches by thumb.
Soft	N-value 2-4 or easily penetrated one inch by thumb.
Medium stiff	N-value 9-15 or indented about ¼ inch by thumb with great effort.
Very stiff	N-value 16-30 or readily indented by thumb nail.
Hard	N-value > than 30 or indented by thumbnail with difficulty

Coarse-grained soil – Density

Description	Criteria
Very loose	N-value 1- 4
Loose	N-value 5-10
Medium dense	N-value 11-30
Dense	N-value 31- 50
Very dense	N-value >50

COLOR

Color should be described using simple basic terminology and modifiers based on the Munsell system. Munsell alpha-numeric codes are required for all samples. If the sample contains layers or patches of varying colors this should be noted and all representative colors should be described. The colors should be described for moist

samples. If the sample is dry it should be wetted prior to comparing the sample to the Munsell chart.

ADDITIONAL COMMENTS (NOTES)

Additional comments should be made where observed and should be presented as notes with reference to a specific depth interval(s) to which they apply. Some of the significant information that may be observed includes the following.

- **Odor** - You should not make an effort to smell samples by placing near your nose since this can result in unnecessary exposure to hazardous materials. However, odors should be noted if they are detected during the normal sampling procedures. Odors should be based upon descriptors such as those used in NIOSH “Pocket Guide to Chemical Hazards”, e.g. “pungent” or “sweet” and should not indicate specific chemicals such as “phenol-like” odor or “BTEX” odor.

- Structure

- Bedding planes (laminated, banded, geologic contacts)

- Presence of roots, root holes, organic material, man-made materials, minerals, etc.

- Mineralogy

- Cementation

- NAPL presence/characteristics, including sheen (based on client-specific guidance)

- Reaction with HCl (typically used only for special soil conditions)

- Origin, if known (capital letters: LACUSTRINE; FILL; etc.)

EXAMPLE DESCRIPTIONS

51.4 to 54.0' Clay, some silt, medium to high plasticity; trace small to large pebbles, subround to subangular up to 2" diameter; moist; stiff; dark grayish brown (10YR 4/2) NOTE: Lacustrine; laminated 0.01 to 0.02 feet thick, laminations brownish yellow (10 YR 4/3).

32.5 to 38.0' Sand, medium to Pebbles, coarse; sub-round to sub-angular; trace silt; poorly sorted; wet; grayish brown (10YR5/2). NOTE: sedimentary, igneous and metamorphic particles.

Unlike the first example where a density of cohesive soils could be estimated, this rotosonic sand and pebble sample was disturbed during drilling (due to vibrations in a loose Sand and Pebble matrix) so no density description could be provided. Neither sample had noticeable odor so odor comments were not included.

The standard generic description order is presented below.

- Depth

- Principal Components
    - Angularity for very coarse sand and larger particles
    - Plasticity for silt and clay
    - Dilatancy for silt and silt-sand mixtures
- Minor Components
- Sorting
- Moisture
- Consistency or Density
- Color
- Additional Comments

VII. Waste Management

Project-specific requirements should be identified and followed. The following procedures, or similar waste management procedures are generally required.

Water generated during cleaning procedures will be collected and contained onsite in appropriate containers for future analysis and appropriate disposal. PPE (such as gloves, disposable clothing, and other disposable equipment) resulting from personnel cleaning procedures and soil sampling/handling activities will be placed in plastic bags. These bags will be transferred into appropriately labeled 55-gallon drums or a covered roll-off box for appropriate disposal.

Soil materials will be placed in sealed 55-gallon steel drums or covered roll-off boxes and stored in a secured area. Once full, the material will be analyzed to determine the appropriate disposal method.

VIII. Data Recording and Management

Upon collection of soil samples, the soil sample should be logged on a standard boring log and/or in the field log book depending on Data Quality Objectives (DQOs) for the task/project. Two examples of standard boring logs are presented below.

The general scheme for soil logging entries is presented above; however, depending on task/project DQOs, specific logging entries that are not applicable to task/project goals may be omitted at the project manager's discretion. In any case, use of a consistent logging procedure is required.

Completed logs and/or logbook will be maintained in the task/project field records file. Digital photographs of typical soil types observed at the site and any unusual features should be obtained whenever possible. All photographs should include a ruler or common object for scale. Photo location, depth and orientation must be recorded in the daily log or log book and a label showing this information in the photo is useful.

ARCADIS Page _____ of _____

Sample Log

Well/Boring _____ Project Name and No. _____

Site Location _____ Drilling Started _____ Drilling Completed _____

Total Depth Drilled _____ feet Hole Diameter _____ inches Sampling Interval _____ feet

Length and Diameter of Sampling Device _____ Type of Sampling Device _____

Drilling Method _____ Drilling Fluid Used _____

Drilling Contractor _____ Driller _____ Helper _____

Prepared By _____ Hammer Weight _____ Hammer Drop _____ inches

Sample Depth (feet below land surface) From	To	Sample Recovery (feet)	Time/Hydraulic Pressure or Blows per 6 inches	Sample Description	PID (ppm)

IX. Quality Assurance

Soil descriptions should be completed only by appropriately trained personnel. Descriptions should be reviewed by an experienced field geologist for content, format and consistency. Edited boring logs should be reviewed by the original author to assure that content has not changed.

X. References

ARCADIS Soil Description Field Guide, 2008 (in progress)

Munsell® Color Chart – available from Forestry Suppliers, Inc.- Item 77341 "Munsell® Color Soil Color Charts

Field Gauge Card that Shows Udden-Wentworth scale – available from Forestry Suppliers, Inc. – Item 77332 "Sand Grain Sizing Folder"

ASTM D-1586, Test Method for Penetration Test and Split-Barrel Sampling of Soils

ASTM D-2488-00, Standard Practice for Description and Identification of Soils (Visual-Manual Procedure)

United States Bureau of Reclamation. Engineering Geology Field Manual. United States Department of Interior, Bureau of Reclamation. http://www.usbr.gov/pmts/geology/fieldmap.htm

Petrology of Sedimentary Rocks, Robert L. Folk, 1980, p. 1-48

NIOSH Pocket Guide to Chemical Hazards

Remediation Hydraulics, Fred C. Payne, Joseph A. Quinnan, and Scott T. Potter, 2008, p 59-63

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Drilling Procedures for Collecting and Screening of Soil Samples

Rev. #: 2

Rev Date: March 24, 2008

Approval Signatures

Prepared by: _____ Date: _____

Reviewed by: _____ Date: _____
(Technical Expert)

I. Scope and Application

This Standard Operating Procedure (SOP) describes the collection and field screening of soils samples using a truck- or track-mounted drill rig using the hollow-stem auger, drive and wash, or mud/water rotary drilling methods after completion of utility clearance procedures. Field screening of the soil samples upon collection may be conducted using a photoionization detector (PID) and/or a flame ionization detector (FID). These instruments are used to measure relative concentrations of volatile organic compounds (VOCs) for the selection of samples for further laboratory or field analysis.

II. Personnel Qualifications

The Project Manager (a qualified geologist, environmental scientist, or engineer) will identify the appropriate soil boring locations, depth and soil sample intervals in a written plan.

Personnel responsible for overseeing drilling operations must have at least 16 hours of prior training overseeing drilling activities with an experienced geologist, environmental scientist, or engineer with at least 2 years of prior experience.

III. Equipment List

- appropriate health and safety equipment;
- PID and FID;
- air-tight sample containers, 8-oz. glass Mason jars or driller's jars, and 40 mL headspace vials;
- aluminum foil;
- extra batteries for the PID;
- calibration gases and regulators;
- spare filter cartridges;
- field notebook and appropriate screening forms; and
- indelible ink pens.

IV. Cautions

Avoid using drilling fluids or materials that could impact groundwater or soil quality, or could be incompatible with the subsurface conditions.

Water used for drilling and sampling of soil or bedrock, decontamination of drilling/sampling equipment, or grouting boreholes upon completion will be of a quality acceptable for project objectives. Testing of water supply should be considered.

Specifications of materials used for backfilling bore hole will be obtained, reviewed and approved to meet project quality objectives.

V. Health and Safety Considerations

To be completed by Preparer and reviewed by Technical Expert.

VI. Procedure

All soil samples will be field screened upon collection with a PID for a relative measure of the total VOCs. Initial PID readings will be recorded in the surface log or field notebook. The true soil sample will be separated from the wash material (if any) by using disposable gloves and a pre-cleaned stainless steel spoon. A representative portion of the sample will be placed in a pre-cleaned air-tight 8-ounce and 40 mL sampling container (as quickly as possible to avoid loss of VOCs), filling the containers half full to allow for the accumulation of vapors above the soil. For the glass 8-ounce jar, an aluminum foil seal will be placed between the glass and metal cap and the cap will be screwed on tightly. For the 40-mL vial, a Teflon septum cap will be placed between the glass and the plastic threaded lid. The sample containers will be stored in a cooler chilled to approximately 4ºC until screening.

Upon completion of sample collection, the headspace of the 8-ounce sample jars will be measured using a PID as follows:

1. Samples will be taken to a warm work space and allowed to equilibrate to room temperature for at least one hour.

2. Prior to measuring the soil vapor headspace concentration, the 8-ounce jar will be shaken.

3. The headspace of the sample will then be measured directly from the 8-ounce sample container with the PID by piercing the aluminum foil seal with the probe

of the PID and measuring the relative concentration of VOCs in the headspace of the soil sample. The initial (peak) reading must be recorded.

Upon completion of sample collection, the headspace of the 40 mL sample vial will be measured using an FID as follows:

1. The 40 mL vials will be placed in a hot water bath for an equal and pre-determined period of time (estimated at 15 minutes).

2. A gas-tight syringe will be used to pierce the teflon septum to extract a volume of headspace (.1 to .5 mL) from the vial.

3. The headspace sample will then be injected directly into the FID of an OVA with a GC attachment. The septum injection port of the OVA should be set on the total field mode. The reading will be recorded on the field screening forms and/or in the field notebook. If a peak is noted in total field mode, a duplicate sample will be injected with the OVA in GC mode and recorded on the strip chart recorder. The retention time will be noted on the GC strip chart, along with the date, time of injection, and the sample identification.

The PID will be calibrated to a benzene-related compound (isobutylene). The FID will be calibrated to methane. The FID/PID must be calibrated according to the manufacturer's specifications at a minimum frequency of once per day prior to collecting FID/PID readings. The time, date, and calibration procedure must be clearly documented in the field notebook and/or the calibration log book. If at any time the FID/PID results appear erratic or inconsistent with field observations, then the unit will be recalibrated. If calibration is difficult to achieve, then the PID's lamp should be checked for dirt or moisture and cleaned. During humid or wet conditions, the unit should be calibrated on a more frequent basis as determined by field personnel. In addition, a blank and a field duplicate will be performed every 10 samples. Maintenance and calibration records will be kept as part of the field quality assurance program.

Sampling for Laboratory Analysis Procedures

Samples will be selected for laboratory analysis based on:

1. Their position in relation to identified source areas;

2. The visual presence of source residues;

3. The relative levels of total VOCs based on field screening measurements; and/or

4. The judgment of the field coordinator.

Samples designated for laboratory analysis will be placed in the appropriate containers. Sample containers for VOC analysis will be filled first. Next, a sufficient amount of the remaining soil will be homogenized by mixing in a stainless steel tray with a clean stainless steel trowel. Then sample containers will be filled for SVOCs, metals, cyanide, and, lastly, for PCBs. For every 20 soil samples obtained, a duplicate soil sample will be obtained by splitting the sample into two sets of sample containers.

VII. Waste Management

Soil cuttings brought to the ground surface during the drilling activities will be handled based on the location of the boring, a visual assessment of the soil, and PID field screening. Soil cuttings from borings located on asphalt or landscaped ground surfaces will be contained in labeled and dated Department of Transportation (DOT)-approved 55-gallon drums. Soil cuttings from borings drilled within the SWMU/disposal areas will be examined and screened with a PID. Soil cuttings will be discarded at ground surface if the soil cuttings consist of cover material above the SWMU/disposal area and no relatively elevated PID readings are measured. If wastes are encountered in the SWMU/disposal area and/or relatively elevated PID readings are measured the soils will be contained in labeled and dated DOT-approved 55-gallon DOT drums.

VIII. Data Recording and Management

A field survey control program will be conducted by a qualified survey crew using standard instrument survey techniques to document boring locations.

IX. Quality Assurance

Equipment cleaning will occur prior to use on the site, between each drilling location, and upon completion of the drilling prior to leaving the site. All drilling equipment and associated tools including augers, drill rods, sampling equipment, wrenches, and any other equipment or tools that may have come in contact with the soils will be cleaned with high-pressure steam cleaning equipment using a tap water source. The drilling equipment will be cleaned after each boring in an area designated by the field coordinator or supervising geologist. Cleaning water will be contained within a water-tight, lined cleaning area. The solids collected on the floor of the cleaning area will be stored in separate labeled and dated DOT-approved 55-gallon drums.

X. References

To be completed by Preparer and reviewed by Technical Expert.

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Monitoring Well Development

Rev. #: 2.2

Rev. Date: March 22, 2010

Approval Signatures

Prepared by: _____ Date: 03/22/2010

Reviewed by: _____ Date: 03/22/2010
(Technical Expert)

I. Scope and Application

Monitoring wells (or piezometers, well points, or micro-wells) will be developed to clear them of fine-grained sediment to enhance the hydraulic connection between the well and the surrounding geologic formation. Development will be accomplished by evacuating well water by either pumping or bailing. Prior to pumping or bailing, the screened interval will be gently surged using a surge block, bailer, or inertia pump with optional surgeblock fitting as appropriate. Accumulated sediment in the bottom of the well (if present) will be removed by bailing with a bottom-loading bailer or via pumping using a submersible or inertia pump with optional surge-block fitting. Wells will also be gently brushed with a weighted brush to assist in removing loose debris, silt or flock attached to the inside of the well riser and/or screen prior to development. Pumping methods will be selected based on site-specific geologic conditions, anticipated well yield, water table depth, and groundwater monitoring objectives, and may include one or more of the following:

- submersible pump
- inertial pump (Waterra™ pump or equivalent)
- bladder pump
- peristaltic pump
- centrifugal pump

When developing a well using the pumping method, the pump (or, with inertial pumps, the tubing) is lowered to the screened portion of the well. During purging, the pump or tubing is moved up and down the screened interval until the well yields relatively clear water.

Submersible pumps have a motor-driven impeller that pushes the groundwater through discharge tubing to the ground surface. Inertial pumps have a check valve at the bottom of stiff tubing which, when operated up and down, lifts water to the ground surface. Bladder pumps have a bottom check valve and a flexible internal bladder that fills from below and is then compressed using pressurized air to force water out the top of the bladder through the discharge tubing to the ground surface. These three types of pumps have a wide range of applicability in terms of well depth and water depth.

Centrifugal and peristaltic pumps use atmospheric pressure to lift water from the well, and therefore can only be practically used where the depth to water is less than 25 feet.

II. Personnel Qualifications

Monitoring well development activities will be performed by persons who have been trained in proper well development procedures under the guidance of an experienced field geologist, engineer, or technician.

III. Equipment List

Materials for monitoring well development using a pump include the following:

- health and safety equipment, as required by the site Health and Safety Plan (HASP):
- cleaning equipment
- photoionization detector (PID) to measure headspace vapors
- pump
- polyethylene pump discharge tubing
- plastic sheeting
- power source (generator or battery)
- field notebook and/or personal digital assistant (PDA)
- graduated pails
- appropriate containers

- monitoring well keys
- water level indicator

Materials for monitoring well development using a bailer include the following:

- personal protective equipment (PPE) as required by the HASP
- cleaning equipment
- PID to measure headspace vapors
- bottom-loading bailer, sand bailer
- polypropylene or nylon rope
- plastic sheeting
- graduated pails
- appropriate containers
- keys to wells
- field notebook and/or PDA
- water level indicator
- weighted brush for well brushing

IV. Cautions

Where surging is performed to assist in removing fine-grained material from the sand pack, surging must be performed in a gentle manner. Excessive suction could promote fine-grained sediment entry into the outside of the sand pack from the formation.

Avoid using development fluids or materials that could impact groundwater or soil quality, or could be incompatible with the subsurface conditions.

In some cases it may be necessary to add potable water to a well to allow surging and development, especially for new monitoring wells installed in low permeability formations. Before adding potable water to a well, the Project Manager (PM) must be notified and the PM shall make the decision regarding the appropriateness and applicability of adding potable water to a well during well development procedures. If potable water is to be added to a well as part of development, the potable water source should be sampled and analyzed for constituents of concern, and the results evaluated by the PM prior to adding the potable water to the well. If potable water is added to a well for development purposes, at the end of development the well will be purged dry to remove the potable water, or if the well no longer goes dry then the well will be purged to remove at least three times the volume of potable water that was added.

V. Health and Safety Considerations

Field activities associated with monitoring well development will be performed in accordance with a site-specific HASP, a copy of which will be present on site during such activities.

VI. Procedure

The procedures for monitoring well development are described below. (Note: Steps 7, 8, and 10 can be performed at the same time using an inertial pump with a surge-block fitting.)

1. Don appropriate PPE (as required by the HASP).

2. Place plastic sheeting around the well.

3. Clean all equipment entering each monitoring well, except for new, disposable materials that have not been previously used.

4. Open the well cover while standing upwind of the well, remove well cap. Insert PID probe approximately 4 to 6 inches into the casing or the well headspace and cover with gloved hand. Record the PID reading in the field notebook. If the well headspace reading is less than 5 PID units, proceed; if the headspace reading is greater than 5 PID units, screen the air within the breathing zone. If the PID reading in the breathing zone is below 5 PID units, proceed. If the PID reading is above 5 PID units, move upwind from well for 5 minutes to allow the volatiles to dissipate. Repeat the breathing zone test. If the reading is still above 5 PID units, don the appropriate respiratory protection in accordance with the requirements of the HASP. Record all PID readings.

5. Obtain an initial measurement of the depth to water and the total well depth from the reference point at the top of the well casing. Record these measurements in the field log book.

6. Prior to redeveloping older wells that may contain solid particulate debris along the inside of the well casing and screen, gently lower and raise a weighted brush along the entire length of the well screen and riser to free and assist in removing loose debris, silt or flock. Perform a minimum of 4 “passes” along the screened and cased intervals of the well below the static water level in the well. Allow the resulting suspended material to settle for a minimum of one day prior to continuing with redevelopment activities.

7. Lower a surge block or bailer into the screened portion of the well. Gently raise and lower the surge block or bailer within the screened interval of the well to force water in and out of the screen slots and sand pack. Continue surging for 15 to 30 minutes.

8. Lower a bottom-loading bailer, submersible pump, or inertia pump tubing with check valve to the bottom of the well and gently bounce the bailer, pump, pump tubing on the bottom of the well to collect/remove accumulated sediment, if any. Remove and empty the bailer, if used. Repeat until the bailed/pumped water is free of excessive sediment and the bottom of the well feels solid. Alternatively, measurement of the well depth with a water level indicator can be used to verify that sediment and/or silt has been removed to the extent practicable, based on a comparison with the well installation log or previous measurement of total well depth.

9. After surging the well and removing excess accumulated sediment from the bottom of the well, re-measure the depth-to-water and the total well depth from the reference point at the top of the well casing. Record these measurements in the field log book.

10. Remove formation water by pumping or bailing. Where pumping is used, measure and record the pre-pumping water level. Operate the pump at a relatively constant rate. Measure the pumping rate using a calibrated container and stop watch, and record the pumping rate in the field log book. Measure and record the water level in the well at least

once every 5 minutes during pumping. Note any relevant observations in terms of water color, visual level of turbidity, sheen, odors, etc. Pump or bail until termination criteria specified in the Field Sampling Plan (FSP) are reached. Record the total volume of water purged from the well.

11. If the well goes dry, stop pumping or bailing. Note the time that the well went dry. After allowing the well to recover, note the time and depth to water. Resume pumping or bailing when sufficient water has recharged the well.

12. Contain all water in appropriate containers.

13. When complete, secure the lid back on the well.

14. Place disposable materials in plastic bags for appropriate disposal and decontaminate reusable, downhole pump components and/or bailer.

VII. Waste Management

Materials generated during monitoring well installation and development will be placed in appropriate labeled containers and disposed of as described in the Work Plan or Field Sampling Plan.

VIII. Data Recording and Management

Well development activities will be documented in a proper field notebook and/or PDA. Pertinent information will include personnel present on site; times of arrival and departure; significant weather conditions; timing of well development activities; development method(s); observations of purge water color, turbidity, odor, sheen, etc.; purge rate; and water levels before and during pumping.

IX. Quality Assurance

All reused, non-disposable, downhole well development equipment will be cleaned in accordance with the procedures outlined in the Field Equipment Cleaning-Decontamination SOP.

X. References

Not applicable.

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Monitoring Well Installation

Rev. #: 3

Rev Date: February 2, 2011

Approval Signatures

Prepared by: _____ Date: 2/2/2011

Reviewed by: _____ Date: 2/2/2011
(Technical Expert)

I. Scope and Application

The procedures set out herein are designed to produce standard groundwater monitoring wells suitable for: (1) groundwater sampling, (2) water level measurement, (3) bulk hydraulic conductivity testing of formations adjacent to the open interval of the well.

Monitoring well boreholes in unconsolidated (overburden) materials are typically drilled using the hollow-stem auger drilling method. Other drilling methods that are also suitable for installing overburden monitoring wells, and are sometimes necessary due to site-specific geologic conditions, include: drive-and-wash, spun casing, Rotasonic, dual-rotary (Barber Rig), and fluid/mud rotary with core barrel or roller bit. Direct-push techniques (e.g., Geoprobe or cone penetrometer) and driven well points may also be used in some cases within the overburden. Monitoring wells within consolidated materials such as bedrock are commonly drilled using water-rotary (coring or tri-cone roller bit), air rotary or Rotasonic methods. The drilling method to be used at a given site will be selected based on site-specific consideration of anticipated drilling/well depths, site or regional geologic knowledge, type of monitoring to be conducted using the installed well, and cost.

No oils or grease will be used on equipment introduced into the boring (e.g., drill rod, casing, or sampling tools). No polyvinyl chloride (PVC) glue/cement will be used in constructing or retrofitting monitoring wells that will be used for water-quality monitoring. No coated bentonite pellets will be used in the well drilling or construction process. Specifications of materials to be installed in the well will be obtained prior to mobilizing onsite, including:

- well casing;
- bentonite;
- sand; and
- grout.

Well materials will be inspected and, if needed, cleaned prior to installation.

II. Personnel Qualifications

Monitoring well installation activities will be performed by persons who have been trained in proper well installation procedures under the guidance of an experienced field geologist, engineer, or technician. Where field sampling is performed for soil or

bedrock characterization, field personnel will have undergone in-field training in soil or bedrock description methods, as described in the appropriate SOP(s) for those activities.

III. Equipment List

The following materials will be available during soil boring and monitoring well installation activities, as required:

- Site Plan with proposed soil boring/well locations;
- Work Plan or Field Sampling Plan (FSP), and site Health and Safety Plan (HASP);
- personal protective equipment (PPE), as required by the HASP;
- traffic cones, delineators, caution tape, and/or fencing as appropriate for securing the work area, if such are not provided by drillers;
- appropriate soil sampling equipment (e.g., stainless steel spatulas, knife);
- soil and/or bedrock logging equipment as specified in the appropriate SOPs;
- appropriate sample containers and labels;
- drum labels as required for investigation derived waste handling;
- chain-of-custody forms;
- insulated coolers with ice, when collecting samples requiring preservation by chilling;
- photoionization detector (PID) or flame ionization detector (FID);
- ziplock style bags;
- water level or oil/water interface meter;
- locks and keys for securing the well after installation;
- decontamination equipment (bucket, distilled or deionized water, cleansers appropriate for removing expected chemicals of concern, paper towels);

- field notebook.

Prior to mobilizing to the site, ARCADIS personnel will contact the drilling subcontractor or in-house driller (as appropriate) to confirm that appropriate sampling and well installation equipment will be provided. Specifications of the sampling and well installation equipment are expected to vary by project, and so communication with the driller will be necessary to ensure that the materials provided will meet the project objectives. Equipment typically provided by the driller could include:

- drilling equipment required by the American Society of Testing and Materials (ASTM) D 1586, when performing split-spoon sampling;
- disposable plastic liners, when drilling with direct-push equipment;
- drums for investigation derived waste;
- drilling and sampling equipment decontamination materials;
- decontamination pad materials, if required; and
- well construction materials.

IV. Cautions

Prior to beginning field work, underground utilities in the vicinity of the drilling areas will be delineated by the drilling contractor or an independent underground utility locator service. See separate SOP for utility clearance.

Some regulatory agencies require a minimum annular space between the well or permanent casing and the borehole wall. When specified, the minimum clearance is typically 2 inches on all sides (e.g., a 2-inch diameter well requires a 6-inch diameter borehole). In addition, some regulatory agencies have specific requirements regarding grout mixtures. Determine whether the oversight agency has any such requirements prior to finalizing the drilling and well installation plan.

If dense non-aqueous phase liquids (DNAPL) are known or expected to exist at the site, refer to the DNAPL Contingency Plan SOP for additional details regarding drilling and well installation to reduce the potential for inadvertent DNAPL remobilization.

Similarly, if light non-aqueous phase liquids (LNAPLs) are known or expected to be present as “perched” layers above the water table, refer to the DNAPL Contingency

Plan. Follow the general provisions and concepts in the DNAPL contingency plan during drilling above the water table at known or expected LNAPL sites.

Avoid using drilling fluids or materials that could impact groundwater or soil quality, or could be incompatible with the subsurface conditions.

Similarly, consider the material compatibility between the well materials and the surrounding environment. For example, PVC well materials are not preferred when DNAPL is present. In addition, some groundwater conditions leach metals from stainless steel.

Water used for drilling and sampling of soil or bedrock, decontamination of drilling/sampling equipment, or grouting boreholes upon completion will be of a quality acceptable for project objectives. Testing of water supply should be considered.

Specifications of materials used for backfilling bore hole will be obtained, reviewed and approved to meet project quality objectives. Bentonite is not recommended where DNAPLs are likely to be present. In these situations, neat cement grout is preferred.

No coated bentonite pellets will be used in monitoring well construction, as the coating could impact the water quality in the completed well.

Monitoring wells may be installed with Schedule 40 polyvinyl chloride (PVC) to a maximum depth of 200 feet below ground surface (bgs). PVC monitoring wells between 200 and 400 feet total depth will be constructed using Schedule 80 PVC. Monitoring wells deeper than 400 feet will be constructed using steel.

V. Health and Safety Considerations

Field activities associated with monitoring well installation will be performed in accordance with a site-specific HASP, a copy of which will be present on site during such activities.

VI. Procedures

The procedures for installing groundwater monitoring wells are presented below:

Hollow-Stem Auger, Drive-and-Wash, Spun Casing, Fluid/Mud Rotary, Rotasonic, and Dual-Rotary Drilling Methods

1. Locate boring/well location, establish work zone, and set up sampling equipment decontamination area.

2. Advance boring to desired depth. Collect soil and/or bedrock samples at appropriate interval as specified in the Work Plan and/or FSP. Collect, document, and store samples for laboratory analysis as specified in the Work Plan and/or FSP. Decontaminate equipment between samples in accordance with the Work Plan and/or FSP. A common sampling method that produces high-quality soil samples with relatively little soil disturbance is the ASTM D 1586 - Standard Test Method for Penetration Test and Split-Barrel Sampling of Soils. Split-spoon samples are obtained during drilling using hollow-stem auger, drive-and-wash, spun casing, and fluid/mud rotary. Rotasonic drilling produces large-diameter soil cores that tend to be more disturbed than split-spoon samples due to the vibratory action of the drill casing. Dual-rotary removes cuttings by compressed air and allows only a general assessment of geology. High-quality bedrock samples can be obtained by coring.

3. Describe each soil or bedrock sample as outlined in the appropriate SOP. Record descriptions in the field notebook and/or personal digital assistant (PDA). It should be noted that PDA logs must be electronically backed up and transferred to a location accessible to other project team members as soon as feasible to retain and protect the field data. During soil boring advancement, document all drilling events in field notebook, including blow counts (number of blows required to advance split-spoon sampler in 6-inch increments) and work stoppages. Blow counts will not be available if Rotasonic, dual-rotary, or direct-push methods are used. When drilling in bedrock, the rate of penetration (minutes per foot) is recorded.

4. If it is necessary to install a monitor well into a permeable zone below a confining layer, particularly if the deeper zone is believed to have water quality that differs significantly from the zone above the confining layer, then a telescopic well construction should be considered. In this case, the borehole is advanced approximately 3 to 5 feet into the top of the confining layer, and a permanent casing (typically PVC, black steel or stainless steel) is installed into the socket drilled into the top of the confining layer. The casing is then grouted in place. The preferred methods of grouting telescoping casings include: pressure-injection grouting using an inflatable packer installed temporarily into the base of the casing, such that grout is injected out the bottom of the casing until it is observed at ground surface outside the casing; displacement-method grouting (also known as the Halliburton method), which entails filling the casing with grout and displacing the grout out the bottom of the casing by pushing a drillable plug, typically made of wood to the bottom of the casing, following by tremie grouting the remainder of the annulus outside the casing; or tremie grouting the annulus surrounding the casing using a tremie pipe installed to the base of the borehole. In all three cases, the casing is grouted to the ground

surface, and the grout is allowed to set prior to drilling deeper through the casing. Site-specific criteria and work plans should be created for the completion of non-standard monitoring wells, including telescopic wells.

5. In consolidated formations such as competent bedrock, a monitoring well may be completed with an open borehole interval without a screen and sandpack. In these cases, the borehole is advanced to the targeted depth of the top of the open interval. A permanent casing is then grouted in place following the procedures described in Step 4 above. After the grout sets, the borehole is advanced by drilling through the permanent casing to the targeted bottom depth of the open interval, which then serves as the monitoring interval for the well. If open-borehole interval stability is found to be questionable or if a specific depth interval is later selected for monitoring, a screened monitoring well may later be installed within the open-borehole interval, depending on the annular space and well diameter requirements.

6. Before installing a screened well – or after drilling an open-bedrock well –, it is important to confirm that the borehole has been advanced into the saturated zone. This is particularly important for wells installed to monitor the water table and/or the shallow saturated zone, as the capillary fringe may cause soils above the water table to appear saturated. If one or more previously installed monitoring wells exist nearby, use the depth to water at such well(s) to estimate the water-table depth at the new borehole location.

   To verify that the borehole has been advanced into the saturated zone, it is necessary to measure the water level in the borehole. For boreholes drilled without using water (e.g., hollow-stem auger, cable-tool, air rotary, air hammer), verify the presence of groundwater (and /or LNAPL, if applicable) in the borehole using an electronic water level probe, oil-water interface probe, or a new or decontaminated bailer. For boreholes drilled using water (e.g., drive and wash, spun-casing with roller-bit wash, rotasonic, or water rotary with core or roller bit), monitor the water level in the borehole as it re-equilibrates to the static level. In low-permeability units like clay, fine-grained glacial tills, shale and other bedrock formations, it may be necessary to wait overnight to allow the water level to equilibrate. To the extent practicable, ensure that the depth of the well below the apparent water table is deep enough so that the installed well can monitor groundwater year-round, accounting for seasonal water-table fluctuations. In most cases, the well should be installed at least five feet below the water-table depth, determined as described above. When in doubt, err on the side of slightly deeper well installation.

If necessary, the borehole should be drilled deeper to ensure that the well may intersects the water table or a permeable water-bearing zone.

7. Upon completing the borehole to the desired depth, if a screened well construction is desired, install the monitoring well by lowering the screen and casing assembly with sump through the augers or casing. Monitoring wells typically will be constructed of 2-inch-diameter, flush-threaded PVC or stainless steel slotted well screen and blank riser casing. Smaller diameters may be used if wells are installed using direct-push methodology or if multiple wells are to be installed in a single borehole. The screen length will be specified in the Work Plan or FSP based on regulatory requirements and specific monitoring objectives. Monitoring well screens are usually 5 to 10 feet long, but may be up to 25 feet long in very low permeability, thick geologic formations. The screen length will depend on the purpose for the well and the objectives of the groundwater investigation. Typically, the slot size will be 0.010 inch and the sand pack will be 20-40, Morie No. 0, or equivalent. In very fine-grained formations where sample turbidity needs to be minimized, it may be preferred to use a 0.006-inch slot size and 30-65, Morie No. 00, or equivalent sand pack. Alternatively, where monitoring wells are installed in coarse-grained deposits and higher well yield is required, a 0.020-inch slot size and 10-20, Morie No. 1, or equivalent sand pack may be preferred. To the extent practicable, the slot size and sand pack gradation may be predetermined in the Work Plan or FSP based on site-specific grain-size analysis or other geologic considerations or monitoring objectives. A blank sump may be attached below the well screen if the well is being installed for DNAPL recovery/monitoring purposes. If so, the annular space around the sump will be backfilled with neat cement grout to the bottom of the well screen prior to placing the sand pack around the screen. A blank riser will extend from the top of the screen to approximately 2.5 feet above grade or, if necessary, just below grade where conditions warrant a flush-mounted monitoring well. For wells greater than 50 feet deep, centralizers may be desired to assist in centralizing the monitoring well in the borehole during construction.

8. When the monitoring well assembly has been set in place and the grout has been placed around the sump (if any), place a washed silica sand pack in the annular space from the bottom of the boring to a height of 1 to 2 feet above the top of the well screen. The sand pack is placed and drilling equipment extracted in increments until the top of the sand pack is at the appropriate depth. The sand pack will be consistent with the screen slot size and the soil particle size in the screened interval, as specified in the Work Plan or FSP. A hydrated bentonite seal (a minimum of 2 feet thick) will then be placed in the annular space above the sand pack. If non-hydrated bentonite is used, the bentonite

should be permitted to hydrate in place for a minimum of 30 minutes before proceeding. No coated bentonite pellets will be used in monitoring well drilling or construction. Potable water may be added to hydrate the bentonite if the seal is above the water table. Monitor the placement of the sand pack and bentonite with a weighted tape measure. During the extraction of the augers or casing, a cement/bentonite or neat cement grout will be placed in the annular space from the bentonite seal to a depth approximately 2 feet bgs.

9. Place a locking, steel protective casing (extended at least 1.5 feet below grade and 2 feet above grade) over the riser casing and secure with a neat cement seal. Alternatively, for flush-mount completions, place a steel curb box with a bolt-down lid over the riser casing and secure with a neat cement seal. In either case, the cement seal will extend approximately 1.5 to 2.0 feet below grade and laterally at least 1 foot in all directions from the protective casing, and should slope gently away to promote drainage away from the well. Monitoring wells will be labeled with the appropriate designation on both the inner and outer well casings or inside of the curb box lid.

   When an above-grade completion is used, the PVC riser will be sealed using an expandable locking plug and the top of the well will be vented by drilling a small-diameter (1/8 inch) hole near the top of the well casing or through the locking plug, or by cutting a vertical slot in the top of the well casing. When a flush-mount installation is used, the PVC riser will be sealed using an unvented, expandable locking plug.

10. During well installation, record construction details and actual measurements relayed by the drilling contractor and tabulate materials used (e.g., screen and riser footages; bags of bentonite, cement, and sand) in the field notebook.

11. After completing the well installation, lock the well, clean the area, and dispose of materials in accordance with the procedures outlined in Section VII below.

Direct-Push Method

The direct-push drilling method may also be used to complete soil borings and install monitoring wells. Examples of this technique include the Diedrich ESP vibratory probe system, GeoProbe®, or AMS Power Probe® dual-tube system. Environmental probe systems typically use a hydraulically operated percussion hammer. Depending on the equipment used, the hammer delivers 140- to 350-foot pounds of energy with each blow. The hammer provides the force needed to penetrate very stiff/medium dense soil formations. The hammer simultaneously advances an outer steel casing that contains a dual-tube liner for sampling soil. The outside diameter (OD) of the outer

casing ranges from 1.75 to 2.4 inches and the OD of the inner sampling tube ranges from 1.1 to 1.8 inches. The outer casing isolates shallow layers and permits the unit to continue to probe at depth. The double-rod system provides a borehole that may be tremie-grouted from the bottom up. Alternatively, the inside diameter (ID) of the steel casing provides clearance for the installation of small-diameter (e.g., 0.75- to 1-inch ID) micro-wells. The procedures for installing monitoring wells in soil using the direct-push method are described below.

1. Locate boring/well location, establish work zone, and set up sample equipment decontamination area.

2. Advance soil boring to designated depth, collecting samples at intervals specified in the Work Plan. Samples will be collected using dedicated, disposable, plastic liners. Describe samples in accordance with the procedures outlined in Step 3 above. Collect samples for laboratory analysis as specified in the Work Plan and/or FSP.

3. Upon advancing the borehole to the desired depth, install the micro-well through the inner drill casing. The micro-well will consist of approximately 1-inch ID PVC or stainless steel slotted screen and blank riser. The sand pack, bentonite seal, and cement/bentonite grout will be installed as described, where applicable, in Step 7 and 8 above.

4. Install protective steel casing or flush-mount, as appropriate, as described in Step 9 above. During well installation, record construction details and tabulate materials used.

5. After completing the well installation, lock the well, clean the area, and dispose of materials in accordance with the procedures outlined in Section VII below.

Driven Well Point Installation

Well points will be installed by pushing or driving using a drilling rig or direct-push rig, or hand-driven where possible. The well point construction materials will consist of a 1- to 2-inch-diameter threaded steel casing with either 0.010- or 0.020-inch slotted stainless steel screen. The screen length will vary depending on the hydrogeologic conditions of the site. The casings will be joined together with threaded couplings and the terminal end will consist of a steel well point. Because they are driven or pushed to the desired depth, well points do not have annular backfill materials such as sand pack or grout.

VII. Waste Management

Investigation-derived wastes (IDW), including soil cuttings and excess drilling fluids (if used), decontamination liquids, and disposable materials (well material packages, PPE, etc.), will be placed in clearly labeled, appropriate containers, or managed as otherwise specified in the Work Plan, FSP, and/or IDW management SOP.

VIII. Data Recording and Management

Drilling activities will be documented in a field notebook. Pertinent information will include personnel present on site, times of arrival and departure, significant weather conditions, timing of well installation activities, soil descriptions, well construction specifications (screen and riser material and diameter, sump length, screen length and slot size, riser length, sand pack type), and quantities of materials used. In addition, the locations of newly-installed wells will be documented photographically or in a site sketch. If appropriate, a measuring wheel or engineer's tape will be used to determine approximate distances between important site features.

The well or piezometer location, ground surface elevation, and inner and outer casing elevations will be surveyed using the method specified in the site Work Plan. Generally, a local baseline control will be set up. This local baseline control can then be tied into the appropriate vertical and horizontal datum, such as the National Geodetic Vertical Datum of 1929 or 1988 and the State Plane Coordinate System. At a minimum, the elevation of the top of the inner casing used for water-level measurements should be measured to the nearest 0.01 foot. Elevations will be established in relation to the National Geodetic Vertical Datum of 1929. A permanent mark will be placed on top of the inner casing to mark the point for water-level measurements.

IX. Quality Assurance

All drilling equipment and associated tools (including augers, drill rods, sampling equipment, wrenches, and any other equipment or tools) that may have come in contact with soil will be cleaned in accordance with the procedures outlined in the appropriate SOP. Well materials will also be cleaned prior to well installation.

X. References

American Society of Testing and Materials (ASTM) D 1586 - *Standard Test Method for Penetration Test and Split-Barrel Sampling of Soils*.

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Standard Groundwater Sampling for Monitoring Wells

Rev. #: 1

Rev Date: July 16, 2008

Approval Signatures

Prepared by: _____ Date: 7/16/08

Reviewed by: _____ Date: 7/16/08
(Technical Expert)

I. Scope and Application

This Standard Operating Procedure (SOP) describes the procedures to be used to collect groundwater samples using traditional purging and sampling techniques. For low-flow purging techniques, please refer to the Low Flow Purging SOP. Monitoring wells must be developed after installation at least 1 week prior to groundwater sample collection. Monitoring wells will not be sampled until the well has been developed. During precipitation events, groundwater sampling will be discontinued until precipitation ceases or a cover has been erected over the sampling area and monitoring well.

Both filtered and unfiltered groundwater samples may be collected using this SOP. Filtered samples may be obtained using a 1.0-, 0.45-, or 0.1-micron disposable filter.

II. Personnel Qualifications

ARCADIS personnel directing, supervising, or leading groundwater sample collection activities should have a minimum of 2 years of previous groundwater sampling experience. Field employees with less than 6 months of experience should be accompanied by a supervisor (as described above) to ensure that proper sample collection techniques are employed.

III. Equipment List

The following materials shall be available, as required, during groundwater sampling:

- site plan of monitoring well locations and site Field Sampling Plan (FSP);
- appropriate health and safety equipment, as specified in the site Health and Safety Plan (HASP);
- photoionization detector (PID) or flame ionization detector (FID), as needed, in accordance with the HASP;
- monitoring well construction logs or tables and historical water level information, if available;
- dedicated plastic sheeting or other clean surface to prevent sample contact with the ground;
- if bailers are to be used in sampling:

  - appropriate dedicated bottom-loading, bottom-emptying bailers (i.e., polyvinyl chloride [PVC], Teflon, or stainless steel);
  - polypropylene rope;
- if submersible pumps are to be used in sampling:
  - dedicated tubing and other equipment necessary for purging;
  - generator or battery for operation of pumps, if required;
  - a pump selected in accordance with the FSP or Work Plan (parameter-specific [e.g., submersible, bladder, peristaltic]);
- graduated buckets to measure purge water;
- water-level or oil/water interface probe, in accordance with the FSP or Work Plan;
- conductivity/temperature/pH meter;
- down-hole dissolved oxygen meter, oxidation reduction potential meter, and/or turbidity meter, if specified in the FSP;
- water sample containers appropriate for the analytical method(s) with preservative, as needed (parameter-specific);
- filter, as needed, in accordance with the analytical method and parameter;
- appropriate blanks (trip blank supplied by the laboratory), as specified in the FSP;
- Ziploc-type freezer bags for use as ice containers;
- appropriate transport containers (coolers) with ice and appropriate labeling, packing, and shipping materials;
- appropriate groundwater sampling log (example attached);
- chain-of-custody forms;
- site map with well locations and groundwater contour maps;

- keys to wells and contingent bolt cutters for rusted locks and replacement keyed-alike locks; and
- drums or other containers for purge water, as specified by the site investigation derived waste (IDW) management plan.

IV. Cautions

If heavy precipitation occurs and no cover over the sampling area and monitoring well can be erected, sampling must be discontinued until adequate cover is provided. Rain water could contaminate groundwater samples.

Remember that field logs and some forms are considered to be legal documents. All field logs and forms should therefore be filled out in indelible ink.

It may be necessary to field filter some parameters (e.g., metals) prior to collection, depending on preservation, analytical method, and project quality objectives.

Check monitoring well logs for use of bentonite pellets. Make note of potential use of bentonite pellets on the groundwater sampling log. Coated bentonite pellets have been found to contaminate monitoring wells with elevated levels of acetone.

Store and/or stage empty and full sample containers and coolers out of direct sunlight.

To mitigate potential cross-contamination, groundwater samples are to be collected in a pre-determined order from least impacted to more impacted based on previous analytical data. If no analytical data are available, samples are to be collected in the following order:

1. First sample the upgradient well(s).
2. Next, sample the well located furthest downgradient of the interpreted or known source.
3. The remaining wells should be progressively sampled in order from downgradient to upgradient, such that the wells closest to the interpreted or known source are sampled last.

Be careful not to over-tighten lids with Teflon liners or septa (e.g., 40 mL vials). Over-tightening can impair the integrity of the seal.

V. Health and Safety Considerations

If thunder or lighting is present, discontinue sampling until 30 minutes have passed after the last occurrence of thunder or lighting.

VI. Procedure

The procedures to sample monitoring wells will be as follows:

1. Don safety equipment, as required in the HASP. Depending on site-specific security and safety considerations, this often must be done prior to entering the work area.

2. Review equipment list (Section III above) to confirm that the appropriate equipment has been acquired.

3. Record site and monitoring well identification on the groundwater sampling log, along with date, arrival time, and weather conditions. Also identify the personnel present, equipment utilized, and other relevant data requested on the log.

4. Label all sample containers with indelible ink.

5. Place plastic sheeting adjacent to the well for use as a clean work area, if conditions allow. Otherwise, prevent sampling equipment from contacting the ground or other surface that could compromise sample integrity.

6. Remove lock from well and if rusted or broken, replace with a new brass keyed-alike lock.

7. Unlock and open the well cover while standing upwind of the well. Remove well cap and place on the plastic sheeting.

8. Set the sampling device,meters, and other sampling equipment on the plastic sheeting. If a dedicated sampling device stored in the well is to be used, this may also be set temporarily on the plastic sheeting, for convenience. However, if a dedicated sampling device is stored below the water table, removing it may compromise water-level data, so water level measurements should be taken prior to removing the device.

9. Obtain a water-level depth and bottom-of-well depth using an electric well probe and record on the groundwater sampling log using indelible ink. Clean the probe(s) after each use in accord with the FSP or the equipment

decontamination SOP.

Note: Water levels may be measured at all wells prior to initiating any sampling activities, depending on FSP requirements.

10. Calculate the number of gallons of water in the well using the length of water column (in feet). Record the well volume on the groundwater sampling log using indelible ink.

11. Remove the required purge volume of water from the well (measure purge water volume in measuring buckets). The required purge volume will be three to five well volumes (the water column in the well screen and casing) unless the well runs dry, in which case, the water that comes into the well will be sampled (USEPA, 1996). In any case, the pumping rate will be decreased during sampling to limit the potential for volatilization of organics potentially present in the groundwater.

12. Field parameter measurements will be periodically collected in accord with FSP specifications. The typical time intervals of field parameter measurement are (1) after each well volume removed, and (2) before sampling. If the field parameters are being measured above-ground (rather than with a downhole probe), then the final pre-sampling parameter measurement should be collected at the reduced flow rate to be used during sampling. The physical appearance of the purged water should be noted on the groundwater sampling log. In addition, water level measurements should be collected and recorded to verify that the well purging is in accord with the guidelines set forth in the previous step.

13. Unless otherwise specified by the applicable regulatory agencies, all purge water will be contained. Contained purge water will be managed in accordance with the FSP or Work Plan. If historical concentrations in the well are less than federal or state regulated concentrations appropriate for current land use, *and permission has been granted by the oversight regulatory agency* to dispose of clean purge water on the ground next to the well(s), then purge water will be allowed to infiltrate into the ground surface downgradient from the monitoring well after the well is sampled.

14. After the appropriate purge volume of groundwater in the well has been removed, or if the well has been bailed dry and allowed to recover, obtain the groundwater sample needed for analysis with the dedicated bailer or from the dedicated sampling tubing, pour the groundwater directly from the sampling device into the appropriate container in the order of volatilization sensitivity of

the parameters sampled, and tightly screw on the cap (snug, but not too tight). The suggested order for sample parameter collection, based on volatilization sensitivity, is presented below:

a. volatile organic compounds (VOCs);

b. semi-volatile organic compounds (SVOCs);

c. polychlorinated biphenyls (PCBs)/pesticides;

d. metals; and

e. wet chemistry.

15. When sampling for volatiles, water samples will be collected directly from the bailer or dedicated tubing into 40 mL vials with Teflon-lined septa.

16. For other analytical samples, sample containers for each analyte type should be filled in the order specified by the FSP. If a bailer is used, then the sample for dissolved metals and/or filtered PCBs should either be placed directly from the bailer into a pressure filter apparatus or pumped directly from the bailer with a peristaltic pump, through an in-line filter, into the pre-preserved sample bottle. If dedicated sample tubing is used, then the filter should be installed in-line just prior to filtered sample collection.

17. If sampling for total and filtered metals and/or PCBs, a filtered and unfiltered sample will be collected. Sample filtration for the filtered sample will be performed in the field utilizing a pump prior to preservation. Attach (clamp) a new 1.0-, 0.45-, or 0.1-micron filter to the discharge tubing of the pump (note the filter flow direction). Turn the pump on and allow 100 mL (or manufacturer recommended amount) of fluid through the filter before sample collection. Dispense the filtered liquid directly into the laboratory sample bottles. If bailers are used for purging and sampling, a proper volume of purge water will be placed in a disposable or decontaminated polyethylene container and pumped through the filter and into the sample container using a peristaltic pump.

18. Place the custody seal around the cap and the sampler container, if required. Note the time on the sample label. Secure with packing material and maintain at approximately 4°C on wet ice contained in double Ziploc-type freezer bags during storage in an insulated, durable transport container.

19. Replace the well cap and lock well, or install a new lock if needed.

20. Record the time sampling procedures were completed on the appropriate field logs (using indelible ink).

21. Complete the procedures for chain-of-custody, handling, packing, and shipping. Chain-of-custody forms should be filled out and checked against the labels on the sample containers progressively after each sample is collected.

22. Place all disposable sampling materials (such as plastic sheeting, disposable tubing or bailers, and health and safety equipment) in appropriate containers.

23. If new locks were installed, forward copies of the keys to the client Project Manager (PM) and ARCADIS PM at the end of the sampling activities.

VII. Waste Management

Purge water will be managed as specified in the FSP or Work Plan, and according to state and/or federal requirements. Personal protective equipment (PPE) and decontaminated fluids will be contained separately and staged at the sampling location. Containers must be labeled at the time of collection. Labels will include date, location(s), site name, city, state, and description of matrix contained (e.g., soil, groundwater, PPE). General guidelines for IDW management are set forth in a separate IDW management SOP.

VIII. Data Recording and Management

Initial field logs and chain-of-custody records will be transmitted to the ARCADIS PM at the end of each day unless otherwise directed by the PM. The groundwater team leader retains copies of the groundwater sampling logs. All field data should be recorded in indelible ink.

IX. Quality Assurance

Field-derived quality assurance blanks will be collected as specified in the FSP, depending on the project quality objectives. Typically, field rinse blanks will be collected when non-dedicated equipment is used during groundwater sampling. Field rinse blanks will be used to confirm that decontamination procedures are sufficient and samples are representative of site conditions. Trip blanks for VOCs, which aid in the detection of contaminates from other media, sources, or the container itself, will be kept with the coolers and the sample containers throughout the sampling activities.

X. References

USEPA. 1986. RCRA Groundwater Monitoring Technical Enforcement Guidance Document (September 1986).

USEPA. 1991. Handbook Groundwater, Volume ii Methodology, Office of Research and Development, Washington, DC. USEPN62S, /6-90/016b (July, 1991).

U.S. Geological Survey (USGS). 1977. National Handbook of Recommended Methods for Water-Data Acquisition: USGS Office of Water Data Coordination. Reston, Virginia.

ARCADIS
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Water Level Measurement

Rev. #: 2

Rev Date: February 24, 2011

Approval Signatures

Prepared by: _____ Date: 02/24/2011

Reviewed by: _____ Date: 02/24/2011
(Technical Expert)

I. Scope and Application

The objective of this Standard Operating Procedure (SOP) is to describe procedures to measure and record groundwater and surface-water elevations. Water levels may be measured using an electronic water-level probe, oil-water level indicator, or a pressure transducer from established reference points (e.g. top of casing). Reference points will be surveyed to evaluate fluid elevations relative to mean sea level (msl). This SOP describes the equipment, field procedures, materials, and documentation procedures to measure and record groundwater and surface-water elevations using the aforementioned equipment.

This is a standard (i.e., typically applicable) operating procedure which may be varied or changed as required, dependent upon site conditions, equipment limitations, or limitations imposed by the procedure. The ultimate procedure employed will be documented in the project work plans or reports.

II. Personnel Qualifications

ARCADIS field sampling personnel will have current health and safety training including 40-hour HAZWOPER training, site supervisor training, site-specific training, first aid, and CPR, as needed. In addition, ARCADIS field sampling personnel will be versed in the relevant SOPs and posses the required skills and experience necessary to successfully complete the desired field work.

III. Equipment List

The following materials, as required, shall be available during water level measurements:

- Appropriate personal protective equipment as specified in the Site Health and Safety Plan
- Equipment decontamination supplies
- Electronic water-level indicator
- Electronic oil-water level indicator
- Mini-Troll® or Troll® pressure transducer
- In-Situ™ data logger

- Laptop computer with the Win-Situ software package installed
- Photoionization detector (PID) and/or organic vapor analyzer
- Non-phosphate laboratory soap (Alconox or equivalent)
- Deionized/distilled water
- 150-foot measuring tape
- Solvent (methanol/acetone) rinse
- Portable containers
- Hacksaw
- Pliers
- Plastic sheeting
- “Write-in-the-Rain” Field logbook and or PDA (Personal Digital Assistant)
- Indelible ink pen.

IV. Cautions

Electronic water-level probes and oil-water interface probes can sometimes produce false-positive readings. For example, if the inside surface of the well has condensation above the water level, then an electronic water-level probe may produce a signal by contacting the side of the well rather than the true water level in the well. To produce reliable data, the electronic water level probe and/or interface probe should be raised and lowered several times at the approximate depth where the instrument produces a tone indicating a fluid interface to verify consistent, repeatable results.

The graduated tape or cable with depth markings is designed to indicate the depth of the electronic sensor that detects the fluid interface, but not the depth of the bottom of the instrument. When using these devices to measure the total well depth, the additional length of the instrument below the electronic sensor must be added to the apparent well depth reading, as observed on the tape or cable of the instrument, to obtain the true total depth of the well. If the depth markings on the tape or cable are

worn or otherwise difficult to read, extra care must be taken in obtaining the depth readings.

V. Health and Safety Considerations

The HASP will be followed, as appropriate, to ensure the safety of field personnel. Access to wells may expose field personnel to hazardous materials such as contaminated groundwater or oil. Other potential hazards include stinging insects that may inhabit well heads, other biologic hazards, and potentially the use of sharp cutting tools (scissors, knife). Appropriate personal protective equipment (PPE) will be worn during these activities. Field personnel will thoroughly review client-specific health and safety requirements, which may preclude the use of fixed/folding-blade knives.

VI. Procedure

Electronic Water-Level Indicators and Oil-Water Indicators

Calibration procedures and groundwater level measurement procedures for electronic water-level indicators and oil-water indicators are described in the sections below.

Calibration Procedures

The indicator probe will be tested to verify that the meter has been correctly calibrated by the manufacturer. The following steps will be used to verify the accuracy of the indicator:

1. Measure the lengths between each increment marker on the indicator with a measuring tape. The appropriate length of indicator measuring tape, suitable to cover the depth range for the wells of interest, will be checked for accuracy.

2. If the indicator measuring tape is inaccurate, the probe will be sent back to the manufacturer.

3. Equipment calibration will be recorded in the field logbook and/or PDA.

Groundwater Level Measurement Procedures

A detailed procedure for obtaining water elevations will be as follows:

1. Identify site and monitoring well number in field notebook along with date, time, personnel and weather conditions using indelible ink.

2. Use safety equipment as specified in the Health and Safety Plan.

3. Decontaminate the indicator probe and tape in accordance with the appropriate cleaning procedures.

4. Place clean plastic sheeting on the ground next to the well.

5. Unlock and open the monitoring well cover while standing upwind from the well.

6. Measure the volatile organics present in the monitoring well head space with a PID and record the PID reading in the field logbook.

7. Allow the water level in the well to equilibrate with atmospheric pressure for a few minutes. Locate a measuring reference point on the monitoring well casing. If one is not found, create a reference point by notching the highest point on the inner casing (or outer if an inner casing is not present) with a hacksaw. All downhole measurements will be taken from the reference point. Document the creation of any new reference point or alteration of the existing reference point.

8. Measure to the nearest 0.01 foot and record the height of the inner and outer casing from reference point to ground level.

9. Slowly lower the level indicator probe until it touches the bottom of the well. Record the total depth of the well from the top of the inner casing (or outer casing if inner casing is not present). Measure depth to water level as the probe is drawn back up through the water column. If used to measure the level of surface water, slowly lower from the surveyed reference point, as appropriate. Double check all measurements and record depths to the nearest 0.01 foot.

10. Decontaminate the instrument using appropriate cleaning procedures.

11. Lock the well when all activities are completed.

Pressure Transducers

The detailed procedure for obtaining water elevations using a Mini-Troll® or Troll® pressure transducer with an In-Situ™ data logger and the Win-Situ software package will be as follows:

<u>Setup Procedures</u>

1. Connect the Mini-Troll® or Troll® transducer to a laptop computer serial port.

2. Open the Win-Situ software package on the laptop computer.

3. Verify that the Win-Situ software recognizes the transducer.

4. Synchronize the clock on the laptop computer with that of the transducer.

5. Add a test to the transducer and input the specifications of the test (e.g., frequency of data collection, start data collection).

6. Disconnect the transducer from the laptop computer, and prepare the transducer for field deployment.

Field Procedures

1. Decontaminate all equipment entering the monitoring well using appropriate cleaning procedures.

2. Connect transducer to laptop computer, and start the Win-Situ program.

3. Lower the transducer gently below the water table or surface-water level.

4. Take a water level reading from the transducer using the Win-Situ software package. Lift the transducer approximately 1-foot, and verify the transducer response on the Win-Situ program (i.e. depth to water should be 1-foot less).

5. Upon verification, set the transducer to the desired depth. Position the instrument below the lowest anticipated water level, but not so low that its range will be exceeded at the highest anticipated water level. The maximum operating depth below water is equal to 2.31 feet times the psi rating of the transducer (e.g., 23.1 feet for a 10 psi transducer).

6. Secure the cable at the well head or fixed object adjacent to surface-water body to prevent drift and movement.

7. Obtain a manual water-level reading using the procedure noted above, and record the measurement in the field notebook or PDA.

8. Set reference point (e.g. depth to water, groundwater elevation) and input it into the Win-Situ software package.

9. Periodically download data and collect additional manual depth-to-water measurements using the same water-level or oil-water indicator probe used during the equipment setup to verify the accuracy of the transducer.

VII. Waste Management

Decontamination fluids, PPE, and other disposable equipment will be properly stored on site in labeled containers and disposed of properly. Be certain that waste containers are properly labeled and documented in the field log book. Review appropriate waste management SOPs, which may be state- or client-specific.

VIII. Data Recording and Management

Groundwater level measurements should be documented in the field logbook and/or PDA. The following information will be documented in the field logbook:

- Sample identification
- Measurement time
- Total well depth
- Depth to water

Groundwater elevations recorded using a Mini-Troll® or Troll® pressure transducer with an In-Situ™ data logger and the Win-Situ software package will be downloaded and stored in the central project file.

IX. Quality Assurance

As described in the detailed procedure, the electronic water-level meter and/or oil-water interface probe will be calibrated prior to use versus an engineer's rule to ensure accurate length demarcations on the tape or cable. Fluid interface measurements will be verified by gently raising and lowering the instrument through each interface to confirm repeatable results.

X. References

No literature references are required for this SOP.

Title: PCB Preparation for Analysis by HRGC/HRMS [Method 1668A, EPA 1668C & CBC01.2]

Approvals (Signature/Date):

Elizabeth Koston Technical Manager	09/05/14 Date	Joe Schairer Health & Safety Manager / Coordinator	9/10/14 Date
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1. SCOPE AND APPLICATION

1.1. This SOP is appropriate for the preparation of samples for analysis of mono- through deca-chlorinated biphenyls in a variety of matrices at low part-per-trillion to part-per-billion levels using high resolution gas chromatography and high resolution mass spectrometry, by EPA Methods 1668A, 1668C and CBC01.2.

1.2. The calibration range of the procedure for 1 L water is 20 to 20000 ppq, 2 to 2000 ppt for 10.0 g soil, sediment or tissue, and 40-40,000 pg/train (assuming 1/2 sample to 20 uL F.V.) for air train samples for mono-deca PCBs. Analysis of dilutions of aliquots of the sample will permit measurements of concentrations above the upper method calibration limit. The practical limits of detection and quantitation may be different from the lower method calibration limit, depending on the complexity of the matrix and the level of PCB contamination of the reagent and absorbent used in the extraction and cleanup procedure.

1.3. All PCB congener labeling in this document is consistent with IUPAC naming conventions.

1.4. When undertaking projects for the Department of Defense (DOD), the relevant criteria in Policy WS-PQA-021, "DOD QSM and AFCEE QAPP Implementation" must be checked and incorporated.

1.5. The detection limits and quantitation limits in this method are driven more by the level of interference and laboratory background than by absolute instrument sensitivity. Reporting limits are discussed in the analysis SOP WS-ID-0013.

2. SUMMARY OF METHOD

2.1. This procedure uses matrix specific extraction and analyte specific cleanup techniques.

2.2. An aliquot of a matrix (water, soil, sediment, XAD Resin, filter) is spiked with the solution containing 27 isotopically 13C-labeled PCBs listed in Table I. The sample is then extracted according to matrix specific extraction procedures.

2.3. After extraction labeled cleanup standards are spiked into the extract. Available cleanup processes include silica gel, florisil, and gel permeation chromatography. Acid and/or base back extraction may also be used.

2.4. The preparation of the final extract for the instrumental analysis is accomplished by adding 5 isotopically ($^{13}C_{12}$) labeled recovery standards (Table I). Quantitation and analysis is performed as described in the analytical method SOP WS-ID-0013.

2.5. After cleanup recovery standards are added and the extract is concentrated to 20uL.

2.6. The extract is then analyzed according to SOP WS-ID-0013.

2.7. Quantitative analysis is performed differently for different congeners:

2.7.1. The Toxic and LOC PCBs are determined using isotope dilution against a 5 point calibration.

2.7.2. For all congeners excluding those in Section 2.6.1 quantitation is carried out by internal standard technique using a single calibration point.

3. DEFINITIONS

3.1. Definitions of terms used in this SOP may be found in the glossary of the Quality Assurance Manual (QAM).

3.2. Data qualifiers are defined on each data report. Commonly used data qualifiers are defined in the QAM.

4. INTERFERENCES

4.1. Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts or elevated baselines that may cause misinterpretation of the chromatographic data. All of these materials must be demonstrated to be free from interferents under the conditions of analysis by running laboratory method blanks. Analysts shall not use PVC gloves.

4.2. The use of high-purity reagents and solvents helps minimize interference problems. Purification of solvents by distillation in all-glass systems may be necessary.

4.3. Reuse of glassware is to be minimized to avoid the risk of contamination. If samples are known or suspected of containing high analyte levels glassware should be segregated and isolated until analytical results are available. Additional cleaning or disposal of glassware may occur dependent upon analyte levels.

4.4. Interferents co-extracted from the sample will vary considerably from matrix to matrix. PCBs are often associated with other interfering chlorinated substances such as polychlorinated dioxins/furans (PCDD/PCDF), polychlorinated diphenyl ethers (PCDPEs), polychlorinated naphthalenes, methoxy biphenyl hydroxydiphenyl ethers, benzylphenyl ethers, brominated diphenyl ethers, polynuclear aromatics and pesticides that may be found at concentrations several orders of magnitude higher than the analytes of interest. Retention times of target analytes must be verified using reference standards. These values must correspond to the retention time windows established. While certain clean-up techniques are provided as part of this method, unique samples may require additional cleanup steps to achieve lower detection limits.

4.5. A high-resolution capillary column (30 m SPB Octyl) is used to resolve as many PCB isomers as possible; however, no single column is known to resolve all isomers.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), the Sacramento Addendum to the Corporate EH&S Manual (WS-PEHS-0002), and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1. Specific Safety Concerns or Requirements

5.1.1. Eye protection that satisfies ANSI Z87.1, laboratory coat, and chemically resistant gloves must be worn while samples, standards, solvents, and reagents are being handled. Latex and vinyl gloves provide no protection against most of the organic solvents used in this method. Nitrile or similar gloves must be used. Latex gloves may be used for methanol.

5.1.2. Exposure to chemicals must be maintained as low as reasonably achievable; therefore all samples must be opened, transferred and prepared in a fume hood. Solvent and waste containers will be kept closed unless transfers are being made.

5.1.3. Laboratory procedures such as repetitive use of pipettes, repetitive transferring of extracts and manipulation of filled separatory funnels and other glassware represent a significant potential for repetitive motion or other ergonomic injuries. Laboratory associates performing these procedures are in the best position to realize when they are at risk for these types of injuries. Whenever a situation is found in which an employee is performing the same repetitive motion, the employee shall immediately bring this to the attention of their supervisor, manager, or the EH&S staff. The task will be analyzed to determine a better means of accomplishing it.

5.1.4. Hearing protection must be worn when using mechanical systems to grind fish or tissue samples.

5.1.5. When dissecting crawfish abdomens with a scalpel, cut from the hand holding the abdomen toward the tail (away from you).

5.1.6. Finely divided dry soils contaminated with PCBs are particularly hazardous because of the potential for inhalation and ingestion. Such samples are to be

processed in a confined environment, such as a hood or a glove box.

5.1.7. Assembly and disassembly of glassware creates a risk of breakage and cuts. All staff members shall wear Kevlar or similar cut-resistant gloves over chemically resistant gloves when assembling and disassembling glassware.

5.1.8. The use of separatory funnels to extract aqueous samples with methylene chloride creates excessive pressure very rapidly. Initial venting should be done immediately after the sample container has been sealed and inverted. Vent the funnel into the hood away from people and other samples. This is considered a high-risk activity, and a face shield must be worn over safety glasses or goggles when it is performed.

5.1.9. The use of vacuum systems during rotovap concentration presents the risk of imploding glassware. All glassware used during vacuum operations must be thoroughly inspected prior to each use. Glass that is chipped, scratched, cracked, rubbed or marred in any manner must not be used under vacuum. It must be removed from service and replaced.

5.1.10. Mercury is a highly toxic compound that must be handled with care. The analyst must be aware of the handling and cleanup techniques before handling this material. Spilled mercury requires that special cleanup tools and procedures be used.

5.2. Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table below contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Table 1: Materials used in this SOP and their Hazards

Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sulfuric Acid (1)	Corrosive Oxidizer Dehydradator	1 mg/m3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.
Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of Sodium Hydroxide dust will cause irritation of the nasal and respiratory system.

Table 1: Materials used in this SOP and their Hazards			
Material	**Hazards**	**Exposure Limit (2)**	**Signs and symptoms of exposure**
Mercury	Poison	0.1 Mg/M3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Iso-octane (2,2,4-trimethylpentane, 2,4,4-trimethylpentane)	Flammable	500 PPM TWA	Causes eye or respiratory tract irritation. Repeated/ prolonged exposure can cause defatting of skin. High concentrations can produce drowsiness
Toluene	Flammable Poison Irritant	200 ppm-TWA 300 ppm-Ceiling	Inhalation may cause irritation of the upper respiratory tract. Symptoms of overexposure may include fatigue, confusion, headache, dizziness and drowsiness. Peculiar skin sensations (e. g. pins and needles) or numbness may be produced. Causes severe eye and skin irritation with redness and pain. May be absorbed through the skin.
Dodecane	Flammable	None listed	May cause respiratory tract, s kin or eye irritation.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Nonane	Flammable	200 ppm	Primary hazard is flammability. May also cause skin irritation, drowsiness and dizziness if inhaled.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

6.1. Equipment for sample preparation

6.1.1. Laboratory fume hood of sufficient size to contain the sample preparation equipment listed below.

6.1.2. Glove box (optional)

6.1.3. Meat grinder - Hobart, or equivalent, with 3-5 mm holes in inner plate.

6.1.4. Analytical Balance - Capable of weighing 0.1 mg

6.1.5. Top Loading Balance- Capable of weighing 10 mg.

6.2. Extraction Apparatus

6.2.1. Water Samples

6.2.1.1. Graduated cylinder, 1L capacity

6.2.1.2. 1L filtration flasks with side arm, for use in vacuum filtration of water samples

6.2.1.3. Separatory funnels - 250, 500 and 2000 mL, with Teflon stopcocks.

6.2.1.4. Glass fiber filters, Whatman GF-D, GF-F, GMF-150 or equivalent

6.2.2. Soxhlet/Dean-Stark (SDS) extractor

6.2.2.1. Soxhlet – 50 mm i.d., 200 mL capacity with 500 mL flask or 70 mm x 240 mm with 1000 mL round bottom flask.

6.2.2.2. Thimble - 30 x 100 or 43 x 123 mm Glass fiber

6.2.2.3. Moisture trap - Dean-Stark or Barret.

6.2.2.4. Heating mantle - hemispherical, to fit 500 mL or 1000 mL round bottom flask (Cal-Glass LG-8801-112, or equivalent).

6.2.2.5. Variable transformer - Powerstat (or equivalent), 110 volts, 10 amps.

6.2.3. Spatulas - Stainless Steel

6.2.4. Soxtherm extraction apparatus (Gerhardt SE416 or equivalent), including glass thimble holders, glass beakers, and gaskets.

6.3. Filtration Apparatus

6.3.1. Sodium sulfate, granular anhydrous

6.3.2. Pyrex glass wool. (pre-rinsed with methylene chloride)

6.3.3. Glass funnel - 125 - 250 mL.

6.3.4. Glass fiber filter paper (Whatman GF/D, or equivalent).

6.3.5. Drying Column - 15 to 20 mm i.d. Pyrex chromatographic column equipped with coarse glass frit or glass wool plug.

6.3.6. Buechner funnel, 15 cm.

6.3.7. Pressure filtration apparatus - Vacuum filtration

6.4. Centrifuge Apparatus

6.4.1. Centrifuge - Capable of rotating 500 mL centrifuge bottles or 15 mL centrifuge tubes at 5000 rpm minimum

6.4.2. Centrifuge tubes - 12-15 mL, with screw caps, to fit centrifuge

6.5. Concentration Apparatus

6.5.1. Rotary evaporator – (Büchi R210 or equivalent) equipped with a variable temperature water bath.

6.5.1.1. A vacuum source is required for use of the rotary evaporator. It must be equipped with a shutoff valve at the evaporator, and preferably, have a vacuum gauge.

6.5.1.2. A recirculation water pump and chiller are recommended, as the use of tap water for cooling the evaporator wastes large volumes of water, and can lead to inconsistent performance because water temperatures and pressures vary.

6.5.1.3. Round bottom flasks - 500 mL and 1000 mL or larger, with ground glass fitting compatible with the rotary evaporator.

6.5.2. Nitrogen blow down apparatus - installed in a fume hood.

6.5.3. Sample vials - 2-5 mL with Teflon-lined screw cap and 200 uL auto-injector insert vials with septum lined screw caps.

7. REAGENTS AND STANDARDS

7.1. Reagents for extraction procedures.

All reagents must be ACS reagent grade or better unless otherwise specified.

7.2. pH adjustment and back extraction

7.2.1. Sodium hydroxide - Dilute 50 mL of 20 N NaOH with 50 mL reagent water.

7.2.2. Sulfuric acid - Reagent grade (specific gravity 1.84)

7.3. Solution drying and evaporation

7.3.1. Solution drying - Sodium sulfate, reagent grade, granular anhydrous (Baker 3375, or equivalent), rinsed with methylene chloride (20 mL/g) and stored in a pre-cleaned glass bottle with a screw cap that prevents moisture from entering.

7.3.2. Prepurified nitrogen, reagent grade

7.4. Extraction Solvents: Acetone, toluene, hexane, dodecane, iso-octane, nonane, methanol and methylene chloride (DCM).

7.5. Absorbents for sample cleanup

7.5.1. Silica gel

7.5.1.1. Activated silica gel - Silica Gel 60-Em Science7734-4, 70-230 mesh, rinsed with methylene chloride, baked at 180ºC for one hour minimum, cooled in a desiccator, and stored at 130°C in a covered flask.

7.5.1.2. Acid silica gel (44 percent w/w) - Thoroughly mix 24 mL (44g) of concentrated sulfuric acid with 56.0 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a screw-capped bottle with a Teflon-lined cap.

7.5.2. Alumina—the standard alumina cleanup procedure employs acidic alumina only. Basic alumina may be substituted or added to the cleanup procedure on a project specific basis, provided that the laboratory can meet the QA/QC requirements specified in Section 10. The same type of alumina must be used for all samples, including those used to demonstrate ongoing precision and accuracy (LCS).

7.5.2.1. Acid Alumina - ICN Super A. This alumina is purchased activated and can be used directly from the bottle. A column profile is performed for each new vendor; otherwise a laboratory control sample is used to re-verify new material from an existing vendor.

7.5.3. Mercury: triple distilled. (Mallinckrodt Baker, Inc. or equivalent)

7.6. Reference matrices

7.6.1. Reagent water - Water in which the PCBs and interfering compounds are not

detected at above ½ the reporting limit by this method.

7.6.2. High solids reference matrix – sodium sulfate.

7.6.3. Filter paper or extraction thimble - Glass fiber filter papers or extraction thimbles in which the PCBs and interfering compounds are not detected by this method.

7.6.4. Other matrices - This method may be verified on any matrix if the following criteria are met. Ideally, the matrix should be free of the PCBs, but in no case shall the background level of the PCBs in the reference matrix exceed three times the minimum levels given in Table II (CC1). If low background levels of the PCBs are present in the reference matrix, the spike level of the analytes used in Table III should be increased to provide a spike-to-background ratio in the range of 1:1 to 5:1.

7.6.5. Tissue reference matrix – Vegetable oil and sodium sulfate.

7.7. Standard solutions - Purchased as solutions or mixtures with certification to their purity, concentration and authenticity, or prepared from materials of known purity and composition. If compound purity is 98 percent or greater, the weight may be used without correction to compute the concentration of the standard. When not being used, standards are stored in the dark in screw-capped vials with Teflon-lined caps in a refrigerator at 3 ± 3 degrees C. A mark is placed on the vial at the level of the solution so that solvent evaporation loss can be detected. If solvent loss has occurred, the solution should be replaced.

7.7.1. Sealed ampoules may be used until the manufacturer's expiration date is exceeded.

7.7.1.1. If no expiration date is provided, then the expiration date will be 10 years from the date the ampoule is opened.

7.7.1.2. The solvent level should be monitored prior to each use to assure there has been no concentration of the standard over time.

7.7.2. All calibration, daily isotope dilution analytes, daily clean up isotope dilution analytes, and daily spiking solutions are stable for one year from preparation.

7.7.2.1. After one year, solutions may be re-verified. The re-verified solution may be used for an additional year, or until there is evidence of compound degradation or concentration.

7.7.2.2. The re-verification must be performed using an unexpired, not previously re-verified solution from a second lot or second vendor.

7.8. Stock solutions

7.8.1. Preparation - Prepare in isooctane or equivalent solvent per the steps below or purchase as dilute solutions (Cambridge Isotope Laboratories, Cambridge, MA, or equivalent).

7.8.2. Stock standard solutions are prepared from dilutions of neat solutions. Dilutions are performed in volumetric flasks and transferred to a clean vial or amber glass bottle with Teflon-lined cap.

7.9. Stock standard solutions should be checked for signs of degradation prior to the preparation of calibration of performance test standards. Reference standards that can be used to determine the accuracy of calibration standards are available from Cambridge Isotope Laboratories.

7.10. Secondary standard - Using stock solutions, prepare secondary standard solutions containing the compounds and concentrations shown in Table I in dodecane.

7.11. Labeled compound stock standard - From stock standard solutions prepared as above, or from purchased mixtures, prepare this standard to contain the labeled compounds at the concentrations shown in Table I in iso-octane.

7.12. Isotope Dilution Analytes (IDA) - Prepare at the concentration shown in Table I in iso-octane.

7.13. Surrogate Standard (SU) - Prepare at the concentration shown in Table I in iso-octane.

7.14. Internal Standard (IS) - Prepare at the concentration shown in Table I in dodecane.

7.15. Native spike solution (SP) - Used for determination of ongoing precision and accuracy, in the form of a laboratory control sample (LCS). This solution contains the analytes and labeled compounds at the concentrations listed in Tables I and III in isooctane.

7.16. Standard solutions will be periodically assayed against reference standards. Continued use of standard solutions past the initially indicated expiration date is acceptable if concentrations are verified versus the reference standard. Upon acceptable verification, a new expiration/evaluation date will be noted in the standards logbook.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. The sample collection, shipping, handling, and chain-of-custody procedures are not described in the document. The complexity of the method is such that, in order to obtain reliable results, testers should be trained and experienced with sampling and preservation procedures.

8.2. There are no demonstrated maximum holding times associated with the PCBs in aqueous, solid, semi-solid, tissues, or other matrices. If stored in the dark at 0-6°C, and

preserved if required, aqueous samples may be stored for up the one year. Similarly, if stored in the dark at <-10 °C, solids, semi-solid, multi-phase, and tissue samples may be stored for up to one year.

8.3. All extracts must be stored capped at <-10°C and completely analyzed within one year of extraction. This holding time is consistent with EPA SOW CBC01.2.(Ref 16.5).

9. QUALITY CONTROL

9.1. One method blank must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. The method blank is an aliquot of reference matrix processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a Non-Conformance memo, then implemented when target analytes are detected in the method blank above the acceptance limit or when surrogate recoveries are outside control limits. The associated samples will be evaluated for adverse impact, and flagged or qualified as appropriate. Re-extraction of the blank, other batch QC, and the affected samples are required when the method blank is deemed unacceptable. For any analyte detected in the blank in any of the homologous series of PCBs, the detection limit in the samples analyzed with that blank for the specific isomer or the total for that homologous series is increased to 5 times of the contamination level. Alternatively, both QC and sample results may be reported and qualified as necessary.

9.1.1. Certain programs, such as DOD, may require a more stringent evaluation of the method blank, for instance, that the blank not contain any analytes of interest at a concentration greater than ½ the reporting limit.

9.2. A laboratory control sample (LCS) must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. The LCS is an aliquot of laboratory matrix (e.g. reagent water, Ottawa sand, sodium sulfate, extraction thimble, filter paper, etc.) spiked with 100 uL of Isotope Dilution Analyte fortification solution (Table 1) and 100 uL of Native Standard fortification solution (Table III). The LCS must be processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a Non-Conformance memo, then implemented when recoveries of any spiked analyte is outside 50-150%, or the control limits provided on the LIMS, or by the client. The associated samples will be evaluated for adverse impact, and flagged or qualified as appropriate. Re-extraction of the blank, other batch QC, and the affected samples are required when the LCS is deemed unacceptable

9.3. A matrix spike/matrix spike duplicate (MS/MSD or MS/SD) pair may be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. MS/MSD are analyzed at the request of the client. An MS/MSD pair is aliquots of a selected field sample spiked with analytes of known identity and concentration. The

MS/MSD pair must be processed in the same manner and at the same time as the associated samples. Spiked analytes must be within control limits 50-150%, or the control limits provided on the LIMS, or by the client. The result obtained from MS and MSD samples analysis should agree within 50 percent relative difference. Corrective actions must be documented on a Non-Conformance memo. Outliers with recoveries or precision outside control limits will be flagged and narrated as appropriate.

10. CALIBRATION

10.1. On a monthly basis, calibrate any auto-pipettes to be used in accordance with SOP WS-QA-0004.

10.2. On a daily basis, calibrate any balances to be used in accordance with SOP WS-QA-0041.

11. PROCEDURE

One time procedural variations are allowed only if deemed necessary in the professional judgment of a supervisor to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Non-Conformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Non-Conformance Memo shall be filed in the project file.

Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.1. Grinding or Blending of Fish Samples.

If not otherwise specified by the client, the whole fish (frozen) should be blended or ground to provide a homogeneous sample. The use of a stainless steel meat grinder with a 3- to 5-mm hole size inner plate is recommended. In some circumstances, analysis of fillet or specific organs of fish may be requested by the client. If so requested by the client, the above whole fish requirement is superseded. Please refer to SOP WS-WI-0018 for further grinding procedure.

WARNING: Hearing protection must be worn when grinding samples.

11.2. Phase Separation

Phase separation on very wet (>25 percent water) soil and sediment samples may be accomplished as follows: Place a 50 g portion in a suitable centrifuge bottle and centrifuge for 30 minutes at 2,000 rpm. Remove the bottle from the centrifuge and mark the interface level on the bottle. Estimate the relative volume of each phase. With a disposable pipette, transfer the liquid layer into a clean bottle. Mix the solid with a stainless steel spatula and remove a portion to be weighed and analyzed (percent moisture determination, extraction). Return the remaining solid portion to the original

sample bottle (if empty) or to a clean sample bottle that is properly labeled, and store it as appropriate. Analyze the solid phase by using only the soil and sediment method. Take note of the estimated volume of liquid before disposing of the liquid as a liquid waste.

WARNING: Finely divided soils and sediments contaminated with PCBs are hazardous because of the potential for inhalation or ingestion of particles containing PCBs. Such samples should be handled in a confined environment (i.e., a closed hood or a glove box).

11.3. Sample Pre-Treatment

11.3.1. Paper pulp sludges are generally air-dried and ground prior to extraction by either Soxhlet (Section 11.4) or Soxtherm (Section 11.5). Because of the drying procedure, a Dean-Stark water separator may or may not be used for extraction.

11.3.2. Non-Paper pulp sludges are extracted as-is using either Soxhlet (Section 11.4) or Soxtherm (Section 11.5) techniques.

11.3.2.1. Sludges. Paper pulp sludges are generally air-dried and ground. Because of the drying procedure, a Dean-Stark water separator may or may not be used for extraction. Extraction is generally done by Soxhlet with 200-300 mL of toluene.

11.3.2.2. Non-Paper pulp sludges are extracted with 200-300 mL of toluene.

11.3.2.3. Soxhlet sample for a minimum of 16 hours. Cool the sample, then filter the toluene extract, if needed, through a glass-fiber filter or equivalent into a round-bottom flask. Rinse the filter with 10 mL toluene, and combine the extract and rinsate. Concentrate the combined solutions to near dryness on a rotary evaporator at 70°C. Use of an inert gas to concentrate the extract is also permitted. Proceed with Section 11.10 as necessary.

11.3.2.4. Still-Bottom/Fuel Oil. All organic liquids, fuel oils, and solids that will dissolve in a solvent and are treated as a solvent dilution will be prepared by dissolving a nominal 1g of sample in 1-10 mL of an appropriate solvent. Spike with appropriate IDA solution and proceed with Section 11.10 as necessary.

11.3.2.5. Fly Ash. Weigh a 2-10 g sample aliquot into a glass fiber extraction thimble. Add 100 uL of the IDA solution. The samples are Soxhlet extracted with toluene for a minimum of 16 hours. 100uL of dodecane can be used as a keeper in the samples, if the lower column cleanup is planned. Concentrate the toluene extract solutions to near dryness on a rotary evaporator at 70°C and 25

pounds vacuum at 120-150 RPM. Proceed with Section 11.10 as necessary.

NOTE: As an option, sodium sulfate may be mixed with the samples to remove moisture before sample extraction.

11.3.3. Solids/Tissues -- Weigh a 2-10 g sample aliquot into a glass fiber extraction thimble. Add 100 uL of IDA solution. Extract the samples in a Soxhlet with a Dean-Stark apparatus with Toluene for a minimum of 16 hours. The solvent must cycle completely through the system at least five times per hour. Concentrate by rotary evaporator at 70ºC and 25 psi vacuum at 120-150 RPM.

11.3.3.1. If tissues requiring % Lipids are to be extracted, for each sample weigh the vessel with label and boiling chips. Record the mass on the bench sheet. When the extraction is complete, proceed to Section 11.6.

NOTE: The matrix for the tissue method blank consists of 9 g of sodium sulfate and 0.25 g of canola oil.

11.4. Soxhlet Extraction (Solids, Tissues, Sludges, and Wipes).

11.4.1. Percent moisture is determined in accordance with SOP WS-OP-0013.

11.4.2. Internal Standard Addition. A 100 uL aliquot, or 2 ng equivalent, of the internal standard mixture is added to all samples, regardless of sample size.

WARNING: Open the chiller supply valves about 15 minutes before turning on the heating element and ensure that all of the condensers are cold before you turn the heating element on. Check all of the condensers about 15 minutes after starting the heating process to ensure that they are still cold and functioning properly. If this cleaning cycle is to be left unattended (e.g., overnight) the first chemist to arrive the next morning is to check all condensers to ensure that they are still cold and functioning properly.

11.4.3. Sludges. Paper pulp sludges are generally air-dried and ground. Because of the drying procedure, a Dean-Stark water separator may or may not be used for extraction. Extraction is generally done by Soxhlet with 200-300 mL of toluene.

11.4.3.1. Non-Paper pulp sludges are extracted with 200-300 mL of toluene.

11.4.3.2. Soxhlet sample for a minimum of 16 hours. Cool the sample, then filter the toluene extract, if needed, through a glass-fiber filter or equivalent into a round-bottom flask. Rinse the filter with 10 mL toluene, and combine the extract and rinsate. Concentrate the combined solutions to near dryness on a rotary evaporator at 70°C.

Use of an inert gas to concentrate the extract is also permitted. Proceed with Section 11.8 as necessary.

11.4.4. Still-Bottom/Fuel Oil. All organic liquids, fuel oils, and solids that will dissolve in a solvent and are treated as a solvent dilution will be prepared by dissolving a nominal 1g of sample in 1-10 mL of an appropriate solvent. Spike with appropriate internal standards and proceed with Section 11.10 as necessary.

11.4.5. Fly Ash. Weigh a 2-10 g sample aliquot into a glass fiber extraction thimble. Add 100 uL of the internal standard mixture. The samples are Soxhlet extracted with toluene for a minimum of 16 hours. 100uL of dodecane can be used as a keeper in the samples, if the lower column cleanup is planned. Concentrate the toluene extract solutions to near dryness on a rotary evaporator at 70°C and 25 pounds vacuum at 120-150 RPM. Proceed with Section 11.10 as necessary.

NOTE: As an option, sodium sulfate may be mixed with the samples to remove moisture before sample extraction.

11.4.6. Solids/Tissues -- Weigh a 2-10 g sample aliquot into a glass fiber extraction thimble. Add 100 uL of internal standard solution. Extract the samples in a Soxhlet with a Dean-Stark apparatus with toluene for a minimum of 16 hours. The solvent must cycle completely through the system at least five times per hour. Concentrate by rotary evaporator at 70ºC and 25 psi vacuum at 120-150 RPM.

11.4.6.1. If tissues requiring % Lipids are to be extracted, for each sample weigh the vessel with label and boiling chips. Record the mass on the bench sheet. When the extraction is complete, proceed to 11.6.

NOTE: The matrix for the tissue method blank consists of 9 g of sodium sulfate and 0.25 g of canola oil.

11.5. Soxtherm Extraction (Solids, Tissues, Sludges, and Wipes)

11.5.1. Prior to loading samples, run the system through 2 cleaning cycles (approximately one hour each).

11.5.2. After pre-extraction, cool, and disassemble the apparatus, and rinse with acetone.

11.5.3. If tissues requiring % Lipids are to be extracted, for each sample weigh the vessel with label and boiling chips. Record the mass on the bench sheet. (If using the Soxtherm, weigh the 35 mm culture tube).

11.5.4. Weigh a well-mixed aliquot of each sample (10 g, unless otherwise specified) into a clean Soxhlet thimble. Record the mass to the nearest 0.01g. Use sodium sulfate for the batch QC (MB, LCS) for solids, and a mixture of 9 g sodium sulfate and 0.25 g canola oil for the batch QC for tissue matrices.

11.5.5. In the case of wipes, place the entire wipe sample into the Soxhlet apparatus (no thimble needed), including any liquid present with the sample. Use pre-cleaned wipes for the batch QC samples.

11.5.6. Place the thimble into the Soxtherm apparatus.

11.5.7. Spike all samples with 100 uL of IDA solution (2 ng), for a final concentration of 200 pg/g (based on a 10 g sample).

11.5.8. Spike the LCS (and MS/MSD, if present) with 100 uL of native spike.

11.5.9. Reassemble the pre-extracted apparatus and add a fresh charge (150 mL) of toluene to the apparatus and boiling stones.

11.5.10. Program the system to boil for 1 hour, and reduce the toluene volume by 70-90 mL (volume < volume of the thimble).

11.5.11. Continue the extraction for one hour fifteen minutes, reducing the toluene volume by another 15 mL.

11.5.12. After refluxing, allow the apparatus to cool.

11.5.13. Pour the samples into round bottom flasks. If %lipids is required proceed to Section 11.6. If % lipid is not required, and an alumina column cleanup (Section 11.10.4) is planned, add 100uL of dodecane to the sample as a solvent keeper.

11.5.14. Proceed with Section 11.10 (Cleanups) as necessary.

11.6. Fish Tissue Lipid Content Determination

The percent lipid of fish samples is determined as follows:

11.6.1. Concentrate the extract from Sections 11.3.3, 11.4.6 or 11.5.13 on a rotary evaporator until volume is low enough to transfer to a culture tube (approx. 5-10mLs) that has been pre-weighed with label. Transfer the sample into the culture tube and continue blowing down the sample until constant weight is attained. An alternative process employing a VOA vial for weighing may be used for samples with expected low lipid amounts. The percent lipid is calculated using the following expression:

Equation 1

$$\text{Percent Lipid} = \frac{\textit{Weight of residue from extraction (g)}}{\textit{Weight of fish tissue portion (g)}} \times 100$$

11.6.2. Proceed with Section 11.10 (Cleanups) as necessary.

11.7. Aqueous Samples.

11.7.1. Determine the sample volume by placing the sample bottle on a top-loading balance and taring the balance. Pour the entire sample (approximately 1 L) into a 2 L separatory funnel. Reweigh the empty bottle and record the sample weight. Record the sample weight to the nearest 1 gram.

11.7.2. Add 100 mL methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel. Add 100 uL of IDA solution to the samples in the separatory funnel. Each aliquot of spike mixture is added similarly. Extract the sample by shaking the funnel for two minutes with periodic venting. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. Extraction is repeated two additional times with 100 mL each of methylene chloride

NOTE: Mechanical techniques could include any or all of the following: running sample through glass-wool, centrifuge, add 50mLs of 10N NaOH, or let sit longer for separation.

WARNING: Methylene chloride creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the sample container has been sealed and inverted. Vent into hood away from analysts and other samples.

WARNING: Separatory funnel extraction is a high risk activity. Analyst will wear a face shield over safety glasses/goggles for this extraction. Alternatively, the extraction can take place behind a closed hood sash.

11.7.2.1. Dry extract with sodium sulfate: Place glass wool in a precleaned filter funnel. Rinse glass wool with DCM and load funnel with DCM-rinsed Na2SO4. Pour extract through Na2SO4 to remove water. Rinse Na2SO4 with fresh DCM and collect in round bottom flask.

11.7.2.2. Transfer the extract to a 500-mL round-bottom and concentrate on a rotary evaporator at 65ºC and <15 lbs vacuum at 120-150 RPM. Proceed to Section 11.10 for cleanup options as needed.

NOTE: If no lower column cleanup is required do not add dodecane as a solvent keeper.

WARNING: Use of vacuum systems creates a significant risk of implosion. Thoroughly inspect all glassware and do not use any that has been chipped, rubbed, cracked, or marred in any fashion.

WARNING: Ensure that the exhaust line from the vacuum pump is secured well inside of a fume hood so that it cannot fall out of the hood.

11.8. Air train sample – based on Method CARB 428 (Option 1).

There are two options for the preparation of air train sample. The first option is all fractions combined for a single analysis, and the second is to prepare and analyze separate front and back-half extracts. Below is Option 1, the Single composite of all air train fractions.

11.8.1. Preparation of Extraction Thimble

Place a glass extraction thimble into the Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it. Remove the extraction thimble system and place it in a glass beaker for air drying and for catching rinses. Alternatively, the thimbles may be used directly from the box if the thimbles have been shown to be free of PCBs or interfering compounds at or above the project required reporting limits.

11.8.2. Preparation of Container No. 1 (filter)

Place the filter and all particulate matter from Container No. 1 into the cleaned extraction thimble.

11.8.3. Preparation of Adsorbent Cartridge

Suspend the adsorbent module directly over the extraction thimble containing the associated filter. The glass frit of the module should be positioned up. Add a small amount of acetone to the module and discharge the XAD-2 resin into the thimble by using a nitrogen blowing apparatus. Rinse the walls of the module with acetone to remove any excess resin, collect the rinse in the thimble. Rinse the module with toluene and collect the rinses in the thimble containing the XAD-2 resin and filter.

11.8.4. Preparation of Container No. 2 (Front and Back-half Acetone and Methylene Chloride rinses)

Transfer the solvent to a round bottom flask. Rinse the sample container 3 times with methylene chloride and add these to the round bottom flask. Concentrate the solvent to a volume of about 1-5 mL using a rotary evaporator, at a temperature of 60ºC and <10 inches of vacuum at 120-150 RPM.

11.8.5. Preparation of Container No. 3 (Front and Back-half Toluene rinses)

This step can be done one of two ways as dictated by the client:

11.8.5.1. Option 1- Add the toluene rinse to the round bottom flask previously used to concentrate Container No. 2. Rinse the samples container three times with toluene and add the rinses to the round bottom flask. Concentrate the solvent to about 1-5 mL using a rotary evaporator at a temperature of 70ºC and 25 inches of vacuum. Add the rinses to the Soxhlet containing the corresponding filter and XAD resin portions.

11.8.5.2. Option 2- Add the toluene rinse to a pre-cleaned round bottom flask. Rinse the sample container three times with toluene and collect rinses in the round bottom flask. Concentrate the solvent to about 1-5 mL using a rotary evaporator at a temperature of 70°C and 25 inches of vacuum. Do not add the concentrated solvent to the Soxhlet containing the corresponding filter and XAD, instead add 100 uL of internal standard (IS) and analyze as a separate sample.

11.8.6. Extraction and Concentration.

11.8.6.1. Surrogate compounds should have been added to the adsorbent cartridge prior to sample collection.

11.8.6.2. Place the extraction thimble containing the filter, XAD resin, and solvent rinses into the Soxhlet extractor. Rinse the beaker three times with toluene and add the rinses to the Soxhlet. Add toluene to the round bottom flask until it is about 2/3 full. Add several Teflon boiling chips to the round bottom flask and assemble the Soxhlet apparatus.

11.8.6.3. Add 100 uL of IDA standard to the thimble, connect the condenser, and adjust the heat source to cause the extractor to cycle approximately three times per hour for a minimum of 16 hours.

Note: Additional 100 uL volume of IDA standard may be added per split (i.e. ½ archive = 200 uL total; 1/3 archive, 1/3 Method 0023A, 1/3 1668A = 300 uL; etc.)

11.8.6.4. Allow the Soxhlet to cool and 100 uL of dodecane may be added as a solvent keeper.

11.8.6.5. Concentrate the extract to near dryness using a rotary evaporator at 70ºC and 25 inches of vacuum. Proceed with clean up or splitting of the samples based on client requirements.

WARNING: Use of vacuum systems creates a significant risk of implosion. Thoroughly inspect all glassware and do not use any that has been chipped, rubbed, cracked, or marred in any fashion.

WARNING: Ensure that the exhaust line from the vacuum pump is secured well inside of a fume hood so that it cannot fall out of the hood.

Option 2- Separate Front and Back-half fractions. The Front-half consists of the filter and front-half solvent rinses, the Back-half consists of the XAD resin and Back-half rinses.

11.8.7. Preparation of Container No. 1 (filter)

Place the filter and all particulate matter from Container No. 1 into the cleaned extraction thimble.

11.8.8. Preparation of the Front-half acetone and methylene chloride rinse

Transfer the solvent to a round bottom flask. Rinse the sample container 3 times with methylene chloride and add these to the round bottom flask. Concentrate the solvent to a volume of about 1-5 mL, using a rotary, at a temperature of 60ºC and <10 inches of vacuum at 120-150 RPM. Quantitatively transfer the solvent to the Soxhlet apparatus containing the corresponding filter fraction.

11.8.9. Preparation of the Front-half toluene rinse

Add the toluene rinse to the round bottom flask previously used to concentrate the acetone/methylene chloride rinses. Rinse the samples container three times with toluene and add the rinses to the round bottom flask. Concentrate the solvent to about 1-5 mL using a rotary evaporator at a temperature of 70ºC and 25 inches of vacuum. Add the rinses to the Soxhlet containing the corresponding filter and acetone/methylene chloride fractions.

11.8.10. Preparation of Adsorbent Cartridge

Suspend the adsorbent module directly over a pre-cleaned extraction thimble. The glass frit of the module should be positioned up. Add a small amount of acetone to the module and discharge the XAD-2 resin into the thimble by using a nitrogen blowing apparatus. Rinse the walls of the module with acetone to remove any excess resin, collect the rinse in the thimble. Rinse the module with toluene and collect the rinses in the thimble containing the XAD-2 resin.

11.8.11. Preparation of the Back-half acetone and methylene chloride rinse

Transfer the solvent to a round bottom flask. Rinse the sample container 3 times with methylene chloride and add these to the round bottom flask. Concentrate the solvent to a volume of about 1-5 mL, using a rotary, at a temperature of 60ºC and <10 inches of vacuum at 120-150 RPM. Quantitatively transfer the solvent to the Soxhlet apparatus containing the corresponding XAD resin fraction.

11.8.12. Preparation of the Back-half toluene rinse

Add the toluene rinse to the round bottom flask previously used to concentrate the acetone/methylene chloride rinses. Rinse the samples container three times with toluene and add the rinses to the round bottom flask. Concentrate the solvent to about 1-5 mL using a rotary evaporator at a temperature of 70ºC and 25 inches of vacuum. Add the rinses to the Soxhlet containing the corresponding XAD resin and acetone/methylene chloride fractions.

11.9. There are several useful methods to decrease or eliminate emulsion in aqueous samples when extracting with DCM. These methods may include stirring with a pipette to manually breakup the emulsions or to transfer the sample into centrifuge tubes and centrifuge at approximately 3000 RPM. The most useful method is to use a 1:1 $NaOH/H_2O$ solution to change the pH enough to disrupt the emulsion phase, which works 90% of the time. The following procedure describes how to prepare and use the solution to decrease or eliminate emulsions in aqueous samples during the liquid/liquid extraction step.

11.9.1. Preparing the solution:

Add 1.0 L of reagent grade NaOH solution to an empty 2.0 L NaOH container. Then add 1.0 L of DI H2O to the container and leave the container in secondary containment with the lid off.

WARNING: The solution will begin to heat so let the solution stand until equilibrium is met and the solution is at room temperature.

When this process is complete, the solution will then be ready for use in the samples.

11.9.2. Using the solution to decrease emulsions:

11.9.2.1. Check the pH of the sample to make sure pH is between 3 and 7, then consult supervisor and client for instructions. Pour approximately 100 mL of 1:1 $NaOH/H_2O$ into a 1.0 L AGB.

11.9.2.2. Pour the solution with DCM back into the same 2.0 L separatory funnel and drain the DCM phase through Na_2SO_4 into a 500mL round bottom. Empty the aqueous waste into the LLE waste drum.

11.10. Cleanup: Depending on the complexity of the matrix, the following clean-up procedures may be employed as necessary or per client requirements.

11.10.1. Add 100 uL of Surrogate Standard to each extract.

11.10.2. Option C (Acid only) (Required for all solid and tissue matrices):

11.10.2.1. Partition the extract in 50-125 mL of hexane against 40 mL concentrated H2SO4 in a separatory funnel. Shake for two minutes. Remove and discard the sulfuric acid layer (bottom).

Repeat the acid washing until no color is visible in the acid layer (perform a maximum of four acid washings).

NOTE: Additional rinses may be performed against sodium hydroxide or reagent water if deemed necessary by the laboratory management.

WARNING: Shaking with a concentrated caustic is a high-risk activity. Analyst must wear a face shield over safety glasses/goggles, or the shaking must take behind a closed hood sash.

11.10.3. Silica Gel Column Cleanup. **(Required for all samples)**

11.10.3.1. Add a plug of glass wool to a 20 mm ID disposable column and add 2 grams of activated silica gel, 4 grams of acidic silica gel, 2 grams of activated silica gel, and 1 cm of sodium sulfate.

11.10.3.2. Pre-rinse the column with at least 20 mL of methylene chloride followed by at least 20 mL of hexane.

11.10.3.3. Add the sample extract to the column, and rinse the sample container with 2 x 2 mL hexane rinses. Add the rinses to the column.

11.10.3.4. Elute the column with hexane and collect a total of 90 mL of hexane.

11.10.3.5. Reduce the volume to about 2 mL under nitrogen and proceed with alumina column cleanup if deemed necessary.

11.10.4. Alumina Column Cleanup. (Required for all sediment and tissue extracts)

11.10.4.1. Put a small plug of glass wool in a 16 mm ID column and add 6 grams of acid alumina followed by 1 cm of sodium sulfate.

11.10.4.2. Pre-rinse the column at least 20 mL of hexane.

11.10.4.3. Transfer the sample (in 2 mL hexane) to the acid alumina column. Rinse sample flask with 2 x 2 mL hexane, transfer to acid alumina column.

11.10.4.4. Elute the column with 10 mL of hexane and discard.

11.10.4.5. Elute the column with 30 mL of 65% methylene chloride/hexane and collect.

11.10.5. Sulfur Removal with Elemental Mercury. **(Optional Cleanup)** The entire sample is used for this process. If the sulfur concentration is such that crystallization occurs in the concentrated extract, residual rings of sulfur appear, centrifuge the extract to settle the crystals, and carefully draw off the sample extract with a disposable pipette, leaving the excess sulfur in the centrifuge tube. Transfer the extract to a clean concentrator tube before proceeding with further sulfur cleanup.

Note: Use mercury sparingly in order to minimize exposure and disposal costs.

11.10.5.1. Transfer 2 mL of sample extract into a clean concentrator tube or Teflon sealed vial.

11.10.5.2. Add one to three drops (about 0.25mL) of mercury to the extract vial and seal.

WARNING: Only nitrile gloves may be used when working with mercury and organic solvents at the same time.

11.10.5.3. Shake well for 15-30 seconds.

11.10.5.4. If black precipitate forms, sulfur was present. Centrifuge, then transfer the supernatant to a clean test tube and repeat steps 11.10.5.2 and 11.10.5.3. Do this until relatively little precipitate remains, or a maximum of five sulfur cleanups has been performed.

WARNING: Do NOT centrifuge glass tubes containing mercury. Due to the density of the mercury, the test tube could break in the centrifuge.

11.10.5.5. If no precipitate is present, remove the extract from the mercury using a disposable pipette and transfer to a clean vial. Rotate the mercury waste out of the laboratory to the Hazardous Waste storage area for lab pack disposal.

11.11. Final Voluming

11.11.1. Reduce the sample volume under nitrogen and proceed to RS.

11.11.2. Add 20 uL of internal standard in dodecane to a vial.

11.11.3. Transfer the sample contents to the vial containing the internal standard with several rinses of hexane.

11.11.4. Reduce under nitrogen to 20 uL.

11.11.5. Transfer to an injection vial and cap.

11.12. Analysis

11.12.1. The extract is ready for analysis by WS-ID-0013.

12. CALCULATIONS/DATA REDUCTION

Not applicable

13. METHOD PERFORMANCE

13.1. Method Detection Limit

Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in WS-QA-0006. MDL are available in the Quality Assurance department.

13.2. Initial Demonstration

Each analyst must make a one time initial demonstration of capability for each individual method. Demonstration of capability for both soils and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid level calibration standard.

13.2.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the historical acceptance criteria.

13.2.3. If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3. Training Qualification

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14. POLLUTION CONTROL

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

14.2. Do not allow waste solvent to evaporate in fume hoods. All solvent waste is stored in capped containers unless transfers are being made.

14.3. The use of rotary evaporator systems to concentrate sample extracts significantly reduces the solvent released into the atmosphere.

15. WASTE MANAGEMENT

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples, and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP WS-EHS-0001. The following waste streams are produced when this method is carried out.

15.1. Assorted solvent and methylene chloride from glassware rinsing, glass fiber and sodium sulfate pre-rinsing, and extract rotary evaporator concentration. Collect the waste solvents in tripours during use. Empty the tripours into a 1-liter to 4-liter carboy at the fume hood. When the carboy is full, or at the end of your shift, whichever comes first, empty the carboy into the steel solvent drum in the H3 closet. When the drum is full to between two and six inches of the top, or after no more than 75 days, move the steel drum to the waste collection area for shipment.

15.2. Miscellaneous disposable glassware, chemical resistant gloves, bench paper and similar materials that may or may not be contaminated/hazardous. Place contaminated materials into a yellow landfill contaminated lab trash bucket. When the bucket is full or after no more than one year, tie the plastic bag liner shut and put the dry lab trash into the appropriate steel dry lab trash collection drum in the H3 closet. When the drum is full or after no more than 75 days, move it to the waste collection area for shipment.

15.3. Extracted PUF filters, sodium sulfate, silica gel, alumina, carbon XAD-2 resin, paper funnel filters, glass wool, thimbles, fish/crawfish, ash and soil contaminated with various solvent and eluents. Dump the materials into an orange “incinerate” extracted soil bucket. When the bucket is full or at the end of the day, tie the plastic bag liner shut and put the lab trash into the incinerate steel extracted solids collection drum in the H3 closet. When the drum is full or after no more than 75 days, move it to the waste collection area for shipment.

15.4. Extracted aqueous samples contaminated with methylene chloride and/or other organic solvents are collected at the fume hood in a 5-gallon or smaller carboy. If the samples are not at a neutral pH, add small quantities of sodium bicarbonate to bring the waste to neutral. Stir well. Once neutralized, immediately pour the carboy contents into a blue plastic LLE drum in the H3 closet. When full to between two and six inches of the top, or after no more than 75 days, move the LLE drum to the waste collection area for shipment.

15.5. Contaminated sulfuric acid used during Option C extract clean-up. Collect the used sulfuric acid in empty, 2.5-liter, plastic coated jars. When full or after no more than

one year, whichever comes first, transfer these jars to the waste collection area for shipment.

15.6. Contaminated mercury used during sulfur clean-up. Collect the used mercury in empty 8 ounce plastic jars. When full or after no more than one year, transfer the jar to the waste collection area for shipment.

16. REFERENCES/CROSS REFERENCES

16.1. State of California Air Resources Board Method 428: Determination of Polychlorinated Dibenzo-p-dioxin (PCDD), Polychlorinated Dibenzofuran (PCDF), and Polychlorinated Biphenyl Emissions from Stationary Sources, September 12, 1990.

16.2. EPA Method 1668: Toxic polychlorinated Biphenyls by Isotope Dilution High Resolution Gas Chromatography/High resolution Mass Spectrometry, March 1997.

16.3. Method 1668, Revision A (Method 1668A): Chlorinated Biphenyl Congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS, August 2003.

16.4. Method 1668C: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS, April 2010.

16.5. EPA SOW CBC01.2, Analysis of Chlorinated Biphenyl Congeners (PCBs)), December 2009.

17. METHOD MODIFICATIONS

17.1. Deviations from reference Method 1668A, Method 1668C, and CBC01.2.

17.1.1. Aqueous samples with < 1% solids are extracted as received, by separatory funnel. Samples with high solids content, > 1% solids, are either shaken well to thoroughly mix the sample followed by extraction by separatory funnel, or separated into two different samples for extraction and analysis, dependent upon client request.

17.1.2. Solid samples are extracted as received, with %-moisture determination performed simultaneously. Dry weight correction to results is applied at the time of data reporting.

17.1.3. Tissue samples are extracted using toluene.

17.1.4. The sample extract cleanup procedures are all optional, except where noted, and based on analyst judgment. The routine cleanup procedures include acidic silica gel and acidic alumina cleanup columns. The laboratory does not routinely use Florisil, GPC, or anthropogenic column cleanup procedures.

17.1.5. Soxtherms are used as an option of extracting that is not listed in the source method, The soxtherm are used instead of soxhlets and microwave.

18. ATTACHMENTS

18.1. Table 1 – Composition of the Sample Fortification Solutions

18.2. Table 2 – Instrument Calibration Solution Concentrations

18.3. Table 3 – Composition of the Matrix Spike Fortification Solution

19. REVISION HISTORY

19.1. WS-IDP-0013, Revision 3.0, Effective 09/12/2014

19.1.1. This SOP was revised to combine WS-IDP-0018 (PCB Preparation for Analysis by HR/GC/HRMS {Method 1668C}) and WS-IDP-0013 (PCB Preparation for Analysis by HR/GC/HRMS {Method 1668A}).

19.1.2. Section 11.6.1 – Inserted "Concentrate the extract from Section 11.3.6 or 11.4.12 on a rotary evaporator until volume is low enough to transfer to a culture tube (approx. 5-10mLs) that has been pre-weighed with label. Transfer the sample into the culture tube and continue blowing down the sample until constant weight is attained" as 1st sentence in section.

19.1.3. Section 11.10.5 – Inserted "The entire sample is used for this process. If the sulfur concentration is such that crystallization occurs in the concentrated extract, residual rings of sulfur appear…" at beginning of sentence.

19.1.4. Added Section 16.4 – "Method 1668C: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS, April 2010."

19.1.5. Added Section 16.5 – "EPA SOW CBC01.2, Analysis of Chlorinated Biphenyl Congeners (PCBs)), December 2009."

19.1.6. Editorial changes.

19.2. WS-IDP-0013, Revision 2.2, Effective 04/26/2013

19.2.1. Renamed Internal Standards to Isotope Dilution Analytes.

19.2.2. Renamed Recovery Standards to Internal Standards.

19.2.3. Editorial changes.

19.3. WS-IDP-0013, Revision 2.2, Effective 03/02/2012

19.3.1. Changed Section 11.5.3 from "1.0g canola oil" to "0.250g corn oil"

19.3.2. Editorial changes.

19.4. WS-IDP-0013, Revision 2.1, Effective 10/14/2011

19.4.1. Inserted Section 11.2 from SOP WS-IDP-0007 as Section 11.7 in this SOP (Aqueous w/filtrate).

19.4.2. Inserted Section 6.2.1.5 – "Glass fiber filters, Whatman GF-D, GF-F, GMF-150 or equivalent."

19.4.3. Editorial revisions.

TABLE I
Composition of the Sample Fortification Solutions

	Sample Fortification Solution Concentration (pg/uL in Isooctane)	Recovery Standard Solution (pg/uL in Dodecane)	Clean-up Recovery Standard Solution (pg/uL in Dodecane)
$^{13}C_{12}$-2-MonoPCB (1)	20	--	--
$^{13}C_{12}$-4-MonoPCB (3)	20	--	--
$^{13}C_{12}$-2,2-DiPCB (4)	20	--	--
$^{13}C_{12}$-2,5-DiPCB (9)	--	100	--
$^{13}C_{12}$-4,4'-DiPCB (15)	20	--	--
$^{13}C_{12}$-2,2',6'-TriPCB (19)	20	--	--
$^{13}C_{12}$-2,4,4'-TriPCB (28)	--	--	100
$^{13}C_{12}$-3,4,4'-TriPCB (37)	20	--	--
$^{13}C_{12}$-2,2',5,5'-TetraPCB (52)	--	100	--
$^{13}C_{12}$-2,2',6,6'-TetraPCB (54)	20	--	--
$^{13}C_{12}$-3,3',4,4'-TetraPCB (77)	20	--	--
$^{13}C_{12}$-3,4,4',5-TetraPCB (81)	20	--	--
$^{13}C_{12}$-2,2',4,5,5'-PentaPCB (101)	--	100	--
$^{13}C_{12}$-2,2',4,6,6'-PentaPCB (104)	20	--	--
$^{13}C_{12}$-2,3,3',4,4'-PentaPCB (105)	20	--	--
$^{13}C_{12}$-2,3,3'5,5'-PentaPCB (111)	--	--	100
$^{13}C_{12}$-2,3,4,4',5-PentaPCB (114)	20	--	--
$^{13}C_{12}$-2,3',4,4'5-PentaPCB (118)	20	--	--
$^{13}C_{12}$-2',3,4,4',5-PentaPCB (123)	20	--	--
$^{13}C_{12}$-3,3',4,4',5-PentaPCB (126)	20	--	--
$^{13}C_{12}$-2,2',3',4,4',5'-HexaPCB (138)	--	100	--
$^{13}C_{12}$-2,2',4,4',6,6'-HexaPCB (155)	20	--	--
$^{13}C_{12}$-2,3,3',4,4',5-HexaPCB (156)	20	--	--
$^{13}C_{12}$-2,3,3',4,4',5'-HexaPCB (157)	20	--	--
$^{13}C_{12}$-2,3',4,4',5,5'-HexaPCB (167)	20	--	--
$^{13}C_{12}$-3,3',4,4',5,5'-HexaPCB (169)	20	--	--
$^{13}C_{12}$-2,2',3,3',5,5',6-HeptaPCB (178)	--	--	100
$^{13}C_{12}$-2,2',3,4',5,6,6'-HeptaPCB (188)	20	--	--
$^{13}C_{12}$-2,3,3',4,4',5,5'-HeptaPCB (189)	20	--	--
$^{13}C_{12}$-2,2',3,3',4,4',5,5'-OctaPCB (194)	--	100	--
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OctaPCB (202)	20	--	--
$^{13}C_{12}$-2,3,3',4,4'5,5',6-OctaPCB (2025	20	--	--
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NonaPCB (206)	20	--	--
$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-NonaPCB (208)	20	--	--
$^{13}C_{12}$-DecaPCB (209)	20	--	--

TABLE 2
Instrument Calibration Solution Concentrations

Compound	IUPAC #(s)	Concentration (pg/uL in Dodecane)				
		CC1	CC2	CC3	CC4	CC5
Unlabelled Analytes						
MonoPCB	1,3	1	5	50	400	2000
DiPCB	4,15	1	5	50	400	2000
TriPCB	19,37	1	5	50	400	2000
TetraPCB	54,77,81	1	5	50	400	2000
PentaPCB	104,105,114,118,123,126	1	5	50	400	2000
HexaPCB	155, 156,157,167,169	1	5	50	400	2000
HeptaPCB	188,189	1	5	50	400	2000
OctaPCB	202,205	1	5	50	400	2000
NonaPCB	206,208	1	5	50	400	2000
DecaPCB	209	1	5	50	400	2000
Internal Standards						
^{13}C-MonoPCB	1,3	100	100	100	100	100
^{13}C-DiPCB	4,15	100	100	100	100	100
^{13}C-TriPCB	19,37	100	100	100	100	100
^{13}C-TetraPCB	54,77, 81	100	100	100	100	100
^{13}C-PentaPCB	104,105,114,118,123,126	100	100	100	100	100
^{13}C-HexaPCB	155,156,157,167,169	100	100	100	100	100
^{13}C-HeptaPCB	188,189	100	100	100	100	100
^{13}C-OctaPCB	202,205	100	100	100	100	100
^{13}C-NonaPCB	206,208	100	100	100	100	100
^{13}C-DecaPCB	209	100	100	100	100	100
Recovery Standards						
^{13}C-DiPCB	9	100	100	100	100	100
^{13}C-TetraPCB	52	100	100	100	100	100
^{13}C-PentaPCB	101	100	100	100	100	100
^{13}C-HexaPCB	138	100	100	100	100	100
^{13}C-OctaPCB	194	100	100	100	100	100
Cleanup Recovery Standards						
^{13}C-TriPCB	28	100	100	100	100	100
^{13}C-PentaPCB	111	100	100	100	100	100
^{13}C-HeptaPCB	178	100	100	100	100	100

TABLE 3
Composition of the Matrix Spike Fortification Solution

Compound (Unlabelled)	IUPAC #(s)	Concentration (pg/uL in isooctane)
MonoPCB	1,3	20
DiPCB	4,15	20
TriPCB	19,37	20
TetraPCB	54,77,81	20
PentaPCB	104,105,114, 118,123,126	20
HexaPCB	155, 156,157,167,169	20
HeptaPCB	188,189	20
OctaPCB	202,205	20
NonaPCB	206,208	20
DecaPCB	209	20

Title: Preparation of Samples for Tetra- through Octa Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS by Method 1613B [Method 1613B, DLM02.2]

Approvals (Signature/Date):

Elizabeth Koston Technical Manager	4/4/14 Date	Joe Schairer Health & Safety Manager / Coordinator	4/7/14 Date
Lisa Stafford Quality Assurance Manager	4/4/2014 Date	Robert Hrabak Laboratory Manager	4/8/14 Date

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1. SCOPE AND APPLICATION

1.1. The procedures outlined within this SOP are appropriate for the preparation of samples for the determination of 2,3,7,8-TCDD/TCDF and tetra-through-octa chlorinated dibenzo-p-dioxins and dibenzofurans associated with the Clean Water Act (as amended 1987); the Resource Conservation and Recovery Act (as amended 1986); and the Comprehensive Environmental Response, Compensation and Liability Act (as amended 1986). Specificity is provided for determination of the seventeen 2, 3, 7, 8-substituted polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). See Table 1 for list of analytes. Analysis is by SOP WS-ID-0007.

1.2. When undertaking projects for the Department of Defense (DOD), the relevant criteria in Policy WS-PQA-021, "DOD QSM and AFCEE QAPP Implementation" must be checked and incorporated.

2. SUMMARY OF METHOD

2.1. Stable isotopically labeled analogs of 15 of the PCDDs and PCDFs are added to each sample prior to extraction. Samples containing coarse solids are prepared for extraction by grinding or homogenization. Drinking water samples are extracted with methylene chloride using separatory funnel procedures. Non drinking water type samples are filtered and then extracted with methylene chloride using separatory funnel procedures; the particulates from the water samples, soils, and other finely divided solids are extracted using a combined Soxhlet (or equivalent) extraction/Dean-Stark azeotropic distillation with toluene (Reference 7, Method 1613). Prior to cleanup and analysis, the extracts of the filtered water and the particulates are combined. This method can also use solid phase extraction (SPE), however, Test America Sacramento is in the developmental stages for this extraction type and is not currently certified for its use.

2.2. After extraction, $^{37}Cl_4$-labeled 2, 3, 7, 8, -TCDD is added to each extract to measure the efficiency of the cleanup process. Samples are then permeated through silica gel, acidic alumina, and activated carbon chromatography columns. High performance liquid chromatography (HPLC), basic alumina, or back extraction with sulfuric acid/water/NaOH/water can be used for further isolation of the 2, 3, 7, 8-isomers or other specific isomers or congeners.

2.3. After cleanup, the extract is concentrated to near dryness and a known amount of recovery standard is added to each extract. The recovery standard contains two $^{13}C_{12}$-labeled analogs ($^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD). Each extract is concentrated to a final volume in tetradecane. The extract is ready for analysis and delivered to the Instrument Group for HRGC/HRMS.

3. DEFINITIONS

3.1. Definitions of terms used in this SOP may be found in the glossary of the Laboratory Quality Assurance Manual (QAM).

3.2. Data qualifiers are defined on each data report. Commonly used data qualifiers are defined in the QAM.

3.3. Isotope Dilution Analyte: An isotope dilution analyte is a ^{13}C-labeled analog of a congener chosen from the compounds listed in Table 2. Isotope dilution analytes are added to all samples including method blanks and quality control samples before extraction, and they are used to quantitate the concentration of the analytes. Nine isotope dilution analytes are used in this method. There is one for each of the dioxin and furan homologs (except for OCDF) with the degree of chlorination ranging from four to eight. Additional isotope dilution analytes may be added to act as retention time references, but they are not used for quantitation.

3.4. Target Analyte: analyte of interest.

3.5. Surrogate Standard (SU): A $^{37}Cl_4$-2,3,7,8-TCDD analog that is added to each sample following extraction to measure the efficiency of the cleanup process.

3.6. Internal Standard (IS): Two recovery standards are used to determine the percent recoveries for the internal standards. The 13C-1,2,3,4-TCDD is used to measure the percent recoveries of the tetra- and pentachlorinated internal standards while 13C-1,2,3,7,8,9-HxCDD is used to determine the recovery of the hexa-hepta- and octachlorinated internal standards. 13C-1,2,3,7,8,9-HxCDD also acts as a retention time reference for the unlabeled analog present in sample extracts. They are added to the final sample extract before HRGC/HRMS instrument analysis.

4. INTERFERENCES

4.1. Solvents, reagents, glassware and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Where possible, reagents are cleaned by extraction or solvent rinse.

4.2. Proper cleaning of glassware is extremely important because glassware may not only contaminate the samples, but may also remove the analytes of interest by absorption on the glassware surface.

4.2.1. Glassware should be rinsed with solvent and washed with a detergent solution as soon after use as practical. Sonication of glassware containing a detergent solution for approximately 30 seconds may aid in cleaning. Glassware with removable parts, particularly separatory funnels with Teflon

stopcocks, must be disassembled prior to detergent washing.

4.2.2. After detergent washing, glassware should be immediately rinsed first with acetone, then with toluene. The toluene rinse is followed by hexane, and then methylene chloride.

4.2.3. Do not bake reusable glassware in an oven as a routine part of cleaning. Baking may be warranted after particularly dirty samples are encountered, but should be minimized, as repeated baking of glassware may cause active sites on the glass surface that will irreversibly absorb PCDDs/PCDFs.

4.2.4. Immediately prior to use, Soxhlet (or equivalent) extraction glassware should be pre-extracted with toluene for approximately 4 hours (1 hour for Soxtherm extraction glassware) (See Method 1613A, Section 11.2.3). Separatory funnels are rinsed sequentially with acetone, toluene, hexane and methylene chloride.

4.3. All materials used in the analysis shall be demonstrated to be free from interferences by running reference blanks initially and with each sample set (samples started through the extraction process on a given 12-hour shift, to a maximum of 20 samples). The reference matrix blank must simulate, as closely as possible, the sample matrix under test. Reagent water is used to simulate water samples; playground sand, white quartz sand, or sodium sulfate can be used to simulate soils; filter paper or Soxhlet extraction thimbles are used to simulate paper and similar materials; other materials can be used to simulate other matrices.

4.4. Interferences co-extracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled. Interfering compounds may be present at concentrations several orders of magnitude higher than the PCDDs and PCDFs. The most frequently encountered interferences are chlorinated-biphenyls, methoxy biphenyls, hydroxy biphenyl ethers, benzyl phenyl ethers, polynuclear aromatics, and pesticides. Because very low levels of PCDDs and PCDFs are measured by this method, the elimination of interferences is essential. The cleanup steps given in Sections 11.13, 11.14, 11.15, and 11.16 can be used to reduce or eliminate these interferences.

4.4.1. If South Carolina samples show diphenyl ethers at levels that could contribute to positive furan hits, a subsequent clean-up to remove them must be performed.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual (CW-E-M-001) and this document. This work may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its

use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum. All work must be stopped in the event of a known or potential compromise to the health or safety of an associate. The situation must be reported immediately to a supervisor, the EH&S Staff, or a senior manager.

5.1. Specific Safety Concerns or Requirements

5.1.1. Microwave ovens used for extraction or digestion of samples can create elevated pressure in the extraction/digestion containers. Microwaves used for these processes must be equipped with an automated vapor sensor and shutoff system that automatically shuts down the digestion/extraction process when vapor pressure reaches pre-specified levels. Users must follow procedures in the microwave operators manual to ensure that the vapor sensor(s) are functional and working properly prior to starting each extraction/digestion batch.

5.1.2. Hearing protection must be worn when using mechanical systems to grind fish or tissue samples.

5.1.3. When dissecting crawfish abdomens with a scalpel, cut from the hand holding the abdomen toward the tail (away from you).

5.1.4. Finely divided dry soils contaminated with PCDDs and PCDFs are particularly hazardous because of the potential for inhalation and ingestion. Such samples are to be processed in a confined environment, such as a hood or a glove box.

5.1.5. The use of vacuum systems during various filtering and/or cleanup steps presents the risk of imploding glassware. All glassware used during vacuum operations must be thoroughly inspected prior to each use. Glass that is chipped, scratched, cracked, rubbed or marred in any manner must not be used under vacuum. It must be removed from service immediately and replaced.

5.1.6. The use of separatory funnels to extract aqueous samples with methylene chloride creates excessive pressure very rapidly. The use of separatory funnels during the partition and back extraction of sample extracts can also create excessive pressure. Initial venting should be done immediately after the sample container has been sealed and inverted. Vent the funnel into the hood away from people and other samples. This is considered a high-risk activity, and a face shield must be worn over safety glasses or goggles when it is performed. Alternately, the extraction can be performed behind a closed fume hood sash on a mechanical shaker.

5.1.7. When Dean-Stark/Soxhlet clean-ups or extractions are performed overnight or unattended, special precautions must be taken. Open the chiller valves to the system about 15 minutes before the heating elements are turned on, and check every condenser to ensure that it is cold and functioning properly before turning the heating elements on. Check every condenser again about 15 minutes after turning the heating elements on to ensure that they are still cold and functioning properly. If the system is left operating overnight or unattended for an extended period, the first chemist to come back into the lab must again check every condenser to ensure that it is still cold and functioning properly.

5.1.8. The effluents of sample splitters for the gas chromatograph and roughing pumps on the HRGC/HRMS system should pass through either a column of activated charcoal or be bubbled through a trap containing oil or high-boiling alcohol.

5.1.9. Assembly and disassembly of glassware creates a risk of breakage and cuts. All staff members shall wear Kevlar or MAPA blue latex cut-resistant gloves over chemically resistant gloves when assembling and disassembling glassware.

5.1.10. Eye protection that satisfies ANSI Z87.1, laboratory coat, and chemically resistant gloves must be worn while samples, standards, solvents, and reagents are being handled. Latex and vinyl gloves provide no protection against most of the organic solvents used in this method. Nitrile gloves must be used. Latex gloves may be used for methanol.

5.1.11. Exposure to chemicals must be maintained as low as reasonably achievable; therefore all samples must be opened, transferred and prepared in a fume hood. Solvent and waste containers will be kept closed unless transfers are being made.

5.1.12. Laboratory procedures such as repetitive use of pipettes, repetitive transferring of extracts and manipulation of filled separatory funnels and other glassware represent a significant potential for repetitive motion or other ergonomic injuries. Laboratory associates performing these procedures are in the best position to realize when they are at risk for these types of injuries. Whenever a situation is found in which an employee is performing the same repetitive motion, the employee shall immediately bring this to the attention of their supervisor, manager, or the EH&S staff. The task will be analyzed to determine a better means of accomplishing it.

5.2. Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Benzene	Flammable Toxic Carcinogen	PEL: 1 PPM TWA ; 5 PPM 15 MIN. STEL	Causes skin irritation. Toxic if absorbed through skin. Causes severe eye irritation. Toxic if inhaled. Vapor or mist causes irritation to mucous membranes and upper respiratory tract. Exposure can cause narcotic effect. Inhalation at high concentrations may have an initial stimulatory effect on the central nervous system characterized by exhilaration, nervous excitation and/or giddiness, depression, drowsiness or fatigue. Victim may experience tightness in the chest, breathlessness, and loss of consciousness.
Cyclohexane	Flammable Irritant	300 ppm TWA	Inhalation of vapors causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. High concentrations have a narcotic effect.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Iso-octane	Flammable Irritant	None established	Inhalation of vapors may cause nausea, headache, dizziness, loss of consciousness, irritation to upper respiratory tract, pain in throat and nose, coughing, wheezing, shortness of breath.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Nonane	Flammable	200 ppm	Primary hazard is flammability.
Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of Sodium Hydroxide dust will cause irritation of the nasal and respiratory system.
Sulfuric Acid (1)	Corrosive Oxidizer Dehydrator	1 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.
Tetradecane	Irritant	None established	Inhalation of vapors may cause difficulty breathing, headache, intoxication and central nervous system damage.

Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Toluene	Flammable Poison Irritant	200 ppm-TWA 300 ppm-Ceiling	Inhalation may cause irritation of the upper respiratory tract. Symptoms of overexposure may include fatigue, confusion, headache, dizziness and drowsiness. Peculiar skin sensations (e. g. pins and needles) or numbness may be produced. Causes severe eye and skin irritation with redness and pain. May be absorbed through the skin.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

Miscellaneous Equipment and Materials. The following list of items does not necessarily constitute an exhaustive compendium of the equipment needed for this analytical method.

6.1. Nitrogen evaporation apparatus with variable flow rate.

6.2. Balances capable of accurately weighing to 0.01 g and 0.0001 g.

6.3. Centrifuge.

6.4. Water bath, equipped with concentric ring covers and capable of maintaining temperature control within ± 2ºC.

6.5. Stainless steel or glass containers large enough to hold contents of one-pint sample containers.

6.6. Drying oven.

6.7. Stainless steel spoons and spatulas.

6.8. Pipettes, disposable, Pasteur, 150 mm long x 5 mm ID.

6.9. Pipettes, disposable, serological, 10 mL, for the preparation of the carbon column.

6.10. Reacti-vial, 2 mL, silanized amber glass.

6.11. Stainless steel meat grinder with a 3- to 5-mm hole size inner plate.

6.12. Separatory funnels, 125 mL and 2 L funnels.

6.13. Kuderna-Danish concentrator, 500 mL, fitted with 10 mL concentrator tube and three-ball Snyder column.

6.14. Teflon® boiling chips (or equivalent), washed with DCM before use.

6.15. Chromatographic column, glass, 300 mm x 10.5 mm, fitted with Teflon® stopcock.

6.16. Adapters for concentrator tubes.

6.17. Glass fiber filters., Whatman GF-D, GF-F, GMF150, or equivalent.

6.18. Solid phase extraction discs, 3M 90mm C18, or equivalent.

6.19. Dean-Stark trap, 5 or 10 mL, with T-joints, condenser and 125 mL flask.

6.20. All-glass Soxhlet apparatus, 500 mL flask.

6.21. Soxtherm extraction apparatus (or equivalent)

6.22. Vacuum extraction device for solid phase extraction, 1 Liter glass funnel with 90mm filter disc holder with a vacuum source, Kontes or equivalent.

6.23. Milestone microwave extraction apparatus (or equivalent)

6.23.1. Automated microwave extractor unit

6.23.2. Plastic extraction vessels with Teflon sample chambers and Teflon pressure release gaskets

6.23.3. 24 position carrousel

6.24. Glass thimble holders for Soxtherm

6.25. Glass beakers for Soxtherm

6.26. Gaskets for Soxtherm

6.27. Glass funnels, sized to hold 170 mL of liquid.

6.28. Desiccator.

6.29. Solvent reservoir (125 mL), Kontes; 12.35 cm diameter (special order item), compatible with gravity carbon column.

6.30. Rotary evaporator with a temperature controlled water bath and vacuum control.

6.31. Turbo evaporator with a temperature controlled water bath and nitrogen pressure control.

6.32. High-speed tissue homogenizer equipped with an EN-8 probe or equivalent.

6.33. pH Strips

6.34. Residual Chlorine Check strips

6.35. HP Scientific Micro 100 Tubidimeter, or equivalent. The turbidimeter consists of a nephelometer with a light source for illuminating the sample and a photo-electric detector (photo-diodes). The intensity of light scattered at right angles to the path of the incident light is measured and a direct reading of turbidity (NTU) is generated.

6.36. Glass wool, extracted with methylene chloride, dried and stored in a clean glass jar.

Note: Re-use of glassware should be minimized to avoid the risk of contamination. All glassware that is re-used must be scrupulously cleaned as soon as possible after use.

7. REAGENTS AND STANDARDS

7.1. Column Chromatography Reagents

7.1.1. Silica Gel - Kieselgel 60 or equivalent, activate for 12 hours at 180°C before use. Store at 130°C in covered flask.

7.1.2. Acid Alumina - ICN or equivalent, activated as necessary.

7.1.3. Basic Alumina - ICN or equivalent. No activation required.

7.1.4. Granular carbon/silica gel - Mix 5 g granular carbon and 95 g activated silica gel; (alternatively, prepare carbon/silica gel (5%/95%)). Store at room temperature in a Teflon® lined jar. The first LCS prepared with a new batch of column packing material is the quality control check of the packing materials. Refer to historical control limits before accepting the new batch of material.

7.1.5. 44% H_2SO_4 /silica gel - Mix 44 mL conc. H_2SO_4 and 56 g activated silica gel. Stir and shake until free flowing. Store at room temperature in a Teflon® lined jar.

7.1.6. 33% NaOH/silica gel (as needed) - Mix 33 mL 1N NaOH and 67 g activated silica gel. Stir and shake until free flowing. Store at room temperature in a Teflon ® lined jar.

7.2. Reagents

7.2.1. Sulfuric acid, concentrated, ACS grade, specific gravity 1.84.

7.2.2. Reagent water is produced by a Millipore nanopure system.

7.2.3. Silica gel.

7.2.4. Solution for breaking emulsions: Slowly add 1.0 L of reagent grade NaOH solution to an 2.0 L NaOH container containing 1.0 L of DI H_2O; leave the

container in secondary containment with the lid off.

Warning: The solution will begin to heat so let the solution stand until equilibrium is met and the solution is at room temperature.

When this process is complete, the solution will then be ready for use in the samples.

7.2.5. Precleaned Ottawa sand (minimum 4 hours toluene Soxhlet Extracted).

7.2.6. 80 mg/mL Sodium Thiosulfate.

7.2.7. Vegetable Oil (for tissue extraction only), or other suitable oils.

7.2.8. Commercially prepared certified calibraton standards: 0.02NTU. 10.0NTU, and 1000NTU.

7.2.9. Second Source Standard (ICV): 5.0NTU

7.2.10. Initial Calibration Blank (ICB): DI water or equivalent.

7.3. Desiccating Agent

7.3.1. Sodium sulfate, granular, anhydrous.

7.4. Solvents and Standards:

7.4.1. High-purity, distilled-in-glass or highest available purity: Methylene chloride (DCM), hexane, benzene, methanol, tetradecane, isooctane, toluene, cyclohexane, nonane and acetone.

7.4.2. All calibration, daily internal standard, daily clean up recovery standards, and daily spiking solutions are stable for one year from preparation. After 1 year, solutions may be re-verified. The re-verified solution may be used for an additional year, or until there is evidence of compound degradation or concentration. The re-verification must be performed using an unexpired, not previously re-verified solution from a second lot or second vendor.

7.4.3. Standards are purchased as solutions or mixtures with certification of their purity, concentration, and authenticity, or prepared from materials of known purity and composition. If the chemical purity is 98% or greater, the weight may be used without correction to compute the concentration of the standard. When not being used, standards can be stored in the dark at room temperature or refrigerated in screw-capped vials with fluoropolymer-lined or Teflon® - lined caps. A mark is placed on the vial at the level of the solution so that solvent loss by evaporation can be detected. If solvent loss has occurred, the solution should be replaced.

7.4.4. Sealed ampules may be used until the manufacturer's expiration date is exceeded. If no expiration date is provided, then the expiration date will be 10 years from the date the ampule is opened. The solvent level should be monitored prior to each use to assure there has been no concentration of the standard over time.

7.5. Stock Solutions

7.5.1. Preparation – Prepare in nonane or equivalent solvent per the steps below or purchase as dilute solutions (Cambridge Isotope Laboratories, Cambridge, MA, or equivalent). Observe standard safety precautions.

7.5.2. Dissolve an appropriate amount of assayed reference material in solvent. For example, weigh 1 to 2 mg of 2,3,7,8-TCDD to three significant numbers in a 10 mL vial with Teflon® - lined cap.

7.5.3. Stock standard solutions should be checked for signs of degradation prior to the preparation of calibration or performance test standards. Reference standards that can be used to determine the accuracy of calibration standards are available from Cambridge Isotope Laboratories and may be available from other vendors.

7.5.4. Secondary standard – Using stock solutions prepare secondary standard solutions if necessary which can be further diluted the spiking standard solutions (see below).

7.6. Precision and Recovery Standard (PAR) – Also referred to as the Native Spike solution later in this SOP. Contains all the 2,3,7,8-substituted unlabeled analytes listed in Table 2. Prepare using the appropriate standards made in Section 7.5 to yield a spiking solution with a concentration of 4.0 ng/ml for the tetra- CDDs/CDFs, 20 ng/ml for the penta-, hexa-, and hepta- CDDs/CDFs, and 40 ng/ml for the octa- CDD/CDF.

7.7. Sample Fortification Solution – Also referred to as the daily Isotope Dilution Analyte (IDA) Solution later in this SOP. From stock solutions or purchased mixtures, prepare this solution in isooctane (or toluene) to contain the fifteen isotopically labeled compounds at the nominal concentrations that are listed in Table 2.

7.8. Recovery Standard Solution – Also referred to as the Internal Standard (IS) Solution later in this SOP. This solution contains the labeled compounds $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD. This solution is preferably prepared in tetradecane. See Table 2 for nominal concentrations.

7.9. Cleanup Recovery Standard Solution (CRS) – Also referred to as the Surrogate Standard. Prepare $^{37}Cl_4$-2,3,7,8-TCDD at the concentration shown in Table 2, in isooctane (or toluene).

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1. The sample collection, shipping, handling, and chain-of-custody procedures are not described in this document. Sample collection personnel will, to the extent possible, homogenize samples in the field before filling the sample containers. This should minimize or eliminate the necessity for sample homogenization in the laboratory. The analyst should make a judgment, based on the appearance of the sample, regarding the necessity for additional mixing. If the sample is clearly non-homogeneous, the entire contents should be transferred to a glass or stainless steel pan for mixing with a stainless steel spoon or spatula before removal of a sample portion for analysis.

8.2. Samples are collected in amber glass containers following conventional sampling practices (Method 1613). Freely flowing aqueous samples are collected in refrigeration bottles using automatic sampling equipment. Solid samples are collected as grab samples using wide mouth jars.

8.3. Grinding or blending of fish samples.

If not otherwise specified by the client, the whole fish (frozen) should be blended or ground to provide a homogeneous sample. The use of a stainless steel meat grinder with a 3- to 5-mm hole size inner plate is recommended. In some circumstances, analysis of fillet or specific organs of fish may be requested by the client. If so requested by the client, the above whole fish requirement is superseded.

Warning: Hearing protection must be worn when grinding samples.

8.4. Samples are stored at 0-4ºC in the dark from the time of collection until extraction (fish tissues must be stored at - 20°C). A measurement of residual chlorine is performed using EPA Methods 330.4 and 330.5. The residual chlorine will be checked at the laboratory for all aqueous samples. If residual chlorine is present in aqueous samples, the sampler or analyst adds 80 mg of sodium thiosulfate per liter of water.

8.5. Sample extraction is performed within 365 days of sampling. Sample analysis is performed within forty (40) days of extraction.

9. QUALITY CONTROL

9.1. The laboratory operates a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of capability (IDOC), analysis of samples spiked with compounds to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision by this method. This ability is established by generating four laboratory control samples that meet recovery criteria. For each alternative sample matrix, four aliquots of the alternative reference matrix are used.

9.1.1. In recognition of advances that are occurring in analytical technology, and to allow the analyst to overcome sample matrix interferences, the analyst is permitted certain options to improve separations or lower costs of measurements. These options include alternate extraction, concentration, cleanup procedures, and changes in columns and detectors. Unique changes are to be documented using a non-conformance memo. Permanent modifications or additions should be documented using an addendum to this SOP.

9.2. One method blank (MB) must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. The method blank is an equivalent aliquot of laboratory reagent water (or appropriate alternate matrix) processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a non-conformance memo, then implemented, when target analytes are detected in the method blank above the reporting limit or when surrogate or internal standard recoveries are outside control limits. Re-extraction of the blank, other batch QC, and the affected samples are required when the method blank is deemed unacceptable.

Certain programs, such as DOD, may require a more stringent evaluation of the method blank, for instance, that the blank not contain any analytes of interest at a concentration greater than ½ the lower calibration limit.

9.2.1. If the accompanying samples are aqueous, use distilled water as a matrix. Take the method blank through all steps detailed in the analytical procedure.

9.2.2. Use Ottawa sand as the method laboratory matrix when solids are extracted. Use a mixture of Ottawa sand and suitable oil as the matrix when tissues are extracted. Take the method blank through all steps detailed in the analytical procedure.

9.2.3. The method blank must be spiked prior to extraction with the same amount of 13C-labeled internal standards as is added to samples.

9.2.4. If method blank contamination is present, check solvents, reagents, fortification solutions, apparatus and glassware to locate and eliminate the source of contamination before any further samples are extracted and analyzed.

9.2.4.1. OCDD is a ubiquitous laboratory contaminant. A method blank and the associated samples are deemed acceptable if the OCDD concentration is less than 5 times the specified reporting limit. Flag data appropriately. The analyst is expected to investigate and eliminate potential sources of systematic contamination.

9.2.4.2. If a target analyte is detected in the blank but the associated

samples are ND (not detected), then the data may be reported, unless otherwise directed by the client. Note the action in the narrative.

9.2.4.3. If a target analyte is detected in the blank, but the concentration of the contaminant in the samples is greater than 10 times the blank concentration, then the data may be reported, unless otherwise directed by the client. Note the action in the narrative.

9.2.4.4. Method blank contamination of non-target analytes (i.e., non-2,3,7,8-substituted isomers) does not require corrective action, but a non-conformance memo is generated explaining the contamination and impact on sample data. "Totals" concentrations are not flagged to reflect blank contamination because totals are considered estimated values.

9.2.4.5. If the method blank is contaminated with any 2,3,7,8-substituted target analyte above the lower calibration limit (other than the exception noted above for OCDD), and the associated sample contains a positive result for that same analyte above the LCL and less than 10 times the blank concentration. Re-extraction of the associated sample is required, unless otherwise stipulated by the client, where the occurrence shall be documented in the non-conformance memo.

9.2.5. If new batches of reagents or solvents contain interfering contaminants, purify or discard them.

9.3. A Laboratory Control Sample (LCS) must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. The LCS is an aliquot of laboratory matrix (e.g. water, Ottawa sand, sodium sulfate, etc.) spiked prior to extraction with analytes of known identity and concentration. The LCS is also spiked prior to extraction with the same amount of $^{13}C_{12}$-labeled internal standards as added to the method blank and samples. The LCS must be processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a Non-Conformance memo, then implemented when recoveries of any spiked analyte is outside control limits provided on the LIMS or by the client. Re-extraction of the blank, other batch QC and all associated samples are required if the LCS is deemed unacceptable. Update the accuracy assessment for each analyte on a periodic basis. Keep control charts for each matrix.

9.4. A second control sample must be prepared for batches containing drinking water samples for the State of Arizona. This will be identified as the laboratory fortified blank (LFB) or low-level LCS (LLCS) to differentiate it from the LCS. The LFB is an

aliquot of water spiked prior to extraction with analytes at the minimum reporting level (MRL). This level is 5 pg/L for 2,3,7,8-TCDD. The LFB must be prepared with each batch containing drinking waters or once per day, whichever is less. The LFB is also spiked prior to extraction with the same amount of $^{13}C_{12}$-labeled internal standards as added to the method blank and samples. The LFB must be processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a Non-Conformance memo, then implemented when recoveries of any spiked analyte is outside control limits provided on the LIMS or by the client. Re-extraction of the blank, other batch QC and all associated samples are required if the LCS is deemed unacceptable. Update the accuracy assessment for each analyte on a periodic basis. Keep control charts for each matrix.

9.5. The assessment of matrix effects on method performance, as required by NELAP, is met in Method 1613, as in all isotope dilution techniques, with the use of isotopically labeled compounds. These isotopically labeled compounds are analogs of target analytes and are spiked into each sample. Therefore, matrix effects on method performance can be judged by the recovery of these analogs. Sample analysis acceptance is controlled by the performance of these analogs in each sample. A Matrix Spike/Matrix Spike Duplicate (MS/MSD or MS/SD) pair is extracted at the client's request only and is not required by Method 1613B. An MS/MSD pair are aliquots of a selected field sample spiked with analytes of known identity and concentration. The MS/MSD are also spiked prior to extraction with the same $^{13}C_{12}$-labeled IDA standards as the method blank, laboratory control sample, and field samples. The MS/MSD pair shall be processed in the same manner and at the same time as the associated samples. The results obtained from the MS and MSD samples (percent recovery and concentrations of 2,3,7,8-substituted PCDDs/PCDFs) should agree within 50 percent relative difference. Report all results, flag any outliers, and file a non-conformance memo for any outliers. Re-extraction is not required when a MS/MSD pair fail to meet one or more QC criteria. An LCS is extracted to show precision of the extraction and analysis process. (An LCS/LCSD pair may be requested by the client, in which case, these usually replace requests for an MS/MSD pair)

9.6. Duplicates – Upon client request, duplicates may be processed. Locate the sample specified for duplicate analysis, and prepare and analyze a second 10 g soil or sediment sample portion or 1 L water sample, or an appropriate amount of the type of matrix under consideration. A duplicate injection of a sample extract may be performed at the clients request to display instrument precision. The results of the laboratory duplicates (percent recovery and concentrations of 2,3,7,8-substituted PCDD/PCDF compounds) should agree within 50 percent relative difference. Report all results and flag any outliers, re-extraction is not required when RPD limits are not met.

9.7. Field Blanks – Each batch of samples may contain a field blank sample of nominally uncontaminated soil, sediment or water that is to be processed for analysis. Treat this sample as all others.

9.8. Rinsate Samples – In addition to the field blank, a batch of samples may include a rinsate, which is a portion of the solvent (usually trichloroethylene) that was used to rinse sampling equipment. The rinsate is analyzed to assure that the samples were not contaminated by the sampling equipment. The rinsate sample must be processed like a regular sample. Take a 100 mL (± 0.5 mL) portion of the sampling equipment rinse solvent (rinsate sample), filter, if necessary, and add the appropriate amount of internal standard to yield 100 pg/µL in the final extract. Using appropriate methods, concentrate to approximately 10 mL. Before analysis, add the appropriate amount of recovery standard to yield 100 pg/µL in the final extract. Reduce the volume to a final volume of 20 µL, as necessary. No column chromatography is required.

9.9. Recommended Corrective Actions and Troubleshooting Steps

9.9.1. If possible, verify that no error was made while weighing the sample portions.

9.9.2. Review the analytical procedures with the performing laboratory personnel.

10. CALIBRATION AND STANDARDIZATION

10.1. On a daily basis, calibrate any balance to be used in accordance with SOP WS-QA-0041.

10.2. When using autopipettors, follow calibration guildines in accordance with SOP WS-QA-0004.

11. PROCEDURE

The sample preparation process involves modifying the physical form of the sample so that the PCDDs and PCDFs can be extracted efficiently. In general, the samples must be in a liquid form or in the form of finely divided solids in order for efficient extraction to take place. Samples containing a solid phase and samples containing particle size larger than 1mm require preparation prior to extraction. Because PCDDs/PCDFs are strongly associated with particulates, the preparation of aqueous samples includes filtering, Soxhlet extraction and separatory funnel shakeout. For samples expected or known to contain high levels of the PCDDs and/or PCDFs, the smallest sample size representative of the entire sample should be used, and the sample extract should be diluted, if necessary.

11.1. Preparation of aqueous samples (liquid/liquid extraction).

The extraction procedure for aqueous samples involves filtering the sample, extracting the particulate phase and filtrate separately, and combining the extracts for analysis. The aqueous portion is extracted by shaking with methylene chloride in a separatory funnel. The particulate material is extracted using Soxhlet extraction with Dean-Stark.

Note- If the samples are noted as drinking water and no visible particulates are present, sample filtration is not required.

Note – Drinking water samples must be checked for pH using pH strips. The pH must be adjusted to pH 7-9 with sulfuric acid, as necessary. If any sample is below this range, the pH must be adjusted with sodium hydroxide.

Note- Drinking wter samples must be checked for residual Chlorine using Chlorine test strips. The Chlorine level must be less than 0.5 mg/L. If the sample fails the residual Chlorine test, add 1mL portions of 80mg/mL Sodium Thiosulfate unitl the sample passes the Residual Chlorine test.

Note- If the samples are noted as Arizona drinking water, the samples must be screened for Turbidity. If the turbidity is found to be greater than 1.0 NTU, the analyst will notify the project manager to see how to proceed with the samples. Please refer to Section 11.2 for Turbidity procedure.

11.1.1. Mark the original level of the sample on the sample bottle for reference. Weigh the sample in the bottle on the top loading balance to ±1g.

11.1.2. For each sample or sample set (to a maximum of 20 samples) to be extracted during the same twelve hour shift, place two 1.0 liter aliquots of reagent water into two clean 1 liter sample bottles. One aliquot will serve as the blank and the other will serve as the laboratory control sample (LCS).

11.1.2.1. Into the blank, add 1mL of daily isotope dilution analyte (IDA) standard dissolved into approximately 2 mL of acetone.

11.1.2.2. Into the LCS, add 1 mL of daily IDA standard and 50 µL of the native spike into 2 mL of acetone.

11.1.3. For each sample, add 1 mL of IDA standard into 2 mL of acetone. Spike the diluted solution into the sample bottle. Cap the bottle and mix the sample by carefully shaking. Allow the sample to equilibrate.

11.1.4. Assemble a Buchner funnel on top of a clean 1 L filtration flask. Apply a vacuum to the flask, and pour the entire contents of the sample bottle through a glass fiber filter in the Buchner funnel, swirling the sample remaining in the bottle to suspend any particulates.

Warning: The use of a vacuum system creates the risk of glassware implosions. Carefully inspect all glassware before each use, and discard or repair any that is cracked, chipped, scratched or otherwise damaged.

11.1.4.1. Rinse the sample bottle twice with 5 mL of DCM. Shake to transfer any remaining particulates onto the filter.

11.1.4.2. Rinse any particulates off the sides of the Buchner funnel, with small quantities of DCM.

11.1.4.3. Pour aqueous sample back into sample container (if not extracted

immediately).

PERFORM THE EXTRACTION USING THE PROCEDURES IN SECTION 11.3

11.2. Turbidity

11.2.1. For best results, it is recommended that the turbidimeter be left on continuously. At minimum, the instrument should be on one hour before analysis.

11.2.2. Standards and samples should be allowed to equilibrate to room temperature prior to analysis. This will prevent condensation on the turbidity cuvette.

11.2.3. All readings are to be recorded in the turbidity screening logbook.

11.2.4. The instrument should be calibrated daily or when in use, as follows:

11.2.4.1. Press the CAL key, which will illuminate the IDENT and CAL block ion the display screen.

11.2.4.2. The "Turbidity Value" displayed on the screen should be 1000NTU.

11.2.4.3. Insert the 1000 NTU Calibration Standard and wait for the reading to stabilize. Press the <ENTER> key. The lower display row will now change to 10.0 NTU, prompting the analyst to place this standard into the sample well.

11.2.4.4. Insert the 10 NTU Calibration standard and wait for the reading to stabilize. Press the <ENTER> key. The lower display row will now change to 0.02 NTU, prompting the analyst to place this standard into the sample well.

11.2.4.5. Insert the 0.02 NTU Calibration standard and wait for the reading to stabilize. Press the <ENTER> key.

11.2.4.6. Press the <ENTER> key., which completes the calibration sequence, and returns the instrument to normal automatic mode. The instrument is now calibrated across the full 0-1000 NTU range and sample analysis can proceed.

Note- All calibration level and standard lot must be recorded in the turbidity screening logbook..

Note – During calibration, the MICRO 100 will perform a system self-diagnosis. Several error messages may appear under the format E-01, E-02, etc. Consult the instrument operating manual for a description of these error codes and rouble-shooting guidance.

11.2.4.7. Measeure the 5.0 NTU ICV standard. The reading must be between 90%-110%.

11.2.4.8. Analyze an aliquot of DI water as the ICB. The turbidity reading must be less than the reporting limit of 1.0 NTU. If not, re-analyze once. Re-calibration may be required.

11.2.4.9. Mix the samples thoroughly to disperse solids. Wait for air bubbles to disappear. Pour samples int clean VOA vials and record the readings.

Note- Vials must be free of fingerprints and air bubbles to ensure accurate results. Clean the outside surface with Kimwipes if necessary.

11.2.4.10. Following every 10 samples, analyze a 5.0 NTU ICV.

11.2.4.11. Samples that pass the turbidity screening can proceed to extraction.

11.3. Extraction of filtrates

Extract the aqueous samples, blanks, and PAR aliquots according to the following procedure.

11.3.1. Pour the filtered aqueous sample from the sample bottle flask into a 2 L separatory funnel. Rinse the bottle twice with 5 mL of DCM and add these rinses to the separatory funnel. Add 100 mL DCM to the sample bottle, seal, and shake 60 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel. Weigh the empty bottle on a top loading balance, and compare to weight from Section 11.1.1 to determine initial volume.

11.3.2. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 minutes with periodic venting.

Warning: Separatory funnel extraction with DCM is a high-risk activity. Pressure may build rapidly in the funnel. It should be vented after several seconds of shaking, and often enough to prevent build-up of pressure. Chemist performing separatory funnel extraction must wear a face shield over their safety glasses/goggles. Alternatively, the extraction can be performed behind a closed fume hood sash.

11.3.3. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between the layers is more than one-third the volume of the solvent layer, employ mechanical techniques to complete this operation (e.g., a glass stirring rod or centrifuge). Drain the DCM extract into the original sample container.

NOTE: Experience with aqueous samples high in dissolved organic materials (e.g., paper mill effluents) has shown that acidification of the sample prior to extraction may reduce the formation of emulsions. Mechanical techniques may still be necessary to complete the phase separation. Refer to Section 11.5 for techniques to decrease or eliminate emulsions.

11.3.4. Extract the water sample two more times using 100 mL of fresh DCM each time. Drain solvent into original container. After the third extraction, rinse the separatory funnel with at least 20 mL of fresh DCM, and drain solvent into original container.

11.3.5. Prepare a funnel plugged with rinsed glass wool and half filled with sodium sulfate. Filter DCM from Section 11.3.4 through funnel and collect directly into 500 mL round bottom flask. Rinse the Na_2SO_4 with DCM and then add as a keeper

11.3.6. Extract the filter portion by Dean-Stark/Soxhlet according to Section 11.7.

11.3.7. Perform macro concentration as detailed in Section 11.17.

11.3.8. If the sample was filtered and the particulate fraction was also extracted, combine the concentrated extracts of filtrate and particulate prior to proceeding with cleanup or micro concentration steps.

11.3.9. Proceed to Section 11.13, Extract Cleanup.

11.4. Aqueous Samples (solid phase extraction).

11.4.1. Weigh the sample in the bottle on the top loading balance to the nearest centigram (0.01g), and record the mass.

11.4.2. Create a blank and LCS by adding 1L of DI water to 2 additional 1L bottles.

11.4.3. For each sample, add 1mL of daily IDA standard in acetone. Add this solution to the sample in the bottles. Each aliquot of spike mixture is added similarly.

11.4.4. To the LCS, add 50µL of the native spike in acetone.

11.4.5. Prepare the C18 extraction discs by first soaking them in toluene for at least 5 minutes.

11.4.6. Assemble the filter holder and vacuum filtration flask and place the extraction disc onto the filter holder. Place a GF-F filter on top of the extraction disc. If the sample has a large amount of particulates, a GF-D filter can be placed on top of the GF-F filter. Alternatively, a GMF-150 filter

can be used in place of the two filters.

11.4.7. Place the filtering funnel onto the disc holder and clamp it in place.

11.4.8. Rinse the filter and discs with approximately 15mL of toluene and allow it to soak for about a minute. Apply vacuum and draw the toluene through the discs. Repeat the wash step using about 15mL of acetone. Apply vacuum and draw the acetone through the discs.

11.4.9. Rinse the filter and discs with approximately 15mL of methanol and allow it to soak for about a minute. Apply vacuum and draw the methanol through the discs, but **DO NOT ALLOW THE DISCS TO GO DRY**. If they do go dry, simply repeat the methanol rinse step, leaving a 1 – 2mm layer of solvent on top of the discs.

11.4.10. Rinse twice with about 50mL of reagent water, leaving a 1 – 2mm layer of water on the surface of the discs.

11.4.11. Pour the spiked method blank, LCS or sample into the reservoir and apply vacuum to begin the extraction. Adjust the vacuum such that the extraction takes approximately 10 minutes. Samples with large amounts of particulates may take much longer.

11.4.12. After most of the sample has been pulled through the discs, rinse the sample bottle with a few mLs of reagent water and add the rinse to the funnel. Rinse down the sides of the funnel with reagent water as well.

11.4.13. Allow the discs to dry, remove them from the holder and extract by soxhlet (Section 11.7) or soxtherm (Section 11.8) and proceed with cleanups.

11.5. Decreasing or Eliminating Emulsions

There are several useful methods to decrease or eliminate emulsion in aqueous samples when extracting with DCM. These methods may include stirring with a pipette to manually breakup the emulsions or to transfer the sample into centrifuge tubes and centrifuge at approximately 3000 RPM.

The most useful method is to use a 1:1 $NaOH/H_2O$ solution to change the pH enough to disrupt the emulsion phase, which works 90% of the time. The following procedure describes how to prepare and use the solution to decrease or eliminate emulsions in aqueous samples during the liquid/liquid extraction step.

11.5.1. Prepare the solution according to Section 7.2.4.

11.5.2. Check the pH of the sample to make sure pH is between 3 and 7. If pH is greater than 7, then consult supervisor and client for instructions. Pour approximately 100 mL of 1:1 $NaOH/H_2O$ into the 1:1 NaOH and let stand.

Empty the aqueous waste in the LLE waste drum.

11.5.3. Pour the solution with DCM back into the same 2 L separatory funnel and drain the DCM phase through Na_2SO_4 into a 500 mL round bottom. Empty the aqueous waste into the LLE waste drum.

11.6. Preparation of pulp, paper and tissue samples which are subject to grinding, homogenization or blending.

The method of reducing particle size to less then 1 mm is matrix dependent. In general, hard particulates can be reduced by grinding with a mortar and pestle. Softer particulates can be reduced by grinding in a Whiley mill or meat grinder, by homogenization, or by blending.

11.6.1. The grinding, homogenization, or blending procedures shall be carried out in a fume hood to prevent particles from contaminating the work environment.

11.6.2. Grinding- Tissue samples, certain papers and pulps, slurries and amorphous solids can be ground in a heavy-duty grinder. In some cases, reducing the temperature of the sample to freezing or to dry ice or liquid nitrogen temperatures can aid in the grinding process. Do not allow the sample temperature to exceed 50ºC.

11.6.3. Homogenization or blending – Particles that are not ground effectively, or particles greater than 1 mm in size after grinding, can often be reduced in size by high-speed homogenization or blending.

11.6.4. Extract the aliquots using the Dean-Stark/Soxhlet procedures in Section 11.7.

11.7. Dean-Stark/Soxhlet (or alternative Soxtherm [Section 11.8] or Microwave Assisted Extraction [Section 11.9]) extraction of solids – Extract the solid samples, particulates, blanks, and PAR aliquots using the following procedure.

11.7.1. Pre-extract the glassware by heating the flask until the toluene is boiling. When properly adjusted, 1-2 drops of toluene per second will fall from the condenser tip into the receiver. Extract the apparatus for a minimum of four hours.

WARNING: Open the chiller supply valves about 15 minutes before turning on the heating element and ensure that all of the condensors are cold before you turn the heating element on. Check all of the condensors about 15 minutes after starting the heating process to ensure that they are still cold and functioning properly. If this cleaning cycle is to be left unattended (e.g., overnight) the first chemist to arrive the next morning is to check all condensers to ensure that they are still cold and functioning properly.

11.7.2. After pre-extraction, cool and disassemble the apparatus.

11.7.3. Weigh a well-mixed aliquot of each sample, generally 2 –10 g, (of the same matrix type) into a clean Soxhlet thimble. If the material to be extracted is the particulate matter from the filtration of an aqueous sample, add the filter paper to the thimble also.

11.7.4. Spike 1.0 mL of the IDA standard into the sample aliquot(s).

11.7.4.1. Do not spike filter/particulate samples from the aqueous filtration step, because theses extracts will be combined with those of the aqueous portion, and the aqueous portion is spiked already.

11.7.5. For each sample or sample set (to a maximum of 20 samples) to be extracted during the same 12-hour shift, weigh two aliquots of the appropriate reference matrix into clean Soxhlet thimbles. One aliquot will serve as the blank and the other will serve as the laboratory control sample (LCS).

11.7.5.1. Into the blank, add 1 mL of daily IDA standard.

11.7.5.2. Into the LCS, add 1 mL of daily IDA standard and 50 µL of the native spike.

11.7.5.3. Normal solid samples are spiked with the appropriate daily IDA standard (the LCS and MS/SD samples are spiked with the daily PAR solution) after the samples are loaded into the Soxhlet (or Soxtherm) apparatus.

11.7.6. Reassemble the pre-extracted apparatus and add a fresh charge of toluene (250 ml – 350 ml) to the receiver and reflux flask.

WARNING: Open the chiller supply valves about 15 minutes before turning on the heating element and ensure that all of the condensors are cold before you turn the heating element on. Check all of the condensors about 15 minutes after starting the heating process to ensure that they are still cold and functioning properly. If this cleaning cycle is to be left unattended (e.g., overnight) the first chemist to arrive the next morning is to check all condensers to ensure that they are still cold and functioning properly.

11.7.7. Apply power to the heating mantle to begin refluxing. Adjust the reflux rate to match the rate of percolation of sand and silica beds until water removal lessens the restriction to toluene flow. Check the apparatus for foaming frequently during the first 2 hours of extraction. If foaming occurs, reduce the reflux rate until foaming subsides.

11.7.8. Drain the water from the receiver if the receiver fills with water. Check and drain when necessary.

Note: If the receiver holds 10 mL of liquid, and 20 g of a approximately 10% solid sample is being extracted, then approximately 9 mL of water will end up in the receiver. In this case, the receiver will not need to be emptied (insufficient liquid to overflow), but it should be checked. If the sample amount is 50, and the percent solids is still 10%, then 45 mL of water will end up in the receiver. In this case, frequent checking is required, and the receiver will need to be emptied at least 5 times.

11.7.9. Reflux the sample for a minimum of 16 hours. Cool and disassemble the apparatus.

11.7.10. Remove the distilling flask. Drain the liquid from the Dean-Stark receiver.

11.7.10.1. The SoxTherm unit will drain all purged solvent and water into the waste solvent reservoir.

11.7.11. For solid samples, the extract must be concentrated to approximately 10 mL prior to additional cleanup. For the particulates filtered from an aqueous sample, the extract must be concentrated prior to combining with the extract of the filtrate. Therefore, add approximately 100 µL of C_{14} to the round bottom flask.

11.7.12. Proceed to Section 11.13, Extract Cleanup.

11.8. SoxTherm Extraction

11.8.1. Prior to loading samples, run the system through a cleaning cycle (approximately 1 hour).

11.8.2. After pre-extraction, cool and disassemble the apparatus.

11.8.3. Place the thimble into the SoxTherm apparatus.

11.8.4. Reassemble the pre-extracted apparatus and add a fresh charge (150 mL) of toluene to the apparatus.

11.8.5. Spike according to Section 11.7.5.1, 11.7.5.2, and 11.7.5.3.

11.8.6. Program the system to boil for 1 hour, and reduce the toluene volume by 70 – 90 mL (volume < volume of the thimble).

11.8.7. Continue the extraction for one hour fifteen minutes, reducing the toluene volume by another 15 mL. The SoxTherm unit will have between 5 mL and 20 mL of solvent following extraction. Transfer the extract from the extract beaker to a 35 mL culture tube and add approximately 100 uL C_{14} to each extract.

11.8.8. Proceed to Section 11.13, Extract Cleanup.

11.9. Microwave Assisted Extraction (MAE)

WARNING: Microwave ovens used for extraction or digestion of samples can create elevated pressure in the extraction/digestion containers. Follow procedures in the operators manual to ensure that the vapor sensor(s) are functional and working properly prior to starting each extraction/digestion batch.

11.9.1. Prior to loading samples, run the system through a cleaning cycle (approximately 35 minutes) using approximately 30 mL 1:1 Toluene:Acetone and the following program (cleaning run.mpr):

Step	Time (min)	Power (W)	Temperature (^{o}C)
1	10	1200	145
2	25	1200	145

11.9.2. After pre-extraction, cool and disassemble the apparatus.

11.9.3. In a clean jar or beaker weigh 10 g (or required sample amount) or each field sample and MS/MSD if required and mix with approximately 5 g to 10 g of diatomaceous earth and let dry for a minimum of one hour. MB, LCS and if required LCSD aliquots are made with only diatomaceous earth.

11.9.4. Place a stir bar at the bottom of each Teflon sample chamber. The number of sample chambers should match the number of field samples and QC samples.

11.9.5. Carefully transfer the mixed samples and QC aliquots from the jars to the Teflon sample chambers.

11.9.6. Add 25 mL of 1:1 Toluene:Acetone to each Teflon sample chambers.

11.9.7. Spike according to Section 11.7.5.1, 11.7.5.2, and 11.7.5.3.

11.9.8. Add the Teflon cap with the Teflon pressure release valve on top of each chamber and place the setup into the plastic pressure vessel and screw on the cap. Into one vessel (that has a special Teflon pressure release valve) carefully add the monitoring probe casing into the top of the chamber. Be careful to not force this probe casing as it is very fragile.

11.9.9. Run the following program for sample extraction (Dioxin.mpr)

Step	Time (min)	Power (W)	Temperature (^oC)
1	10	1200	115
2	25	1200	115
3	10	0	0

11.9.10. Following extraction filter the extract through Na_2SO_4 and collect in a round bottom flask, rinse twice more with approximately 5 mL to 10 mL of Toluene for a total of about 50 mL.

11.9.11. Add approximately 100 uL C_{14} to each round bottom flask.

11.9.12. Proceed to Section 11.13, Extract Cleanup,

11.10. Tissue samples follow the same solid extraction procedure described in Section 11.3, except where % Lipids are needed, C_{14} is not added to the sample extract (only to the method blank and LCS). The matrix for the method blank consists of 9 g of pre-cleaned Ottawa sand and 1 g of a suitable oil.

11.10.1. Weigh the concentration vessel with label and boiling chips prior to extraction and record on the benchsheet.

Note: If Soxtherm was used, weigh the 35 mL culture tube.

11.10.2. Weigh the appropriate sample size into the glass fiber thimble and mix thoroughly with sodium sulfate. Extract according to Section 11.7. Concentrate the sample using a rotary evaporator until toluene has been completely removed. Add approximately 25 mL hexane and repeat the concentration via rotary-evaporation to ensure only lipids are present.

Note: If Soxtherm was used, transfer the sample to 35 mL culture tubes and turbo-evaporate to near dryness. Add approximately 5 mL hexane and repeat the concentration via turbo-evaporation until only lipids are present.

11.10.3. Dry the concentration vessel and let stand at room temperature. Re-weigh the concentration vessel and record on the benchsheet.

11.10.4. %Lipids are calculated by the following:

$$\%Lipids = \frac{Final\ Vessel\ Weight - Initial\ Vessel\ Weight}{Sample\ Size} \times 100$$

11.10.5. Proceed to Section 11.12, Wipe Extractions, Soxhlet Method.

11.11. Wipe Extractions - Jar Shake Method

11.11.1. Place a pre-cleaned wipe in a French Square jar. This will be the method blank aliquot. Place an additional pre-cleaned wipe in yet another French Square. This will be the LCS aliquot.

11.11.2. Transfer each wipe sample and all accompanying liquid into separate French Square jars or appropriate sized containers

Note: If the container used to deliver the wipe to the laboratory can contain 100 ml of solvent, then the container can be used for the extraction.

11.11.3. Spike all samples, method blank and LCS with an appropriate amount of daily IDA standard. Additionally, spike the LCS with the appropriate amount of native standard.

11.11.4. Add 100 mL of toluene to each jar and secure with a Teflon-lined cap. Place the closed container onto the flatbed shaker and secure in place. Turn the shaker on such that the shaking motion is aggressive enough to move the liquid through the wipe. Shake for 4 hours.

11.11.5. Filter each sample through a filter funnel with a glasswool plug. Capture the sample into a 500 ml round bottom flask. Add approximately 100 µL of tetradecane and concentrate to approximately 100 µL on a rotary evaporator or TurboVap.

11.11.6. Add approximately 1 mL of hexane or toluene to rinse the sides of the round bottom flask. Using a pipette, withdraw the sample from the round bottom flask and transfer the liquid into a test-tube. Use additional amounts of solvents to rinse the flask. Transfer all the liquid into the test-tube. Insure that all traces of sample in the round bottom flask have been thoroughly rinsed from all surfaces. Bring the sample volume to 8.0 mL or 10.0 mL (or appropriate volume) with the addition of rinse solvent.

11.11.7. Upon completion of the rinsing, cap the test tube and shake vigorously. Take ½ of each sample (or an appropriate amount deemed from the client or other method) and transfer to a culture tube. Archive the remaining sample for future use.

11.11.7.1. If only one analysis is required, then ½ of the sample is archived and the other half is analyzed.

11.11.7.2. If two analyses are required, then 1/3 is archived, 1/3 is used for one test, and 1/3 is used for the second test. For additional analyses, adjust the fractions accordingly.

11.11.8. Proceed to section 11.13.

11.12. Wipe Extractions – Soxhlet/Soxtherms Method

11.12.1. Place a pre-cleaned wipe in a pre-cleaned Soxhlet extraction apparatus. This will be the method blank aliquot. Place an additional pre-cleaned wipe in yet another pre-cleaned Soxhlet/Soxtherm extraction apparatus. This will be the LCS aliquot.

11.12.2. Transfer each wipe sample and all accompanying liquid into separate precleaned Soxhlet/Soxtherm extraction apparatus.

11.12.3. Spike all samples, method blank and LCS with an appropriate amount of internal standard. Additionally, spike the LCS with the appropriate amount of native standard.

11.12.4. Charge the Soxhlet with approximately 300 mL toluene or 150 mL toluene for Soxtherms, and completely assemble the Soxhlet/Soxtherm apparatus. For Soxhlet, follow procedure in Section 11.7.6 to 11.7.11. For Soxtherm follow procedure outlined in Section 11.8.

WARNING: Open the chiller supply valves about 15 minutes before turning on the heating element and ensure that all of the condensors are cold before you turn the heating element on. Check all of the condensors about 15 minutes after starting the heating process to ensure that they are still cold and functioning properly. If this cleaning cycle is to be left unattended (e.g., overnight) the first chemist to arrive the next morning is to check all condensers to ensure that they are still cold and functioning properly.

11.12.5. After cycling is complete, turn the heat off and allow the glassware to cool. Remove the round bottom flask. Add approximately 100 µL of tetradecane and concentrate to approximately 100 µL on a rotary evaporator or TurboVap.

11.12.6. Add approximately 1 mL of hexane or toluene to rinse the sides of the round bottom flask. Using a pipette, withdraw the sample from the round bottom flask and transfer the liquid into a test tube. Use additional amounts of solvents to rinse the flask. Transfer all the liquid into the test tube. Insure that all traces of sample in the round bottom flask have been thoroughly rinsed from all surfaces. Bring the sample volume to 8.0 mL or 10.0 mL (or appropriate volume) with the addition of rinse solvent.

11.12.7. Upon completion of the rinsing, cap the test tube and shake vigorously. Take ½ of each sample (or an appropriate amount deemed from the client or other method) and transfer to a culture tube. Archive the remaining sample for future use.

11.12.7.1. If only one analysis is required, then ½ of the sample is archived and the other half is analyzed.

11.12.7.2. If two analyses are required, then 1/3 is archived, 1/3 is used for one test, and 1/3 is used for the second test. For additional analyses, adjust the fractions accordingly.

11.12.8. Proceed to section 11.13, Extract cleanup..

11.13. Extract cleanup

11.13.1. Cleanup may not be necessary for relatively clean samples (e.g., drinking water). If a cleanup procedure is required, the analyst may use any or all of the procedures below or any other appropriate procedure. Before using a cleanup procedure, the analyst must demonstrate that the requirements of Section 13 can be met using the cleanup procedure. Cleanup may include: back extraction with H_2S0_4 and H_2O, acid and neutral silica gel and alumina are used to remove nonpolar and polar interferences, and/or 5% Carbon/Silica is used to remove nonpolar interferences.

11.13.2. Spike 1.0 mL of the surrogate (SU)) prior to any cleanup into the round bottom flasks containing the samples and QC extracts. Concentrate samples according to Section 11.17 for the macro-concentration of round bottom flasks or Section 11.18 for the micro-concentration of culture tubes.

11.14. Optional Acid Cleanup (if required). This extract clean-up procedure is employed if the extract is dark in color, smells of hydrocarbons or is known to contain high levels of organic materials.

WARNING: Do not deliberately smell the extract. If there is a strong odor, close the fume hood sash to a smaller opening, move the work further back into the hood and ensure that the hood is operating properly.

11.14.1. Partition the extract against approximately 50 mL of concentrated sulfuric acid. Shake for 2 minutes, periodically venting into a hood. Remove and discard the acid layer. Repeat the acid washing until no color is visible in the aqueous layer, to a maximum of 4 washings. (Minimize contact time between the extract and the acid to prevent dehydration of the PCDDs and PCDFs).

WARNING: The use of separatory funnels during these cleanups is a high-risk activity. A face shield must be worn over safety glasses or goggles.

11.14.2. Repeat the partitioning against DI water and discard the aqueous layer. Most samples will not need the base partition and Sections 11.14.3 and 11.14.4 can be skipped. Consult with department manager or lead analyst if unsure.

11.14.3. Partition the extract against 50 mL of sodium hydroxide in the same way as with the acid. Repeat with base washing until no color is visible in the aqueous layer, to a maximum of four washings.

11.14.4. Repeat the partitioning against DI water and discard the aqueous layer.

11.14.5. Pour each extract through a filling funnel column containing 7 to 10 cm of anhydrous sodium sulfate. Rinse the separatory funnel with 30-50 mL of hexane and pour through the filling funnel. Collect and cleanup the samples and QC aliquots.

11.14.6. See Section 11.17 for macro-concentration procedure.

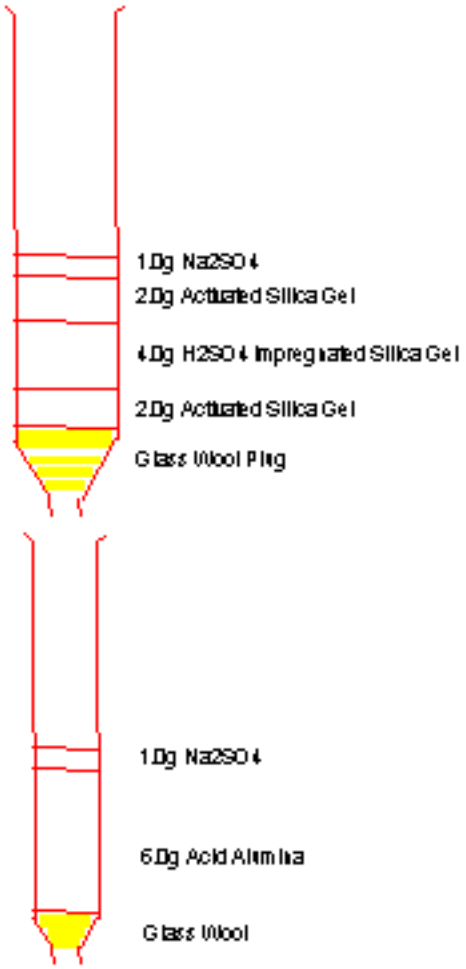
11.15. IFB Column Cleanup

The most frequently used clean-up procedure is the IFB column clean-up.

Exhibit A

IFB COLUMN CLEANUP

Use 20 mm column for upper column
Use 15 mm column for lower column



11.15.1. Pre-rinse both columns with hexane - 40 mL Top and 20 mL Bottom.

11.15.2. Put one column above the other.

11.15.3. Add extract to the top column - rinse the extract vessel 2 times with 1 mL each of hexane and add to column.

11.15.4. Elute the top column directly onto the bottom column with 50 mL hexane.

11.15.5. Disconnect the upper column from the lower column and elute the lower column with 10 mL of 20/80% DCM/hexane. Discard the 20/80% DCM/hexane.

11.15.6. Elute the lower column with 30 mL of 65/35% DCM/hexane into a 35 mL culture tube and save as the final extract eluate.

11.16. If further clean-up is necessary then use this procedure. Carbon Column Cleanup - Prepare an Activated Carbon on Silica Gel column as described below. The carbon column is used to remove non-polar interferences, DPE and should be used on sediment samples.

11.16.1. Use a pre-cut D2 column made from vendor

11.16.2. Push a glass wool plug down to the 3 inch mark.

11.16.3. Add 1 g of 5% Activated Carbon/silica and top with another glasswool plug.

11.16.4. Pre-elute with 5 mL 1:1 DCM: Cyclohexane. Direction "A" (carbon on lower end of the column)

11.16.5. Turn column over to the “B” direction (carbon on the top end of the column) and pre-elute with 5 mL 1:1 DCM: Cyclohexane.

11.16.6. Discard pre-eluates.

11.16.7. Dilute extract to 1 mL with hexane and transfer to the column.

11.16.8. Rinse sample vial onto the column with 2 x 2 mL 1:1 DCM: Cyclohexane.

11.16.9. Elute with: 6 mL 1:1 DCM:Cyclohexane then with 5 mL 75:20:5 DCM:MeOH:Benzene.

11.16.10. Discard eluates.

11.16.11. Turn the column over to the “A” Direction and elute with 25 mL toluene.

11.16.12. See Section 11.18 for micro-concentration procedure.

11.16.13. See Section 11.19 for N_2 concentration procedure.

11.16.14. Collect the sample and proceed to concentration step. 100 µl of tetradecane can be used as keeper if proceeding to IFB cleanup (Section 11.15).

11.17. Macro-concentration

Concentrate the extracts in separate 500 mL round bottom flasks on rotary evaporator.

11.17.1. Assemble the rotary evaporator according to manufacture’s instructions, and warm the water bath (60° C for DCM and 75° C for toluene and hexane). On a daily basis, preclean the rotary evaporator by solvent rinsing. Between samples, 2-3 rinses of toluene followed by a 2-3 mL rinse of hexane should be rinsed down the feed tube into a waste beaker.

11.17.2. Attach the round bottom flask containing the sample extract to the rotary evaporator. Slowly apply vacuum to the system, and begin rotating the sample flask.

11.17.3. Lower the flask into the water bath and adjust the speed of rotation and the temperature as required. At the proper rate of concentration, the flow of solvent into the receiving flask will be steady, but no bumping or visible boiling of the extract will occur.

NOTE: If the rate of concentration is too fast, analyte loss may occur.

11.18. Micro-concentration

Concentrate the extracts in 35 mL culture tubes in a turbo-evaporator. The turbo-evaporator model that the laboratory uses can hold up to 50-35 mL culture tubes. Other turbo-evaporator models can be used that may or may not have the same culture tube sizes and/or capacity. Adjust temperature according to solvent (65ºC for toluene and 45ºC for hexane or hexane/DCM mixtures)

11.18.1. The evaporating times are dependent on sample volume and solvent. The following are examples and can change from sample to sample. Each sample should be checked in intermittent intervals to make sure samples do not go dry.

11.18.2. When evaporating 30 mL toluene, it will normally take approximately 30-50 minutes with the temperature setting described above.

11.18.3. When evaporating 30 mL hexane/DCM, it will normally take approximately 10-20 minutes with the temperature setting described above.

11.19. N_2 concentration.

11.19.1. Transfer extracts to a micro concentration vial (test tubes and other small vessels may also be used), and spike extract with 20 µL of internal standard

11.19.2. Fit a glass concentration apparatus (or equivalent – apparatus can also be made of alternative material free from interferences) with multiple ports.

11.19.2.1. If the concentration apparatus has large orifices for each port, an interference free tube can be placed on each tube fitted with a Pasteur pipette to reduce the size of each port.

11.19.3. Apply a gentle stream of N_2 to the samples making sure turbulence is kept to a minimum.

11.19.4. Concentrate the sample to the necessary volume. Standard volume is 20 µL. Alternative final volumes may be used with client request and/or approval.

11.19.5. Transfer extract to 2 mL vial with inserts.

12. CALCULATIONS/DATA REDUCTION

12.1. Not applicable

13. METHOD PERFORMANCE

13.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate, who has been properly trained in its use and has the required experience.

13.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QC files.

14. POLLUTION CONTROL

It is TestAmerica policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.1. Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards that must be discarded.

14.2. The use of Roto-vaps and Turbo-vaps for some concentration steps, rather than Kuderna-Danish reduction, allows extraction solvents to be collected and disposed of rather than released to the atmosphere.

14.3. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

14.4. Do not allow waste solvent to vent into the hoods. All solvent waste is stored in capped containers unless they are being filled.

14.5. Transfer waste solvent from collection cups (tri-pour and similar containers) to jugs and/or carboys as quickly as possible to minimize evaporation.

15. WASTE MANAGEMENT

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP WS-EHS-0001.

The following waste streams are produced when this method is carried out.

15.1. Extracted aqueous/leachate samples contaminated with methylene chloride are collected at the fume hood in a 5-gallon or smaller carboy. If the samples are not at a neutral pH, add small quantities of sodium bicarbonate to bring the waste to neutral. Stir well. Once neutralized, immediately pour the carboy contents into a blue plastic LLE drum in the H3 closet. When full to between two and six inches of the top, or after no more than 75 days, move the LLE drum to the waste collection area for shipment.

15.2. Miscellaneous disposable glassware, test tubes, syringes, filter disks, chemical rsistant gloves, bench paper and simiilar materials that may or may not be contaminated hazardous. Place contaminated materials into a yellow contaminated lab trash bucket. When the bucket is full or after no more than one year, tie the plastic bab liner shut and put the lab trash into the appropriate steel collection drum in the H3 closet. When the drum is full or after no more than 75 days, move it to the waste collection area for shipment.

15.3. Extracted soil samples, used sodium sulfate, paper funnel tubes, glass wool, thimbles, and extracted solids contaminated with solvents. Dump these materials into an orange contaminated lab trash bucket. When the bucket is full or after no more than one year, tie the plastic bag liner shut and put the lab trash into the appropriate steel collection drum in the H3 closet. When the drum if full or after no more than 75 days, move it to the waste collection area for shipment.

15.4. Assorted solvent and methylene chloride waste generated during glassware and sodium sulfate cleaning. Solvent collected during roto-vap/turbo-vap reduction of extracted samples. Collect the waste solvents in tripours during use. Empty the tripours into a 1-liter to 4-liter carboy at the fume hood. When the carboy is full, or at the end of your shift, whichever comes first, empty the carboy into the steel solvent drum in the H3 closet. When full to between two and six inches of the top, or after no more than 75 days, move the steel drum to the waste collection area for shipment.

15.5. Contaminated sulfuric acid used during extract cleanup. Collect the used sulfuric acid in empty, 2.5-liter, plastic coated jars. When full or after one year, whichever comes first, transfer these jars to the waste collection area for shipment.

15.6. Contaminated sodium hydroxide used during extract cleanup. Collect the used sodium hydroxide in empty, 2.5-liter, plastic coated jars. When full or after one year, whichever comes first, transfer these jars to the waste collection area for shipment.

15.7. Contaminated distilled water used during extract cleanup. Collect the contaminated water in a 1-liter to 4-liter carboy at the fume hood. When the carboy is full, or at the end of your shift, whichever comes first, empty the carboy into the plastic LLE drum in

the H3 closet. When full to between two and six inches of the top, or after no more than 75 days, move the plastic drum to the waste collection area for shipment.

16. REFERENCES/CROSS REFERENCES

16.1. EPA Method 1613, Revision A, October 1990.

16.2. EPA Method 1613, Revision B, October 1994.

16.3. Federal Register, 40 CFR Part 136 App. A (July 2005).

16.4. Dioxins SOW, Exhibits A-C (Rev 2.2) Summary of Requirements, Reporting and Deliverables Requirements, and Target Compound List with Contract Required Quantitation Limits

16.5. Dioxins SOW, Exhibit D (Rev 2.2)) Analytical Method for Dioxins/Furans CLPs

17. METHOD MODIFICATIONS

17.1. Deviations from EPA 1613B

17.1.1. Tetradecane instead of nonane is used as the final solvent to increase the stability of extracts and standards. Tetradecane is less volatile than nonane. Loss of analyte as a result of solvent incompatibility is monitored through recovery checks and calibration acceptance criteria

17.1.2. Microwave Assisted Extraction (MAE) and Soxtherm extraction increase the efficiency of the extraction by decreasing the amount of sample required for analysis and reducing the time required for extraction of CDDS/CDDFs.

18. ATTACHMENTS

18.1. Table 1 - Analyte List

18.2. Table 2 - Concentration of Stock and Spiking Solutions Containing CDDS/CDDFs and Labeled Compounds

18.3. Table 3 - Suggested Sample Quantities to be Extracted for Various Matrices

19. REVISON HISTORY

19.1. WS-IDP-0007, Revision 1.9, Effective 04/11/2014

19.1.1. Inserted Section 11.16.14 - Collect the sample and proceed to concentration step. 100 µl of tetradecane can be used as keeper if proceeding to IFB

cleanup (Section 11.15).

19.1.2. Editorial changes.

19.2. WS-IDP-0007, Revision 1.8, Effective 03/07/2014

19.2.1. Inserted Section 11.2 –Turbidity

19.2.2. Editorial changes.

19.3. WS-IDP-0007, Revision 1.7, Effective 8/26/2013

19.3.1. Updated naming convention for IDA, IS, and native spike.

19.3.2. Modified Section 11.2.5 to reflect current laboratory practice regarding sample size, extraction volume, and spiking concentrations and amounts..

19.3.3. Editorial changes.

19.4. WS-IDP-0007, Revision 1.6, Effective 03/20/2012

19.4.1. Appended to Section 2.1: "This method can also use solid phase extraction (SPE) however, TestAmerica Sacramento is in the developmental stages for this extraction type and is not currently certified for its use.

19.4.2. Editorial changes.

19.5. WS-IDP-0007, Revision 1.5, Effective 06/10/2011

19.5.1. Modified Section 6.17: Whatman GF-D, GF-F, GMF150, or equivalent.

19.5.2. Inserted Section 6.18: Solid phase extraction discs, 3M 90mm C18, or equivalent.

19.5.3. Inserted Section 6.23: Vacuum extraction device for solid phase extraction, 1 Liter glass funnel with 90mm filter disc holder with a vacuum source, Kontes or equivalent.

19.5.4. Inserted Section 11.3: Aqueous Samples (solid phase extraction).

19.5.5. Inserted new Section 5.1.1 dealing with microwave oven safety.

19.5.6. Added new safety warning at Section 11.8

19.5.7. Editorial revisions.

Table 1
Analyte List

CDD/CDF
2,3,7,8-TCDF
2,3,7,8-TCDD
1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF
1,2,3,7,8-PeCDD
1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF
2,3,4,6,7,8-HxCDF
1,2,3,4,7,8-HxCDD
1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD
1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF
1,2,3,4,6,7,8-HpCDD
OCDF
OCDD

Table 2
Concentration of Stock and Spiking Solutions Containing CDDS/CDDFs and Labeled Compounds

Analyte	Type	Labeled Compound Stock Solution (ng/mL=pg/uL)	Labeled Compound Spiking Solution[a] (ng/mL=pg/uL)	PAR Stock Solution (ng/mL=pg/uL)	PAR Spiking Solution[b] (ng/mL=pg/uL)
Isotope Diluton Analyts (IDA)					
$^{13}C_{12}$-2,3,7,8-TCDD	IDA	100	2	--	--
$^{13}C_{12}$-1,2,3,7,8-PeCDD	IDA	100	2	--	--
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	IDA	100	2	--	--
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	IDA	100	2	--	--
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	IDA	100	2	--	--
$^{13}C_{12}$-OCDD	IDA	100	4	--	--
$^{13}C_{12}$-2,3,7,8-TCDF	IDA	100	2	--	--
$^{13}C_{12}$-1,2,3,7,8-PeCDF	IDA	100	2	--	--
$^{13}C_{12}$-2,3,4,7,8-PeCDF	IDA	100	2	--	--
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	IDA	100	2	--	--
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	IDA	100	2	--	--
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	IDA	100	2	--	--
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	IDA	100	2	--	--
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	IDA	100	2	--	--
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	IDA	100	2	--	--
Internal Standard (IS)					
$^{13}C_{12}$-1,2,3,4-TCDD	IS	200	100[d]	--	--
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	IS	200	100[d]	--	--
Surrogate (SU)					
$^{37}Cl_4$-2,3,7,8-TCDD	SU	200	0.8[c]	--	--
Target Analyte (TA)					
2,3,7,8-TCDD	TA	--	--	40	4
1,2,3,7,8-PeCDD	TA	--	--	200	20
1,2,3,4,7,8-HxCDD	TA	--	--	200	20
1,2,3,6,7,8-HxCDD	TA	--	--	200	20
1,2,3,7,8,9-HxCDD	TA	--	--	200	20
1,2,3,4,6,7,8-HpCDD	TA	--	--	200	20
OCDD	TA	--	--	400	40
2,3,7,8-TCDF	TA	--	--	40	4
1,2,3,7,8-PeCDF	TA	--	--	200	20
2,3,4,7,8-PeCDF	TA	--	--	200	20
1,2,3,4,7,8-HxCDF	TA	--	--	200	20
1,2,3,6,7,8-HxCDF	TA	--	--	200	20
2,3,4,6,7,8-HxCDF	TA	--	--	200	20
1,2,3,7,8,9-HxCDF	TA	--	--	200	20
1,2,3,4,6,7,8-HpCDF	TA	--	--	200	20
1,2,3,4,7,8,9-HpCDF	TA	--	--	200	20
OCDF	TA	--	--	400	40

(a) typical spike amount is 1.0 mL
(b) typical spike amount is 50 uL
(c) typical spike amount is 1.0 mL
(d) typical spike amount is 20 uL

Table 3
Suggested Sample Quantities to be Extracted for Various Matrices [1]

Sample Matrix [1]		**Example**	**Percent Solids**	**Phase**	**Quantity**
Single-Phase					
	Aqueous	Drinking water	<1% Solid	[3]	1000mL
		Ground water	<1% Solid	[2]	1000mL
		Treated wastewater	<1% Solid	[2]	1000mL
	Solid	Dry Soil	>20% Solid	Solid	10g
		Compost	>20% Solid	Solid	10g
		Ash	>20% Solid	Solid	10g
	Organic	Waste solvent	<1% Solid	Organic	0.1g
		Waste oil	<1% Solid	Organic	0.1g
		Organic polymer	<1% Solid	Organic	0.1g
	Tissue	Fish & Wildlife		Organic	10g
		Food stuff		Organic	10g
		Human adipose		Organic	10g
Multi-Phase					
Liquid/Solid	Aqueous/Solid	Wet soil	1% Solid<x<30% Solid	Solid	10g
		Untreated effluent	1% Solid<x<30% Solid	Solid	10g
		Digested municipal sludge	1% Solid<x<30% Solid	Solid	5g
		Paper pulp	Dry and homogenize	Solid	10g
		Paper pulp-Sludge	Dry and homogenize	Solid	5g
	Organic/Solid	Industrial sludge	All	All	5g
		Oily waste	All	All	1g
Liquid/Liquid	Aqueous/Organic	In-process effluent	<1% Solid	Organic	1g
		Untreated effluent	<1% Solid	Organic	1g
		Drum waste	<1% Solid	Organic	1g
	Aqueous/Organic /Solid	Untreated effluent	>1% Solid	Organic/Solid	1g
		Drum waste	>1% Solid	Organic/Solid	1g

(1) The sample matrix may be amorphous for some samples. In general, when the CDDs/CDFs are in contact with a multiphase system in which one of the phases is water, they will be preferentially dispersed in or adsorbed on the alternate phase because of their low solubility in water.
(2) Aqueous samples are filtered after spiking with the labeled compounds. The filtrate and the solid phase trapped on the filter are extracted separately, and the extracts are combined for cleanup and analysis.
(3) Drinking water is filtered only if there are particulates and or have color.

Title: PCB Analysis by HRGC/HRMS [Methods 1668A & 1668C]

Approvals (Signature/Date):

5/2/14	4/23/14
Sylvia Krenn Technical Manager Date	Joe Schairer Health & Safety Manager / Coordinator Date
for 5/7/14	5/7/14
Lisa Stafford Interim Quality Assurance Manager Date	Robert Hrabak Laboratory Manager Date

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1. SCOPE AND APPLICATION

1.1. This SOP is appropriate for the detection and quantitative measurement of mono- through deca-chlorinated biphenyls in a variety of matrices at low part-per-trillion to part-per-billion levels using high resolution gas chromatography and high resolution mass spectrometry, by Method 1668A or Method 1668C. Sample preparation procedures are defined in SOP WS-IDP-0013 (Method 1668A) and WS-IDP-0018 (Method 1668C)..

1.2. The CBs determined in this method are the 12 polychlorinated biphenyls (PCBs) designated as toxic by the World Health Organization (WHO). These are congeners 77, 81,105, 114, 118, 123, 126, 156, 157, 167, 169, and 189. This method also determines the remaining 197 PCBs, of which 128 are resolved on the SPB-octyl column to be determined as individual congeners. The remaining 69 congeners are determined as mixtures of isomers (co-elutions). This method can also be used to determine the 20 PCBs on the National Oceanic and Atmospheric Administration (NOAA) list.

1.3. The 12 toxic WHO congeners as well as the first and last eluted congener at each level of chlorination (LOC) are determined by the isotope dilution method using the corresponding labeled analogue. The remaining congeners are determined by using an average of the labeled analogues of each level of chlorination (LOC).

1.4. This method allows the determination of PCB toxicity equivalent factors (TEQPCB)

1.5. The calibration range of the procedure for 1 L water is 20 to 20000 ppq, 2 to 2000 ppt for 10.0 g soil, sediment or tissue, and 40-40,000 pg/train (assuming 1/2 sample to 20 uL F.V.) for air train samples for mono-deca PCBs. Analysis of dilutions of aliquots of the sample will permit measurements of concentrations above the upper method calibration limit. The practical limits of detection and quantitation may be different from the lower method calibration limit, depending on the complexity of the matrix and the level of PCB contamination of the reagent and absorbent used in the extraction and cleanup procedure.

1.6. The PCB naming convention is given in Table VII.

1.7. This SOP should be used by analysts who are experienced and skilled in HRGC/HRMS trace analysis.

1.8. When undertaking projects for Department of Defense (DoD) the relevant criteria in QA Policy WS-PQA-021 “DoD QSM and AFCEE QAPP Implementation” must be checked and incorporated.

2. SUMMARY OF METHOD

2.1. This procedure uses matrix specific extraction, analyte specific cleanup and HRGC/HRMS analysis techniques.

2.2. An aliquot of a matrix (water, soil, sediment, XAD Resin, filter) is spiked with the solution containing 27 isotopically ^{13}C-labeled PCBs Isotope Dilution Analytes (IDAs) listed in Table I. The sample is then extracted according to matrix specific extraction procedures in SOP WS-IDP-0013.for Method 1668A or SOP WS-IDP-0018 for Method 1668C.

2.3. The preparation of the final extract for the instrumental analysis is accomplished by adding 5 isotopically (13 C12) labeled internal standards (ISS -Table I). The internal standard 13C-2,5-DiCB (EPA#9) is used to quantitate the mono and di chlorinated biphenyls and 13C-TrCB-19.. The internal standard 13C-2,2',5,5'-TCB (EPA #52) is used to determine the percent recoveries of 13C-TrCB-37- biphenyls and tetra-chlorinated biphenyls. The 13C-2,2',4,5,5'-PeCB (EPA #101) is used to determine the percent recoveries of penta chlorinated biphenyls. The 13C-2,2',3,4,4',5'-HxCB (EPA #138) is used to determine the percent recoveries of the hexa chlorinated biphenyls. The 13C-2,2',3,3',5,5',6,6'-OCB (EPA #194) internal standard is used to determine the percent recoveries of hepta-deca chlorinated biphenyls.

2.4. One to two microliters (uL) of the final concentrated extract are injected into the HRGC/HRMS.

2.5. The identification of those PCB congeners for which a ^{13}C-labeled isotope dilution analyte is available in the sample fortification solution (IDA solution) is based on their elution time compared to the corresponding labeled isotope dilution analyte and the simultaneous detection of the two most abundant ions in the molecular ion isotopic cluster.

2.6. The identification of those PCB congeners for which no ^{13}C-labeled isotope dilution analyte is available in the sample fortification solution (IDA solution) is based on their elution time measured in the routine calibration standard and the simultaneous detection of the two most abundant ions in the molecular ion isotopic cluster. Confirmation is based on a comparison of the integrated ion abundance of the molecular ions to their theoretical abundance ratios (Table II).

2.7. Quantitation of the individual congeners for which a ^{13}C-labeled isomer is available in the curve is achieved by using the Relative Response Factor (RRF) determined in the 5 point initial calibration curve (ICAL). The quantitation of specific congeners not included in the five point initial calibration solutions is calculated using a RF determined from a single point calibration of a solution containing all 209 PCB compounds. The quantitation of the total for each homologous series is achieved by using the average RRFs of the first and last eluting isomers in the curve at the corresponding chlorination level, determined by the ICAL using the average response of all ^{13}C-labeled isotope dilution analytes in that homologous series. The sole exception is $^{13}C_{12}$-3,3',4,4',5-penta PCB (EPA #126) which is not used in the average response for the penta-PCB homologous series.

3. DEFINITIONS

3.1. Definitions of terms used in this SOP may be found in the glossary of the Quality Assurance Manual (QAM).

3.2. Data qualifiers are defined on each data report. Commonly used data qualifiers are defined in the QAM.

3.3. Isotope Dilution Analyte (IDA) is used in this SOP to refer to what Method 1668 calls an Internal Standard.

3.4. Internal Standard (IS) is used in this SOP to refer to what Method 1668 calls a Recovery Standard.

4. INTERFERENCES

4.1. Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts or elevated baselines that may cause misinterpretation of the chromatographic data. All of these materials must be demonstrated to be free from interferents under the conditions of analysis by running laboratory method blanks. Analysts shall not use PVC gloves.

4.2. The use of high-purity reagents and solvents helps minimize interference problems. Purification of solvents by distillation in all-glass systems may be necessary.

4.3. Reuse of glassware is to be minimized to avoid the risk of contamination.

4.4. Interferents co-extracted from the sample will vary considerably from matrix to matrix. PCBs are often associated with other interfering chlorinated substances such as polychlorinated dioxins/furans (PCDDs/PCDFs), polychlorinated diphenyl ethers (PCDPEs), polychlorinated naphthalenes, methoxy biphenyl hydroxydiphenyl ethers, benzylphenyl ethers, brominated diphenyl ethers, polynuclear aromatics and pesticides that may be found at concentrations several orders of magnitude higher than the analytes of interest. Retention times of target analytes must be verified using reference standards. These values must correspond to the retention time windows established. While certain clean-up techniques are provided as part of this method, unique samples may require additional cleanup steps to achieve lower detection limits.

4.5. A high-resolution capillary column (30 m SPB Octyl) is used to resolve as many PCB isomers as possible; however, no single column is known to resolve all isomers.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), the Sacramento Addendum to the Corporate EH&S Manual (WS-PEHS-0002), and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and

health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1. Specific Safety Concerns or Requirements

5.1.1. Eye protection that satisfies ANSI Z87.1, laboratory coat, and chemically resistant gloves must be worn while samples, standards, solvents, and reagents are being handled. Latex and vinyl gloves provide no protection against most of the organic solvents used in this method. Nitrile or similar gloves must be used.

5.1.2. Exposure to chemicals must be maintained as low as reasonably achievable; therefore all samples must be opened, transferred and prepared in a fume hood. Solvent and waste containers will be kept closed unless transfers are being made.

5.1.3. Laboratory procedures such as repetitive use of pipettes, repetitive transferring of extracts and manipulation of filled separatory funnels and other glassware represent a significant potential for repetitive motion or other ergonomic injuries. Laboratory associates performing these procedures are in the best position to realize when they are at risk for these types of injuries. Whenever a situation is found in which an employee is performing the same repetitive motion, the employee shall immediately bring this to the attention of their supervisor, manager, or the EH&S staff. The task will be analyzed to determine a better means of accomplishing it.

5.2. Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table below contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Table 1: Materials used in this SOP, and their Hazards.

Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Dodecane	Flammable	None listed	May cause respiratory tract, skin or eye irritation.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

6.1. Gas Chromatograph - Shall have splitless or on-column injection port for capillary column, temperature program with isothermal hold, and shall meet all of the performance specifications in Section 10.1.

6.1.1. GC Column for mono- through deca- chlorinated biphenyls - 30 m x 0.25 mm i.d.; 0.25um fused silica capillary column (Supelco SPB-Octyl, or equivalent).

6.1.2. The SPB-Octyl column must resolve congeners 34 from 23 and congeners 187 from 182. The valley height must be less than 40% of the shorter of the two peaks when the diluted 209 congener solution is analyzed.

6.2. Mass Spectrometer - 28-40 eV electron impact ionization, shall be capable of repetitively and selectively monitoring 18 or more exact m/z ratios at high resolution (>10,000) during a period of approximately one second, and shall meet all of the performance specifications in Section 10.2.

6.3. GC/MS Interface - The mass spectrometer (MS) shall be interfaced to the GC such that the end of the capillary column terminates within 1 cm of the ion source and does not intercept the electron or ion beams.

6.4. Data System- Capable of collecting, recording and storing MS data. The system utilizes MassLynx version 4.1 software and Chrom Peak Review, version 2.1 or equivalent.

7. REAGENTS AND STANDARDS

7.1. Standard solutions - Purchased as solutions or mixtures with certification to their purity, concentration and authenticity, or prepared from materials of known purity and composition. If compound purity is 98 percent or greater, the weight may be used without correction to compute the concentration of the standard. When not being used, standards are stored in the dark in screw-capped vials with Teflon-lined caps in a refrigerator at 4 degrees C. A mark is placed on the vial at the level of the solution so that solvent evaporation loss can be detected. If solvent loss has occurred, the solution should be replaced.

7.2. Stock solutions

7.2.1. Preparation - Prepare in isooctane or equivalent solvent per the steps below or purchase as dilute solutions (Cambridge Isotope Laboratories, Cambridge, MA, or equivalent).

7.2.2. Stock standard solutions are prepared from dilutions of neat solutions. Dilutions are performed in volumetric flasks and transferred to a clean 15 mL vial or amber glass bottle with Teflon-lined cap.

7.3. Stock standard solutions should be checked for signs of degradation prior to the preparation of calibration of performance test standards. Reference standards that can be used to determine the accuracy of calibration standards are available from Cambridge Isotope Laboratories.

7.4. Sealed ampoules may be used until the manufacturer's expiration date is exceeded.

7.4.1. If no expiration date is provided, then the expiration date will be 10 years from the date the ampoule is opened.

7.4.2. The solvent level should be monitored prior to each use to assure there has been no concentration of the standard over time.

7.5. All calibration, daily isotope dilution analyte (IDA) standards, daily clean up recovery surrogate (SU) standards, internal (IS) standards, and daily target analyte (TA) spiking solutions are stable for one year from preparation.

7.5.1. After 1 year, solutions may be re-verified. The re-verified solution may be used for an additional year, or until there is evidence of compound degradation or concentration.

7.5.2. The re-verification must be performed using an unexpired, not previously re-verified solution from a second lot, second vendor, or SRM.

7.6. Secondary standard - Using stock solutions, prepare secondary standard solutions containing the compounds and concentrations shown in Table I in dodecane.

7.7. Labeled compound stock standard - From stock standard solutions prepared as above, or from purchased mixtures, prepare this standard to contain the labeled compounds at the concentrations shown in Table I in isooctane.

7.8. Isotope Dilution Analyte (IDA) Standard - Prepare at the concentration shown in Table I in isooctane.

7.9. Calibration standards (CS-1 through CS-6) - Combine the solutions in Tables I and V to produce the six calibration solutions shown in Table V in dodecane. These solutions permit the relative response (labeled to unlabeled) and response factor to be measured as a function of concentration. The 209 congener standard (CS-4) is used for continuing calibration verification (CCV).

7.9.1. A second source standard with all 209 congeners is used for initial calibration verification (ICV).

7.10. GC retention time window defining mix (WDM) (209 congener standard CS-4) - Used to define the beginning and ending retention times for mono-deca chlorinated homologue groups.

7.11. Standard solutions will be periodically assayed against reference standards. Continued use of standard solutions past the initially indicated expiration date is acceptable if

concentrations are verified versus the reference standard. Upon acceptable verification, a new expiration/evaluation date will be noted in the standards reagent database.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. The sample collection, shipping, handling, and chain-of-custody procedures are not described in the document. The complexity of the method is such that, in order to obtain reliable results, testers should be trained and experienced with sampling and preservation procedures.

8.2. There are no demonstrated maximum holding times associated with the PCBs in aqueous, solid, semi-solid, tissues, or other matrices. If stored in the dark at 0-6°C and preserved if required, aqueous samples may be stored for up to one year. Similarly, if stored in the dark at <-10 °C, solids, semi-solid, multi-phase, and tissue samples may be stored for up to one year.

8.3. All extracts must be stored capped at <-10 °C and completely analyzed within one year of extraction. This holding time is consistent with EPA Method 8082 (ref 16.5) and EPA SOW CBC01.2.(Ref 16.6)

9. QUALITY CONTROL

9.1. One method blank must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. The method blank is an aliquot of reference matrix processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a Non-Conformance memo, then implemented when target analytes are detected in the method blank above the acceptance limit or when surrogate recoveries are outside control limits. The associated samples will be evaluated for adverse impact, and flagged or qualified as appropriate. Re-extraction of the blank, other batch QC, and the affected samples are required when the method blank is deemed unacceptable. For any analyte detected in the blank in any of the homologous series of PCBs, the detection limit in the samples run with that blank for the specific isomer or the total for that homologous series is increased to 5 times of the contamination level. Alternatively, both QC and sample results may be reported and qualified as necessary.

NOTE: When laboratory contamination is suspected sample results can be assumed to be maximum possible concentrations. It may be useful to consult project action limits to see if these concentrations may be acceptable to the client. This does NOT preclude the immediate need to initiate contamination clean-up procedures in the sample preparation area.

9.1.1. Certain programs, such as DOD, may require a more stringent evaluation of the method blank, for instance, that the blank not contain any target analytes of interest at a concentration greater than ½ the reporting limit.

9.2. A laboratory control sample (LCS) must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. The LCS is an aliquot of laboratory matrix (e.g. water, sodium sulfate, extraction thimble, filter paper, etc.) spiked with 100 uL of IDA solution (Table 1) and 100 uL of TA solution (Table VI). The LCS must be processed in the same manner and at the same time as the associated samples.

9.2.1. **Method 1668A** - Corrective actions must be documented on a Non-Conformance memo, then implemented when recoveries of any spiked analyte is outside 50-150%, or the control limits provided on the LIMS, or by the client. The associated samples will be evaluated for adverse impact, and flagged or qualified as appropriate. Re-extraction of the blank, other batch QC, and the affected samples are required when the LCS is deemed unacceptable

9.2.2. **Method 1668C** - Corrective actions must be documented on a Non-Conformance memo, then implemented when recoveries of any spiked analyte is outside the control limits in Table VIII.

9.3. A matrix spike/matrix spike duplicate (MS/MSD or MS/SD) pair may be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. MS/MSD are prepared and analyzed at the request of the client. An MS/MSD pair are aliquots of a selected field sample spiked with analytes of known identity and concentration. The MS/MSD pair must be processed in the same manner and at the same time as the associated samples. Spiked analyte recoveries and precision must be within control limits 50-150%, or the control limits provided on the LIMS, or by the client. The result obtained from MS and MSD samples analysis should agree within 50 percent relative difference. Corrective actions must be documented on a Non-Conformance memo. Outliers will be flagged and narrated as appropriate.

9.4. The IDA recovery for each sample and method blank should be between 25 and 150 percent (15 and 150 percent for ^{13}C-PCB-1 and ^{13}C-PCB-3) for Method 1668A and within the recovery limits outlined in Table VIII for Method 1668C. Signal-to-noise of IDA's is also evaluated to assess data usability. Signal-to-noise should exceed 10:1 for all IDA's.

9.5. Positive results for the 12 coplanar PCBs are reported at the lower calibration limit of 2.0 pg/g for solids assuming a 10.0 g aliquot, 20 pg/L for aqueous assuming a 1.0 liter aliquot, and 40 pg/sample for air train samples assuming a one half split of the sample. For all remaining congeners the reporting limit is ten times the lower calibration limit, unless otherwise specified. Detection limits are reported on a sample specific basis and all results are recovery corrected per the isotope dilution technique. For an analyte reported as 'Not Detected' the associated reporting limit represents its maximum possible concentration.

10. CALIBRATION

10.1. For details of the calculations used to generate the regression equations, and how to use the factors generated by these equations, refer to SOP CA-Q-S-005 "Calibration Curves (General)".

10.2. Chromatographic/Mass Spectrometric Conditions and Data Acquisition Parameters

10.2.1. Gas Chromatograph

Column coating SPB-Octyl

Film thickness: 0.25 um

Column dimension: 30 m X 0.25mm

Injector temperature: 260°C

Splitless valve time: 1.0

Interface temperature: 270°C

Recommended Temperature program: (see Table III)

10.2.2. The mass spectrometer is operated in selective ion monitoring (SIM) mode. The ions listed in Table IV for each of the six SIM descriptors are monitored. Some of the ions are monitored in more than one SIM descriptor due to overlapping of the GC elution windows of the different homologous series.

10.2.3. The mass spectrometer is tuned by using a PFK molecular bleed. The instrument is tuned to a resolving power of 10,000 (10 percent valley) at m/z 293.9165, or other appropriate PFK mass, at 8 kV. The intensity of this peak is qualitatively checked at 6 and 8 kV.

NOTE: Commercially available PFK can contain varying levels of contamination. A minor PFK mass (223.9872) is known to interfere with the dichloro PCB secondary quantitation ion (M+2). If this interferent is present it may not be possible to meet the S/N and ion ratio criteria for CS-2 In these cases the calibration/verification is considered acceptable if the CS-3 through CS-6 levels meet all criteria and the CS-2 meets RT criteria and the primary quantitation ion meets 10:1 signal to noise.

10.2.4. A hardcopy of the PFK reference peaks covering the mass range of 6 descriptors is produced, at the start of a run sequence, to document the mass resolution at that range.

10.2.5. A mass resolution is also taken at the completion of a 12 hour period. The mass resolution must have a resolving power of at least 5,000. If the end mass resolution cannot be taken the data will be evaluated for usability and flagged or narrated appropriately. Also a Non-Conformance memo will also be completed.

10.3. Window Defining Mixture (WDM)

A solution containing all 209 PCBs is injected to determine the elution window for each homologous series. Two ions for each homologous series are monitored in each corresponding SIM descriptor.

NOTE: Injection of the WDM/CCV begins the 12 hour analysis bracket. All samples must be injected within 12 hours.

10.3.1. The WDM/CCV is also used to verify that acquisition windows for each function group are correct and to monitor and verify column performance criteria is achieved.

10.4. Initial Calibration

10.4.1. Calibration is required prior to starting sample analysis. Initial calibration is also required if the routine (daily) calibration fails to meet the criteria for acceptable routine calibration.

10.4.2. A minimum of five high-resolution concentration solutions (listed in Table V) are used for initial calibration. (CS-1 optional)

10.4.3. The relative response factors (RRF) for native target analytes (TA) [RRF(n)] relative to their appropriate IDAs and the relative response factor of ^{13}C- IDA [RRF(m)] relative to the internal standards (IS) are calculated according to the following formulae:

Equation 1

$$RRF(n) = \frac{A_{TA} \times Q_{IDA}}{Q_{TA} \times A_{IDA}}$$

Equation 2

$$RRF(m) = \frac{A_{is} \times Q_{rs}}{Q_{is} \times A_{rs}}$$

Where:

A_{TA} = Sum of the integrated ion areas of the quantitation ions for unlabeled PCBs,

A_{IDA} = Sum of the integrated ion areas of the quantitation ions for the labeled isotope dilution analyates.

A_{IS} = Sum of the integrated ion areas of the quantitation ions for the labeled internal standards,

Q_{IDA} = Quantity of the isotope dilution analyte injected (pg),

Q_{IS} = Quantity of the internal standard injected (pg), and

Q_{TA} = Quantity of the unlabeled PCB target injected (pg)

The RRF (n) and RRF (m) are dimensionless quantities; the units used to express Q_{IDA}, Q_{IS}, and Q_{TA} must be the same.

The RRF for the total PCBs for each homologous series is calculated as the average of RRFs of the first and last eluting isomers of the corresponding

homologous series. The sole exception is $^{13}C_{12}$-3,3',4,4',5-penta PCB (EPA #126) which is not used in the average response for the penta-PCB homologous series.

10.4.4. The initial calibration is accepted if the relative standard deviation (% RSD) for the Toxic and LOC native compounds listed in Method 1668A does not exceed ± 20 percent. The second source criterion for the natives (TA) is ±30% deviation from the curve. The first eluting congeners for each chlorination level are not Toxic congeners, and are only used for retention time reference and in the estimated calculation of homolog concentrations. The calibration for the labeled isotope dilution analytes (IDAs) is acceptable if the %RSD does not exceed ± 40 percent.

Note- The incorporation of alternate calibration analytes and acceptance criteria may be implemented on a project specific basis.

10.4.5. The signal to noise ratio (s/n) for the GC signals present in every selected ion current profile must be > 2.5:1.

10.4.6. An injection of the 209 PCB congener mix will be performed annually at concentration at or near the laboratory reporting limit for the congeners not included in the multi-point calibration curve. Solution must be 1 – 2 times the reporting limit. For DoD compliant work a quarterly LOD check at the CS-2 level and an LOQ check at 1-4X the DL level must be performed.

10.5. Daily Calibration Check (CS4)

10.5.1. 1668A Calibration Criteria

10.5.1.1. Daily calibration check is required every 12 hours. The daily calibration check is acceptable if the % Difference in RRF for the Toxic and LOC native compounds listed in Method 1668A are not greater than ± 30% from the initial calibration. The first eluting congeners for each chlorination level are not Toxic congeners, and are only used for retention time reference and in the estimated calculation of homolog concentrations. The daily calibration check of IDAs is acceptable if the RRFs are not greater than ± 50 % of the mean RRF calculated from the initial calibration curve, unless otherwise directed in the client's SOW. The daily calibration check of the cleanup recovery surrogates (SU) is acceptable if the RRFs are not greater than -40 % or +30% of the mean RRF calculated from the initial calibration curve, unless otherwise directed in the client's SOW. The ratio of the ions for the target analytes (TA) and isotope dilution analytes (IDAs) must be within the limits specified in Table II. If the daily calibration check fails to meet the above criteria, a new initial calibration curve is required.

10.5.1.2. For 1668C QC acceptance criteria see Table VIII.

10.5.2. The valley height between the shorter of the two peaks for the congener pairs 34/23 and 187/182 must be less than 40%. Congeners 156 and 157 must co-elute within 2 seconds of the peak maximum.-

10.5.3. If the criteria in Section 10.5.2 are not met, maintenance must be performed. If a second injection fails the column should be replaced.

10.5.3.1. The retention times and response factors should be updated after the criteria for Section 10.5.2 is met.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of a supervisor to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Non-Conformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Non-Conformance Memo shall be filed in the project file.

Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.2. Analysis

11.2.1. 1-2 uL of the final 20 uL extract of the sample is injected into the GC.

11.2.2. Acquire SIM data under the same acquisition and mass spectrometer conditions that the initial calibration curve was acquired.

12. CALCULATIONS/DATA REDUCTION

12.1. For a gas chromatographic peak to be identified as a PCB peak, the following criteria must be met:

12.1.1. For the PCB congeners (a total of 27 congeners) which have an isotopically labeled IDAs in the sample extract, the retention time must be within -1 to +3 seconds of the related IDA.

12.1.2. For the Toxic/LOC congeners (27 congeners) that are present in the five initial calibration solutions, the retention time must be within 0.0005 retention time units of the relative limits measured in the routine calibration (CS4 standard).

12.1.3. For the remaining 182 PCB congeners (mono-nona) which do not have an isotopically labeled internal standard and are not in the five point initial calibration

solutions, the retention time should be within 0.005 retention time units of the relative times measured in the 209 PCB single point calibrations solution. If mono-nona totals are being reported for all or just the remaining isomers the retention time for these compounds should be within the corresponding homologous retention time windows which are established by analyzing either a calibration solution or the 209 single point calibration solution..

12.1.4. For the two ions monitored for each analyte, the apex of the peaks must occur within +/- 2 seconds of each other.

12.1.5. The ratio of the relative intensity of the selected isotopic ions is required to be within the limits (Table II).

12.1.6. A GC/MS peak must be 2.5 times higher than the noise level for positive identification of a PCB compound, and 10 times higher than the noise level for all labeled compounds.

12.1.7. For total isomers to be positively identified they must be within the retention time window of their respective homologous series as specified by the 209 PCB calibration standard.

12.1.8. The loss of one or more chlorines from high chlorinated congeners may contribute to the less-chlorinated congeners peaks that elute at the same retention time which can have an adverse effect on the quantitation of the less-chlorinated congeners. Also in the analysis of total PCBs the extra erroneous peaks in the chromatogram of less-chlorinated congeners produced by the fragment of the high–chlorinated congeners may lead to a high bias in the concentration of the less-chlorinated congeners. If identification is ambiguous, an experienced analyst will determine the presence or absence of the congeners to be reported and the data flagged or narrated appropriately. (The flags will include but are not limited to an elevated detection limit or an estimated positive concentration).

12.2. For gas chromatographic peaks that have met the criteria in Section 12.1, the concentration of the PCBs is calculated by using the following formula:

Equation 3

$$C_{TA} = \frac{A_{TA} \times Q_{IDA}}{A_{IDA} \times W \times RRF_{(TA)}}$$

Where:

C_{TA} = Concentration of unlabeled TA PCB congener,
A_{TA} = Sum of the integrated ion areas of quantitation ions for unlabeled PCBs,
A_{IDA} = Sum of the integrated ion areas of the quantitation ions for the labeled IDAs,
Q_{IDA} = Quantity, in pg, of the IDAs added to the sample before extraction,
W = Sample size in g (if solid) or L (if liquid), and

$RR_{(TA)}$ = Calculated mean relative response factor for the TA.

12.3. The percent recovery of the IDAs is calculated by using the following formula:

Equation 4

$$\text{IDA Percent Recovery} = \frac{A_{IDA} \times Q_{IS}}{Q_{IDA} \times A_{IS} \times RRF_{(IDA)}} \times 100$$

Where:

A_{IDA} = Sum of the integrated ion areas of the quantitation ions for the labeled isotope dilution analyte (IDA).

A_{IS} = Sum of the integrated ion areas of the quantitation ions for the labeled internal standard (IS).

Q_{IDA} = Quantity, in pg, of the isotope dilution analyte (IDA) added to the sample before extraction,

Q_{IS} = Quantity, in pg, of the internal standard (IS) added to the cleaned up sample extract before HRGC/HRMS analysis, and

$RRF(_{IDA})$ = Mean relative response factor for the labeled IDA relative to the appropriate internal standard

12.4. The total concentration for each homologous series of PCBs calculated by summing up the concentration of all positively identified isomers of each homologous series.

12.5. Target compounds that exceed the upper calibration range of the calibration solutions, will be qualified as estimated unless otherwise directed by specific project request. A dilution factor appropriate to bringing the toxic congeners within the calibration range should be used. For other congeners a dilution that, at a minimum, brings the response to a concentration within the detector's response range is acceptable. If possible, the dilution should bring the concentration within the calibration range of the initial calibration solutions. Results for PCB congeners in a sample that has been diluted are reported at the least dilute level at which the area at the quantitation m/z is in the linear response range and the corresponding labeled compound recovery is within the acceptance range.

12.6. Reporting Results

12.6.1. Unless otherwise directed TestAmerica Sacramento will report results in the following units: aqueous samples (pg/L), solids and sediments (pg/g), air samples (pg/sample). Tissues are reported in pg/g wet weight.

12.6.2. Unless otherwise requested the Toxic/LOC congeners will be reported to an RL consistent with the CS-2 calibration level. Other congeners will be reported to an RL of 10X the CS-2 level. Reporting limits for coeluting groups will be multiplied by the number of congeners present. EPA CLP work will be reported per Exhibit C Table 1 of the statement of Work (CBC1-x). Results below the reporting limit will be reported only upon specific request and the reporting process must be agreed upon with the client before samples are processed.

13. METHOD PERFORMANCE

13.1. Method Detection Limit

Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in WS-QA-0006. MDLs are available in the Quality Assurance department.

13.2. Initial Demonstration

Each analyst must make a one time initial demonstration of capability for each individual method. Demonstration of capability for both soils and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid level calibration standard.

13.2.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the historical acceptance criteria.

13.2.3. If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.2.4. A passing PT sample can be substituted for the 4 aliquots in Section 13.2.1.

13.3. Training Qualification

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14. POLLUTION CONTROL

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

14.2. Do not allow waste solvent to evaporate in fume hoods. All solvent waste is stored in capped containers unless transfers are being made.

15. WASTE MANAGEMENT

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples, and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP WS-EHS-0001. The following waste streams are produced when this method is carried out.

15.1. Autovials contaminated with dodecane. As the autovials are removed from the instrument after analysis, they are stored in vial files in the instrument lab for at least ninety days, depending on client requirements. After at least ninety days, the vial files are transferred to the waste disposal area where they are drummed and shipped as PCB waste after no more than ninety days.

15.2. Miscellaneous disposable glassware, chemical resistant gloves, bench paper and similar materials that may or may not be contaminated/hazardous. Place contaminated materials into a yellow contaminated lab trash bucket. When the bucket is full or after no more than one year, tie the plastic bag liner shut and put the lab trash into the appropriate steel collection drum in the H3 closet. When the drum is full or after no more than 75 days, move it to the waste collection area for shipment.

16. REFERENCES/CROSS REFERENCES

16.1. State of California Air Resources Board Method 428: Determination of Polychlorinated Dibenzo-p-dioxin (PCDD), Polychlorinated Dibenzofuran (PCDF), and Polychlorinated Biphenyl Emissions from Stationary Sources, September 12, 1990.

16.2. EPA Method 1668: Toxic polychlorinated Biphenyls by Isotope Dilution High Resolution Gas Chromatography/High resolution Mass Spectrometry, March 1997.

16.3. Method 1668, Revision A (Method 1668A): Chlorinated Biphenyl Congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS, August 2003.

16.4. :Method 1668C: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS, April 2010.

16.5. Method 8082A: Polychlorinated Biphenyls (PCBs) By Gas Chromatography, February 2007.

16.6. EPA SOW CBC01.2: Analysis of Chlorinated Biphenyl Congeners (PCBs), December 2009.

17. METHOD MODIFICATIONS

17.1. Deviations from reference Method 1668A

17.1.1. The acceptance criteria of not greater than +/- 20% and +/- 30% for the Initial Calibration and Continuing Calibration Check respectively, includes the Toxic and LOC native compounds listed in Method 1668A and 1668C,

17.1.2. The retention time for PCB-209 does not have to be greater than 55 minutes if all criteria listed in Section 10.5 is achieved. The laboratory uses GC conditions different than those recommended in Method 1668A.

17.1.3. The retention time windows used to identify the chlorination levels is established from the analysis of the native window defining mix included in the calibration curve and native spiking mix.

17.1.4. The laboratory routinely uses a SPB-Octyl column for primary analysis.

18. ATTACHMENTS

18.1. Table I- Composition of the Sample Fortification Solutions

18.2. Table II- Ion-Abundance Ratio Acceptable Ranges

18.3. Table III- GC Temperature Program

18.4. Table IV- Ions Monitored for HRGC/HRMS Analysis of PCBs

18.5. Table V- High-Resolution Concentration Calibration Solution

18.6. Table VI- Composition of the Matrix Spike Fortification Solution

18.7. Table VII- Analyte List

18.8. Table VIII – Acceptance Criteria for VER, IPR, OPR, and Labeled Compounds in Samples

19. REVISION HISTORY

19.1. WS-ID-0013, Revision 4.4, Effective 05/07/2014

19.1.1. Revised Section 8.3 to read - “All extracts must be stored capped at <-10 °C and completely analyzed within one year of extraction. This holding time is consistent with EPA Method 8082 (ref 16.5) and EPA SOW CBC01.2.(Ref 16.6).”

19.1.2. Inserted Section 16.5 – “Method 8082A: Polychlorinated Biphenyls (PCBs) By Gas Chromatography, February 2007.”

19.1.3. Inserted Section 16.6 – "EPA SOW CBC01.2: Analysis of Chlorinated Biphenyl Congeners (PCBs), December 2009."

19.1.4. Editorial changes.

19.2. WS-ID-0013, Revision 4.3, Effective 05/10/2013

19.2.1. Incorporated SOP (WS-ID-0018 – Method 1668C) into this SOP.

19.2.2. Added Table VIII with Method 1668C acceptance criteria.

19.2.3. Editorial changes.

19.3. WS-ID-0013, Revision 4.2, Effective 03/19/2013

19.3.1. Updated selected ion masses in Table IV

19.3.2. Editorial changes..

19.4. WS-ID-0013, Revision 4.1, Effective 11/11/2011

19.4.1. Updated Table(s) 2, 3, and 4.

19.4.2. Editorial changes.

19.5. WS-ID-0013, Revision 4, Effective 8/31/2010

19.5.1. Deleted the last sentence in Section 2.6.

19.5.2. Deleted all references to the DB-5 column type in Sections 4.5, 6.2.1 and 10.2.1.

19.5.3. Deleted all references to extraction equipment or requirements.

19.5.4. Deleted Section 6.2.3.

19.5.5. Deleted Reference 16.1.

19.5.6. Editorial changes.

19.5.7. Tables I, II, III, V and VI were updated.

TABLE I
Composition of the Sample Fortification Solutions

	Isotope Dilution Analytes (IDA's) Concentration (pg/uL in Isooctane)	Internal Standards (IS's) Solution (pg/uL in Dodecane)	Clean-up Recovery Surrogates (SU) (pg/uL in Dodecane)
$^{13}C_{12}$-2-MonoPCB (1)	20	--	--
$^{13}C_{12}$-4-MonoPCB (3)	20	--	--
$^{13}C_{12}$-2,2-DiPCB (4)	20	--	--
$^{13}C_{12}$-2,5-DiPCB (9)	--	100	--
$^{13}C_{12}$-4,4'-DiPCB (15)	20	--	--
$^{13}C_{12}$-2,2',6'-TriPCB (19)	20	--	--
$^{13}C_{12}$-2,4,4'-TriPCB (28)	--	--	100
$^{13}C_{12}$-3,4,4'-TriPCB (37)	20	--	--
$^{13}C_{12}$-2,2',5,5'-TetraPCB (52)	--	100	--
$^{13}C_{12}$-2,2',6,6'-TetraPCB (54)	20	--	--
$^{13}C_{12}$-3,3',4,4'-TetraPCB (77)	20	--	--
$^{13}C_{12}$-3,4,4',5-TetraPCB (81)	20	--	--
$^{13}C_{12}$-2,2',4,5,5'-PentaPCB (101)	--	100	--
$^{13}C_{12}$-2,2',4,6,6'-PentaPCB (104)	20	--	--
$^{13}C_{12}$-2,3,3',4,4'-PentaPCB (105)	20	--	--
$^{13}C_{12}$-2,3,3'5,5'-PentaPCB (111)	--	--	100
$^{13}C_{12}$-2,3,4,4',5-PentaPCB (114)	20	--	--
$^{13}C_{12}$-2,3',4,4'5-PentaPCB (118)	20	--	--
$^{13}C_{12}$-2',3,4,4',5-PentaPCB (123)	20	--	--
$^{13}C_{12}$-3,3',4,4',5-PentaPCB (126)	20	--	--
$^{13}C_{12}$-2,2',3',4,4',5'-HexaPCB (138)	--	100	--
$^{13}C_{12}$-2,2',4,4',6,6'-HexaPCB (155)	20	--	--
$^{13}C_{12}$-2,3,3',4,4',5-HexaPCB (156)	20	--	--
$^{13}C_{12}$-2,3,3',4,4',5'-HexaPCB (157)	20	--	--
$^{13}C_{12}$-2,3',4,4',5,5'-HexaPCB (167)	20	--	--
$^{13}C_{12}$-3,3',4,4',5,5'-HexaPCB (169)	20	--	--
$^{13}C_{12}$-2,2',3,3',5,5',6-HeptaPCB (178)	--	--	100
$^{13}C_{12}$-2,2',3,4',5,6,6'-HeptaPCB (188)	20	--	--
$^{13}C_{12}$-2,3,3',4,4',5,5'-HeptaPCB (189)	20	--	--
$^{13}C_{12}$-2,2',3,3',4,4',5,5'-OctaPCB (194)	--	100	--
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OctaPCB (202)	20	--	--
$^{13}C_{12}$-2,3,3',4,4'5,5',6-OctaPCB (205)	20	--	--
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NonaPCB (206)	20	--	--
$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-NonaPCB (208)	20	--	--
$^{13}C_{12}$-DecaPCB (209)	20	--	--

TABLE II
Ion-Abundance Ratio Acceptable Ranges

Number of Halogen Atoms	Theoretical Ion Type	Ratio	Control Limits Lower	Upper
1 Cl	M/M+2	3.13	2.66	3.60
2 Cl	M/M+2	1.56	1.33	1.79
3 Cl	M/M+2	1.04	0.88	1.20
4 Cl	M/M+2	0.77	0.65	0.89
5 Cl	M/M+2	1.55	1.32	1.78
6 Cl	M+2/M+4	1.24	1.05	1.43
7 Cl	M+2/M+4	1.05	0.89	1.21
8 Cl	M+2/M+4	0.89	0.76	1.02
9 Cl	M+2/M+4	0.77	0.65	0.89
10 Cl	M+4/M+6	1.16	0.99	1.33

TABLE III
GC Temperature Program

Parameter	SPB-Octyl
Run time (m)	71.6
Initial Temp (°C)	150
Initial Time (m)	2.0
Rate #1 (°C/m)	2.0
Temp #1 (°C)	256
Time #1 (m)	0.0
Rate #2 (°C/m)	15
Temp #2 (°C)	275
Time #2 (m)	12
Rate #3 (°C)	120
Final Temp (°C)	120
Final Time (m)	2

TABLE IV
Ions Monitored for HRGC/HRMS Analysis of PCBs

Descriptor	Accurate Mass	Ion I.D.	Analyte
1	188.0393	M	MonoCB
	190.0363	M+2	MonoCB
	200.0795	M	MonoCB IDA
	202.0766	M+2	MonoCB IDA
	218.9856	Lock	PFK
	222.0003	M	DiCB
	223.9974	M+2	DiCB
	225.9944	M + 4	DiCB
	234.0406	M	DiCB IDA
	236.0376	M+2	DiCB IDA
2	222.0003	M	DiCB
	223.9974	M+2	DiCB
	225.9944	M + 4	DiCB
	234.0406	M	DiCB IDA
	236.0376	M+2	DiCB IDA
	242.9856	Lock	PFK
	255.9613	M	TriCB
	257.9584	M+2	TriCB
	259.9554	M + 4	TriCB
	268.0016	M	TriCB IDA
	269.9986	M+2	TriCB IDA
	289.9224	M	TetraCB
	291.9194	M+2	TetraCB
	293.9165	M + 4	TetraCB
	301.9626	M	TetraCB IDA, IS
	303.9597	M+2	TetraCB IDA, IS
3	255.9613	M	TriCB
	257.9584	M+2	TriCB
	259.9554	M + 4	TriCB
	268.0016	M	TriCB IDA
	269.9986	M+2	TriCB IDA
	280.9825	Lock	PFK
	289.9224	M	TetraCB
	291.9194	M+2	TetraCB
	293.9165	M + 4	TetraCB
	301.9626	M	TetraCB IDA, IS
	303.9597	M+2	TetraCB IDA
	323.8834	M	PentaCB
	325.8804	M+2	PentaCB
	327.8775	M + 4	PentaCB
	337.9207	M+2	PentaCB IDA, IS

Descriptor	Accurate Mass	Ion I.D.	Analyte
	339.9178	M + 4	PentaCB IDA, IS
4	289.9224	M	TetraCB
	291.9194	M+2	TetraCB
	293.9165	M + 4	TetraCB
	301.9626	M	TetraCB IDA, IS
	303.9597	M+2	TetraCB IDA
	323.8834	M	PentaCB
	325.8804	M+2	PentaCB
	327.8775	M + 4	PentaCB
	330.9792	Lock	PFK
	337.9207	M+2	PentaCB IDA, IS
	339.9178	M + 4	PentaCB IDA, IS
	359.8415	M+2	HexaCB
	361.8385	M+4	HexaCB
	363.8356	M + 6	HexaCB
	371.8817	M+2	HexaCB IDA
	373.8788	M+4	HexaCB IDA
	393.8025	M+2	HeptaCB
	395.7995	M+4	HeptaCB
	397.7966	M + 6	HeptaCB
	405.8428	M+2	HeptaCB IDA
	407.8398	M+4	HeptaCB IDA
5	354.9792	Lock	PFK
	359.8415	M+2	HexaCB
	361.8385	M+4	HexaCB
	363.8356	M + 6	HexaCB
	371.8817	M+2	HexaCB IDA
	373.8788	M+4	HexaCB IDA
	393.8025	M+2	HeptaCB
	395.7995	M+4	HeptaCB
	397.7966	M + 6	HeptaCB
	405.8428	M+2	HeptaCB IDA
	407.8398	M+4	HeptaCB IDA
	427.7635	M+2	Octa CB
	429.7606	M+4	Octa CB
	431.7576	M + 6	Octa CB
	439.8038	M+2	OctaCB IDA
	441.8008	M+4	OctaCB IDA
	454.9782	Lock	PFK
6	393.8025	M+2	HeptaCB
	395.7995	M+4	HeptaCB
	397.7966	M + 6	HeptaCB
	405.8428	M+2	HeptaCB IDA
	407.8398	M+4	HeptaCB IDA

Descriptor	Accurate Mass	Ion I.D.	Analyte
	427.7635	M+2	Octa CB
	429.7606	M+4	Octa CB
	431.7576	M + 6	Octa CB
	439.8038	M+2	OctaCB IDA
	441.8008	M+4	OctaCB IDA
	442.9728	QC	PFK
	454.9782	Lock	PFK
	461.7246	M + 2	NonaCB
	463.7216	M + 4	NonaCB
	465.7187	M + 6	NonaCB
	473.7648	M + 2	NonaCB IDA
	475.7619	M + 4	NonaCB IDA
	495.6856	M + 2	DecaCB
	497.6826	M + 4	DecaCB
	499.6797	M + 6	DecaCB
	507.7258	M + 2	DecaCB IDA
	509.7229	M + 4	DecaCB IDA
	511.7199	M + 6	DecaCB IDA

TABLE V
High-Resolution Concentration Calibration Solution

Compound	IUPAC #(s)	Concentration (pg/µL in dodecane)					
		Optional CS1	CS2	CS3	CC4	CS5	CS6
Target Analytes (TA's)							
MonoPCB	1,3	0.2	1	5	50	400	1000
DiPCB	4,15	0.2	1	5	50	400	1000
TriPCB	19,37	0.2	1	5	50	400	1000
TetraPCB	54,77,81	0.2	1	5	50	400	1000
PentaPCB	104,105,114,118,123,126	0.2	1	5	50	400	1000
HexaPCB	155, 156,157,167,169	0.2	1	5	50	400	1000
HeptaPCB	188,189	0.2	1	5	50	400	1000
OctaPCB	202,205	0.2	1	5	50	400	1000
NonaPCB	206,208	0.2	1	5	50	400	1000
DecaPCB	209	0.2	1	5	50	400	1000
Isotope Dilution Analytes (IDA's)							
^{13}C-MonoPCB	1,3	100	100	100	100	100	100
^{13}C-DiPCB	4,15	100	100	100	100	100	100
^{13}C-TriPCB	19,37	100	100	100	100	100	100
^{13}C-TetraPCB	54,77, 81	100	100	100	100	100	100
^{13}C-PentaPCB	104,105,114,118,123,126	100	100	100	100	100	100
^{13}C-HexaPCB	155,156,157,167,169	100	100	100	100	100	100
^{13}C-HeptaPCB	188,189	100	100	100	100	100	100
^{13}C-OctaPCB	202,205	100	100	100	100	100	100
^{13}C-NonaPCB	206,208	100	100	100	100	100	100
^{13}C-DecaPCB	209	100	100	100	100	100	100
Internal Standards (IS's)							
^{13}C-DiPCB	9	100	100	100	100	100	100
^{13}C-TetraPCB	52	100	100	100	100	100	100
^{13}C-PentaPCB	101	100	100	100	100	100	100
^{13}C-HexaPCB	138	100	100	100	100	100	100
^{13}C-OctaPCB	194	100	100	100	100	100	100
Cleanup Recovery Surrogates (SU's)							
^{13}C-TriPCB	28	100	100	100	100	100	100
^{13}C-PentaPCB	111	100	100	100	100	100	100
^{13}C-HeptaPCB	178	100	100	100	100	100	100

Table VI
Composition of the Matrix Spike Fortification Solution

Compound (Unlabelled)	IUPAC #(s)	Concentration (pg/uL in Dodecane)
MonoPCB	1,3	20
DiPCB	4,15	20
TriPCB	19,37	20
TetraPCB	54,77,81	20
PentaPCB	104,105,114, 118,123,126	20
HexaPCB	155, 156,157,167,169	20
HeptaPCB	188,189	20
OctaPCB	202,205	20
NonaPCB	206,208	20
DecaPCB	209	20

Table VII
Analyte List

SYNAME	Compound	CAS No	SYNAME	Compound	CAS No
PCB 1 (BZ)	2-Chlorobiphenyl	2051-60-7	PCB 106 (BZ)	2,3,3',4,5-Pentachlorobiphenyl	70424-69-0
PCB 2 (BZ)	3-Chlorobiphenyl	2051-61-8	PCB 107 (BZ) 109 (IUPAC)	2,3,3',4',5-Pentachlorobiphenyl	70424-68-9
PCB 3 (BZ)	Biphenyl, 4-chloro	2051-62-9	PCB 108 (BZ) 107 (IUPAC)	2,3,3',4,5'-Pentachlorobiphenyl	70362-41-3
PCB 4 (BZ)	2,2'-Dichlorobiphenyl	13029-08-8	PCB 109 (BZ) 108 (IUPAC)	2,3,3',4,6-Pentachlorobiphenyl	74472-35-8
PCB 5 (BZ)	2,3-Dichlorobiphenyl	16605-91-7	PCB 110 (BZ)	2,3,3',4',6-Pentachlorobiphenyl	38380-03-9
PCB 6 (BZ)	2,3'-Dichlorobiphenyl	25569-80-6	PCB 111 (BZ)	2,3,3',5,5'-Pentachlorobiphenyl	39635-32-0
PCB 7 (BZ)	2,4-Dichlorobiphenyl	33284-50-3	PCB 112 (BZ)	2,3,3',5,6-Pentachlorobiphenyl	74472-36-9
PCB 8 (BZ)	2,4'-Dichlorbiphenyl	34883-43-7	PCB 113 (BZ)	2,3,3',5',6-Pentachlorobiphenyl	68194-10-5
PCB 9 (BZ)	2,5-Dichlorobiphenyl	34883-39-1	PCB 114 (BZ)	2,3,4,4',5-Pentachlorobiphenyl	74472-37-0
PCB 10 (BZ)	2,6-Dichlorobiphenyl	33146-45-1	PCB 115 (BZ)	2,3,4,4',6-Pentachlorobiphenyl	74472-38-1
PCB 11 (BZ)	3,3'-Dichlorobiphenyl	2050-67-1	PCB 116 (BZ)	2,3,4,5,6-Pentachlorobiphenyl	18259-05-7
PCB 12 (BZ)	3,4-Dichlorobiphenyl	2974-92-7	PCB 117 (BZ)	2,3,4',5,6-Pentachlorobiphenyl	68194-11-6
PCB 13 (BZ)	3,4'-Dichlorobiphenyl	2974-90-5	PCB 118 (BZ)	2,3',4,4',5-Pentachlorobiphenyl	31508-00-6
PCB 14 (BZ)	3,5-Dichlorobiphenyl	34883-41-5	PCB 119 (BZ)	2,3',4,4',6-Pentachlorobiphenyl	56558-17-9
PCB 15 (BZ)	4,4'-Dichlorobiphenyl	2050-68-2	PCB 120 (BZ)	2,3',4,5,5'-Pentachlorobiphenyl	68194-12-7
PCB 16 (BZ)	2,2',3-Trichlorobiphenyl	38444-78-9	PCB 121 (BZ)	2,3',4,5',6-Pentachlorobiphenyl	56558-18-0
PCB 17 (BZ)	2,2',4-Trichlorobiphenyl	37680-66-3	PCB 122 (BZ)	2',3,3',4,5-Pentachlorobiphenyl	76842-07-4
PCB 18 (BZ)	2,2',5-Trichlorobiphenyl	37680-65-2	PCB 123 (BZ)	2',3,4,4',5-Pentachlorobiphenyl	65510-44-3
PCB 19 (BZ)	2,2',6-Trichlorobiphenyl	38444-73-4	PCB 124 (BZ)	2',3,4,5,5'-Pentachlorobiphenyl	70424-70-3
PCB 20 (BZ)	2,3,3'-Trichlorobiphenyl	38444-84-7	PCB 125 (BZ)	2',3,4,5,6'-Pentachlorobiphenyl	74472-39-2
PCB 21 (BZ)	2,3,4-Trichlorobiphenyl	55702-46-0	PCB 126 (BZ)	3,3',4,4',5-Pentachlorobiphenyl	57465-28-8
PCB 22 (BZ)	2,3,4'-Trichlorobiphenyl	38444-85-8	PCB 127 (BZ)	3,3',4,5,5'-Pentachlorobiphenyl	39635-33-1
PCB 23 (BZ)	2,3,5-Trichlorobiphenyl	55720-44-0	PCB 128 (BZ)	2,2',3,3',4,4'-Hexachlorobiphenyl	38380-07-3
PCB 24 (BZ)	2,3,6-Trichlorobiphenyl	55702-45-9	PCB 129 (BZ)	2,2',3,3',4,5-Hexachlorobiphenyl	55215-18-4
PCB 25 (BZ)	2,3',4-Trichlorobiphenyl	55712-37-3	PCB 130 (BZ)	2,2',3,3',4,5'-Hexachlorobiphenyl	52663-66-8
PCB 26 (BZ)	2,3',5-Trichlorobiphenyl	38444-81-4	PCB 131 (BZ)	2,2',3,3',4,6-Hexachlorobiphenyl	61798-70-7
PCB 27 (BZ)	2,3',6-Trichlorobiphenyl	38444-76-7	PCB 132 (BZ)	2,2',3,3',4,6'-Hexachlorobiphenyl	38380-05-1
PCB 28 (BZ)	2,4,4'-Trichlorobiphenyl	7012-37-5	PCB 133 (BZ)	2,2',3,3',5,5'-Hexachlorobiphenyl	35694-04-3
PCB 29 (BZ)	2,4,5-Trichlorobiphenyl	15862-07-4	PCB 134 (BZ)	2,2',3,3',5,6-Hexachlorobiphenyl	52704-70-8
PCB 30 (BZ)	2,4,6-Trichlorobiphenyl	35693-92-6	PCB 135 (BZ)	2,2',3,3',5,6'-Hexachlorobiphenyl	52744-13-5
PCB 31 (BZ)	2,4',5-Trichlorobiphenyl	16606-02-3	PCB 136 (BZ)	2,2',3,3',6,6'-Hexachlorobiphenyl	38411-22-2
PCB 32 (BZ)	2,4',6-Trichlorobiphenyl	38444-77-8	PCB 137 (BZ)	2,2',3,4,4',5-Hexachlorobiphenyl	35694-06-5
PCB 33 (BZ)	2',3,4-Trichlorobiphenyl	38444-86-9	PCB 138 (BZ)	2,2',3,4,4',5'-Hexachlorobiphenyl	35065-28-2
PCB 34 (BZ)	2',3,5-Trichlorobiphenyl	37680-68-5	PCB 139 (BZ)	2,2',3,4,4',6-Hexachlorobiphenyl	56030-56-9
PCB 35 (BZ)	3,3',4-Trichlorobiphenyl	37680-69-6	PCB 140 (BZ)	2,2',3,4,4',6'-Hexachlorobiphenyl	59291-64-4
PCB 36 (BZ)	3,3',5-Trichlorobiphenyl	38444-87-0	PCB 141 (BZ)	2,2',3,4,5,5'-Hexachlorobiphenyl	52712-04-6
PCB 37 (BZ)	3,4,4'-Trichlorobiphenyl	38444-90-5	PCB 142 (BZ)	2,2',3,4,5,6-Hexachlorobiphenyl	41411-61-4
PCB 38 (BZ)	3,4,5-Trichlorobiphenyl	53555-66-1	PCB 143 (BZ)	2,2',3,4,5,6'-Hexachlorobiphenyl	68194-15-0
PCB 39 (BZ)	3,4',5-Trichlorobiphenyl	38444-88-1	PCB 144 (BZ)	2,2',3,4,5',6-Hexachlorobiphenyl	68194-14-9
PCB 40 (BZ)	2,2',3,3'-Tetrachlorobiphenyl	38444-93-8	PCB 145 (BZ)	2,2',3,4,6,6'-Hexachlorobiphenyl	74472-40-5
PCB 41 (BZ)	2,2',3,4-Tetrachlorobiphenyl	52663-59-9	PCB 146 (BZ)	2,2',3,4',5,5'-Hexachlorobiphenyl	51908-16-8
PCB 42 (BZ)	2,2',3,4'-Tetrachlorobiphenyl	36559-22-5	PCB 147 (BZ)	2,2',3,4',5,6-Hexachlorobiphenyl	68194-13-8
PCB 43 (BZ)	2,2',3,5-Tetrachlorobiphenyl	70362-46-8	PCB 148 (BZ)	2,2',3,4',5,6'-Hexachlorobiphenyl	74472-41-6
PCB 44 (BZ)	2,2',3,5'-Tetrachlorobiphenyl	41464-39-5	PCB 149 (BZ)	2,2',3,4',5',6-Hexachlorobiphenyl	38380-04-0
PCB 45 (BZ)	2,2',3,6-Tetrachlorobiphenyl	70362-45-7	PCB 150 (BZ)	2,2',3,4',6,6'-Hexachlorobiphenyl	68194-08-1

SYNAME	Compound	CAS No	SYNAME	Compound	CAS No
PCB 46 (BZ)	2,2',3,6'-Tetrachlorobiphenyl	41464-47-5	PCB 151 (BZ)	2,2',3,5,5',6-Hexachlorobiphenyl	52663-63-5
PCB 47 (BZ)	2,2',4,4'-Tetrachlorobiphenyl	2437-79-8	PCB 152 (BZ)	2,2',3,5,6,6'-Hexachlorobiphenyl	68194-09-2
PCB 48 (BZ)	2,2',4,5-Tetrachlorobiphenyl	70362-47-9	PCB 153 (BZ)	2,2',4,4',5,5'-Hexachlorobiphenyl	35065-27-1
PCB 49 (BZ)	2,2',4,5'-Tetrachlorobiphenyl	41464-40-8	PCB 154 (BZ)	2,2',4,4',5,6'-Hexachlorobiphenyl	60145-22-4
PCB 50 (BZ)	2,2',4,6-Tetrachlorobiphenyl	62796-65-0	PCB 155 (BZ)	2,2',4,4',6,6'-Hexachlorobiphenyl	33979-03-2
PCB 51 (BZ)	2,2',4,6'-Tetrachlorobiphenyl	68194-04-7	PCB 156 (BZ)	2,3,3',4,4',5-Hexachlorobiphenyl	38380-08-4
PCB 52 (BZ)	2,2',5,5'-Tetrachlorobiphenyl	35693-99-3	PCB 157 (BZ)	2,3,3',4,4',5'-Hexachlorobiphenyl	69782-90-7
PCB 53 (BZ)	2,2',5,6'-Tetrachlorobiphenyl	41464-41-9	PCB 158 (BZ)	2,3,3',4,4',6-Hexachlorobiphenyl	74472-42-7
PCB 54 (BZ)	2,2',6,6'-Tetrachlorobiphenyl	15968-05-5	PCB 159 (BZ)	2,3,3',4,5,5'-Hexachlorobiphenyl	39635-35-3
PCB 55 (BZ)	2,3,3',4-Tetrachlorobiphenyl	74338-24-2	PCB 160 (BZ)	2,3,3',4,5,6-Hexachlorobiphenyl	41411-62-5
PCB 56 (BZ)	2,3,3',4'-Tetrachlorobiphenyl	41464-43-1	PCB 161 (BZ)	2,3,3',4,5',6-Hexachlorobiphenyl	74472-43-8
PCB 57 (BZ)	2,3,3',5-Tetrachlorobiphenyl	70424-67-8	PCB 162 (BZ)	2,3,3',4',5,5'-Hexachlorobiphenyl	39635-34-2
PCB 58 (BZ)	2,3,3',5'-Tetrachlorobiphenyl	41464-49-7	PCB 163 (BZ)	2,3,3',4',5,6-Hexachlorobiphenyl	74472-44-9
PCB 59 (BZ)	2,3,3',6-Tetrachlorobiphenyl	74472-33-6	PCB 164 (BZ)	2,3,3',4',5',6-Hexachlorobiphenyl	74472-45-0
PCB 60 (BZ)	2,3,4,4'-Tetrachlorobiphenyl	33025-41-1	PCB 165 (BZ)	2,3,3',5,5',6-Hexachlorobiphenyl	74472-46-1
PCB 61 (BZ)	2,3,4,5-Tetrachlorobiphenyl	33284-53-6	PCB 166 (BZ)	2,3,4,4',5,6-Hexachlorobiphenyl	41411-63-6
PCB 62 (BZ)	2,3,4,6-Tetrachlorobiphenyl	54230-22-7	PCB 167 (BZ)	2,3',4,4',5,5'-Hexachlorobiphenyl	52663-72-6
PCB 63 (BZ)	2,3,4',5-Tetrachlorobiphenyl	74472-34-7	PCB 168 (BZ)	2,3',4,4',5',6-Hexachlorobiphenyl	59291-65-5
PCB 64 (BZ)	2,3,4',6-Tetrachlorobiphenyl	52663-58-8	PCB 169 (BZ)	3,3',4,4',5,5'-Hexachlorobiphenyl	32774-16-6
PCB 65 (BZ)	2,3,5,6-Tetrachlorobiphenyl	33284-54-7	PCB 170 (BZ)	2,2',3,3',4,4',5-Heptachlorobiphenyl	35065-30-6
PCB 66 (BZ)	2,3',4,4'-Tetrachlorobiphenyl	32598-10-0	PCB 171 (BZ)	2,2',3,3',4,4',6-Heptachlorobiphenyl	52663-71-5
PCB 67 (BZ)	2,3',4,5-Tetrachlorobiphenyl	73575-53-8	PCB 172 (BZ)	2,2',3,3',4,5,5'-Heptachlorobiphenyl	52663-74-8
PCB 68 (BZ)	2,3',4,5'-Tetrachlorobiphenyl	73575-52-7	PCB 173 (BZ)	2,2',3,3',4,5,6-Heptachlorobiphenyl	68194-16-1
PCB 69 (BZ)	2,3',4,6-Tetrachlorobiphenyl	60233-24-1	PCB 174 (BZ)	2,2',3,3',4,5,6'-Heptachlorobiphenyl	38411-25-5
PCB 70 (BZ)	2,3',4',5-Tetrachlorobiphenyl	32598-11-1	PCB 175 (BZ)	2,2',3,3',4,5',6-Heptachlorobiphenyl	40186-70-7
PCB 71 (BZ)	2,3',4',6-Tetrachlorobiphenyl	41464-46-4	PCB 176 (BZ)	2,2',3,3',4,6,6'-Heptachlorobiphenyl	52663-65-7
PCB 72 (BZ)	2,3',5,5'-Tetrachlorobiphenyl	41464-42-0	PCB 177 (BZ)	2,2',3,3',4',5,6-Heptachlorobiphenyl	52663-70-4
PCB 73 (BZ)	2,3',5',6-Tetrachlorobiphenyl	74338-23-1	PCB 178 (BZ)	2,2',3,3',5,5',6-Heptachlorobiphenyl	52663-67-9
PCB 74 (BZ)	2,4,4',5-Tetrachlorobiphenyl	32690-93-0	PCB 179 (BZ)	2,2',3,3',5,6,6'-Heptachlorobiphenyl	52663-64-6
-PCB 75 (BZ)	2,4,4',6-Tetrachlorobiphenyl	32598-12-2	PCB 180 (BZ)	2,2',3,4,4',5,5'-Heptachlorobiphenyl	35065-29-3
PCB 76 (BZ)	2',3,4,5-Tetrachlorobiphenyl	70362-48-0	PCB 181 (BZ)	2,2',3,4,4',5,6-Heptachlorobiphenyl	74472-47-2
PCB 77 (BZ)	3,3',4,4'-Tetrachlorobiphenyl	32598-13-3	PCB 182 (BZ)	2,2',3,4,4',5,6'-Heptachlorobiphenyl	60145-23-5
PCB 78 (BZ)	3,3',4,5-Tetrachlorobiphenyl	70362-49-1	PCB 183 (BZ)	2,2',3,4,4',5',6-Heptachlorobiphenyl	52663-69-1
PCB 79 (BZ)	3,3',4,5'-Tetrachlorobiphenyl	41464-48-6	PCB 184 (BZ)	2,2',3,4,4',6,6'-Heptachlorobiphenyl	74472-48-3
PCB 80 (BZ)	3,3',5,5'-Tetrachlorobiphenyl	33284-52-5	PCB 185 (BZ)	2,2',3,4,5,5',6-Heptachlorobiphenyl	52712-05-7
PCB 81 (BZ)	3,4,4',5-Tetrachlorobiphenyl	70362-50-4	PCB 186 (BZ)	2,2',3,4,5,6,6'-Heptachlorobiphenyl	74472-49-4
PCB 82 (BZ)	2,2',3,3',4-Pentachlorobiphenyl	52663-62-4	PCB 187 (BZ)	2,2',3,4',5,5',6-Heptachlorobiphenyl	52663-68-0

SYNAME	Compound	CAS No	SYNAME	Compound	CAS No
PCB 83 (BZ)	2,2',3,3',5-Pentachlorobiphenyl	60145-20-2	PCB 188 (BZ)	2,2',3,4',5,6,6'-Heptachlorobiphenyl	74487-85-7
PCB 84 (BZ)	2,2',3,3',6-Pentachlorobiphenyl	52663-60-2	PCB 189 (BZ)	2,3,3',4,4',5,5'-Heptachlorobiphenyl	39635-31-9
PCB 85 (BZ)	2,2',3,4,4'-Pentachlorobiphenyl	65510-45-4	PCB 190 (BZ)	2,3,3',4,4',5,6-Heptachlorobiphenyl	41411-64-7
PCB 86 (BZ)	2,2',3,4,5-Pentachlorobiphenyl	55312-69-1	PCB 191 (BZ)	2,3,3',4,4',5',6-Heptachlorobiphenyl	74472-50-7
PCB 87 (BZ)	2,2',3,4,5'-Pentachlorobiphenyl	38380-02-8	PCB 192 (BZ)	2,3,3',4,5,5',6-Heptachlorobiphenyl	74472-51-8
PCB 88 (BZ)	2,2',3,4,6-Pentachlorobiphenyl	55215-17-3	PCB 193 (BZ)	2,3,3',4',5,5',6-Heptachlorobiphenyl	69782-91-8
PCB 89 (BZ)	2,2',3,4,6'-Pentachlorobiphenyl	73575-57-2	PCB 194 (BZ)	2,2',3,3',4,4',5,5'-Octachlorobiphenyl	35694-08-7
PCB 90 (BZ)	2,2',3,4',5-Pentachlorobiphenyl	68194-07-0	PCB 195 (BZ)	2,2',3,3',4,4',5,6-Octachlorobiphenyl	52663-78-2
PCB 71 (BZ)	2,3',4',6-Tetrachlorobiphenyl	41464-46-4	PCB 176 (BZ)	2,2',3,3',4,6,6'-Heptachlorobiphenyl	52663-65-7
PCB 72 (BZ)	2,3',5,5'-Tetrachlorobiphenyl	41464-42-0	PCB 177 (BZ)	2,2',3,3',4',5,6-Heptachlorobiphenyl	52663-70-4
PCB 73 (BZ)	2,3',5',6-Tetrachlorobiphenyl	74338-23-1	PCB 178 (BZ)	2,2',3,3',5,5',6-Heptachlorobiphenyl	52663-67-9
PCB 74 (BZ)	2,4,4',5-Tetrachlorobiphenyl	32690-93-0	PCB 179 (BZ)	2,2',3,3',5,6,6'-Heptachlorobiphenyl	52663-64-6
PCB 75 (BZ)	2,4,4',6-Tetrachlorobiphenyl	32598-12-2	PCB 180 (BZ)	2,2',3,4,4',5,5'-Heptachlorobiphenyl	35065-29-3
PCB 76 (BZ)	2',3,4,5-Tetrachlorobiphenyl	70362-48-0	PCB 181 (BZ)	2,2',3,4,4',5,6-Heptachlorobiphenyl	74472-47-2
PCB 77 (BZ)	3,3',4,4'-Tetrachlorobiphenyl	32598-13-3	PCB 182 (BZ)	2,2',3,4,4',5,6'-Heptachlorobiphenyl	60145-23-5
PCB 78 (BZ)	3,3',4,5-Tetrachlorobiphenyl	70362-49-1	PCB 183 (BZ)	2,2',3,4,4',5',6-Heptachlorobiphenyl	52663-69-1
PCB 79 (BZ)	3,3',4,5'-Tetrachlorobiphenyl	41464-48-6	PCB 184 (BZ)	2,2',3,4,4',6,6'-Heptachlorobiphenyl	74472-48-3
PCB 80 (BZ)	3,3',5,5'-Tetrachlorobiphenyl	33284-52-5	PCB 185 (BZ)	2,2',3,4,5,5',6-Heptachlorobiphenyl	52712-05-7
PCB 81 (BZ)	3,4,4',5-Tetrachlorobiphenyl	70362-50-4	PCB 186 (BZ)	2,2',3,4,5,6,6'-Heptachlorobiphenyl	74472-49-4
PCB 82 (BZ)	2,2',3,3',4-Pentachlorobiphenyl	52663-62-4	PCB 187 (BZ)	2,2',3,4',5,5',6-Heptachlorobiphenyl	52663-68-0
PCB 83 (BZ)	2,2',3,3',5-Pentachlorobiphenyl	60145-20-2	PCB 188 (BZ)	2,2',3,4',5,6,6'-Heptachlorobiphenyl	74487-85-7
PCB 84 (BZ)	2,2',3,3',6-Pentachlorobiphenyl	52663-60-2	PCB 189 (BZ)	2,3,3',4,4',5,5'-Heptachlorobiphenyl	39635-31-9
PCB 85 (BZ)	2,2',3,4,4'-Pentachlorobiphenyl	65510-45-4	PCB 190 (BZ)	2,3,3',4,4',5,6-Heptachlorobiphenyl	41411-64-7
PCB 86 (BZ)	2,2',3,4,5-Pentachlorobiphenyl	55312-69-1	PCB 191 (BZ)	2,3,3',4,4',5',6-Heptachlorobiphenyl	74472-50-7
PCB 87 (BZ)	2,2',3,4,5'-Pentachlorobiphenyl	38380-02-8	PCB 192 (BZ)	2,3,3',4,5,5',6-Heptachlorobiphenyl	74472-51-8
PCB 88 (BZ)	2,2',3,4,6-Pentachlorobiphenyl	55215-17-3	PCB 193 (BZ)	2,3,3',4',5,5',6-Heptachlorobiphenyl	69782-91-8
PCB 89 (BZ)	2,2',3,4,6'-	73575-57-2	PCB 194 (BZ)	2,2',3,3',4,4',5,5'-	35694-08-7

SYNAME	Compound	CAS No	SYNAME	Compound	CAS No
	Pentachlorobiphenyl			Octachlorobiphenyl	
PCB 90 (BZ)	2,2',3,4',5-Pentachlorobiphenyl	68194-07-0	PCB 195 (BZ)	2,2',3,3',4,4',5,6-Octachlorobiphenyl	52663-78-2
PCB 91 (BZ)	2,2',3,4',6-Pentachlorobiphenyl	68194-05-8	PCB 196 (BZ)	2,2',3,3',4,4',5,6'-Octachlorobiphenyl	42740-50-1
PCB 92 (BZ)	2,2',3,5,5'-Pentachlorobiphenyl	52663-61-3	PCB 197 (BZ)	2,2',3,3',4,4',6,6'-Octachlorobiphenyl	33091-17-7
PCB 93 (BZ)	2,2',3,5,6-Pentachlorobiphenyl	73575-56-1	PCB 198 (BZ)	2,2',3,3',4,5,5',6-Octachlorobiphenyl	68194-17-2
PCB 94 (BZ)	2,2',3,5,6'-Pentachlorobiphenyl	73575-55-0	PCB 199 (BZ) 200 (IUPAC)	2,2',3,3',4,5,6,6'-Octachlorobiphenyl	52663-73-7
PCB 95 (BZ)	2,2',3,5',6-Pentachlorobiphenyl	38379-99-6	PCB 200 (BZ) 201 (IUPAC)	2,2',3,3',4,5',6,6'-Octachlorobiphenyl	40186-71-8
PCB 96 (BZ)	2,2',3,6,6'-Pentachlorobiphenyl	73575-54-9	PCB 201 (BZ) 199 (IUPAC)	2,2',3,3',4,5,5',6'-Octachlorobiphenyl	52663-75-9
PCB 97 (BZ)	2,2',3',4,5-Pentachlorobiphenyl	41464-51-1	PCB 202 (BZ)	2,2',3,3',5,5',6,6'-octachlorobiphenyl	2136-99-4
PCB 98 (BZ)	2,2',3',4,6-Pentachlorobiphenyl	60233-25-2	PCB 203 (BZ)	2,2',3,4,4',5,5',6-Octachlorobiphenyl	52663-76-0
PCB 99 (BZ)	2,2',4,4',5-Pentachlorobiphenyl	38380-01-7	PCB 204 (BZ)	2,2',3,4,4',5,6,6'-Octachlorobiphenyl	74472-52-9
PCB 100 (BZ)	2,2',4,4',6-Pentachlorobiphenyl	39485-83-1	PCB 205 (BZ)	2,3,3',4,4',5,5',6-Octachlorobiphenyl	74472-53-0
PCB 101 (BZ)	2,2',4,5,5'-Pentachlorobiphenyl	37680-73-2	PCB 206 (BZ)	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	40186-72-9
PCB 102 (BZ)	2,2',4,5,6'-Pentachlorobiphenyl	68194-06-9	PCB 207 (BZ)	2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl	52663-79-3
PCB 103 (BZ)	2,2',4,5',6-Pentachlorobiphenyl	60145-21-3	PCB 208 (BZ)	2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl	52663-77-1
PCB 104 (BZ)	2,2',4,6,6'-Pentachlorobiphenyl	56558-16-8	PCB 209 (BZ)	Decachlorobiphenyl	2051-24-3
PCB 105 (BZ)	2,3,3',4,4'-Pentachlorobiphenyl	32598-14-4			

Table VIII
Method 1668C QC Acceptance Criteria for VER, IPR, OPR and Labeled compounds in samples

Congener Name	Test Concentration (ng/ml)	VER (%)	IPR RSD (%)	IPR Mean Recovery (%)	OPR Recovery (%)	Labeled compound Recovery in Samples (%)
PCB-1	100	75-125	25	70-130	60-135	NA
PCB-3	100	75-125	25	70-130	60-135	
PCB-4	100	75-125	25	70-130	60-135	
PCB-15	100	75-125	25	70-130	60-135	
PCB-19	100	75-125	25	70-130	60-135	
PCB-37	100	75-125	25	70-130	60-135	
PCB-54	100	75-125	25	70-130	60-135	
PCB-77	100	75-125	25	70-130	60-135	
PCB-81	100	75-125	25	70-130	60-135	
PCB-104	100	75-125	25	70-130	60-135	
PCB-105	100	75-125	25	70-130	60-135	
PCB-114	100	75-125	25	70-130	60-135	
PCB-118	100	75-125	25	70-130	60-135	
PCB-123	100	75-125	25	70-130	60-135	
PCB-126	100	75-125	25	70-130	60-135	
PCB-155	100	75-125	25	70-130	60-135	
PCB-156	100	75-125	25	70-130	60-135	
PCB-157	100	75-125	25	70-130	60-135	
PCB-167	100	75-125	25	70-130	60-135	
PCB-169	100	75-125	25	70-130	60-135	
PCB-188	100	75-125	25	70-130	60-135	
PCB-189	100	75-125	25	70-130	60-135	
PCB-202	100	75-125	25	70-130	60-135	
PCB-205	100	75-125	25	70-130	60-135	
PCB-206	100	75-125	25	70-130	60-135	
PCB-208	100	75-125	25	70-130	60-135	
PCB-209	100	75-125	25	70-130	60-135	
Internal Standards						
$^{13}C_{12}$-PCB-1	100	50-145	70	20-135	15-145	5-145
$^{13}C_{12}$-PCB-3	100	50-145	70	20-135	15-145	5-145
$^{13}C_{12}$-PCB-4	100	50-145	70	20-135	15-145	5-145
$^{13}C_{12}$-PCB-15	100	50-145	70	20-135	15-145	5-145
$^{13}C_{12}$-PCB-19	100	50-145	70	20-135	15-145	5-145
$^{13}C_{12}$-PCB-37	100	50-145	70	20-135	15-145	5-145
$^{13}C_{12}$-PCB-54	100	50-145	70	20-135	15-145	5-145
$^{13}C_{12}$-PCB-77	100	50-145	50	45-135	40-145	10-145
$^{13}C_{12}$-PCB-81	100	50-145	50	45-135	40-145	10-145
$^{13}C_{12}$-PCB-104	100	50-145	50	45-135	40-145	10-145
$^{13}C_{12}$-PCB-105	100	50-145	50	45-135	40-145	10-145
$^{13}C_{12}$-PCB-114	100	50-145	50	45-135	40-145	10-145
$^{13}C_{12}$-PCB-118	100	50-145	50	45-135	40-145	10-145

$^{13}C_{12}$-PCB-123	100	50-145	50	45-135	40-145	10-145
$^{13}C_{12}$-PCB-126	100	50-145	50	45-135	40-145	10-145
$^{13}C_{12}$-PCB-155	100	50-145	50	45-135	40-145	10-145
$^{13}C_{12}$-PCB-156	100	50-145	50	45-135	40-145	10-145
$^{13}C_{12}$-PCB-157	100	50-145	50	45-135	40-145	10-145
$^{13}C_{12}$-PCB-167	100	50-145	50	45-135	40-145	10-145
$^{13}C_{12}$-PCB-169	100	50-145	50	45-135	40-145	10-145
$^{13}C_{12}$-PCB-188	100	50-145	50	45-135	40-145	10-145
$^{13}C_{12}$-PCB-189	100	50-145	50	45-135	40-145	10-145
$^{13}C_{12}$-PCB-202	100	50-145	50	45-135	40-145	10-145
$^{13}C_{12}$-PCB-205	100	50-145	50	45-135	40-145	10-145
$^{13}C_{12}$-PCB-206	100	50-145	50	45-135	40-145	10-145
$^{13}C_{12}$-PCB-208	100	50-145	50	45-135	40-145	10-145
$^{13}C_{12}$-PCB-209	100	50-145	50	45-135	40-145	10-145
Cleanup Standards						
$^{13}C_{12}$-PCB-28	100	65-135	70	20-135	15-145	5-145
$^{13}C_{12}$-PCB-111	100	75-125	50	45-135	40-145	10-145
$^{13}C_{12}$-PCB-178	100	75-125	50	45-135	40-145	10-145

Title: Analysis of Tetra- Through Octa Chlorinated Dioxins and Furans By Isotope Dilution HRGC/HRMS By Method 1613B [Method 1613B]

Approvals (Signature/Date):

2/6/14	2/7/14
Sylvia Krenn — Date	Joe Schairer — Date
Area Supervisor	Health & Safety Manager / Coordinator
2/10/14	2/13/14
Karla Buechler — Date	Robert Hrabak — Date
Quality Assurance Manager	Laboratory Manager

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1. SCOPE AND APPLICATION

1.1. The procedures outlined within this SOP are appropriate for the analysis of samples and the determination of tetra-through-octa chlorinated dibenzo-p-dioxins and dibenzofurans, and 2,3,7,8-TCDD/TCDF associated with the Clean Water Act (CWA – as amended 1987); the Resource Conservation and Recovery Act (RCRA - as amended 1986); and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA - as amended 1986). Preparation of samples is addressed in SOP WS-IDP-0007.

1.2. Specificity is provided for determination of the seventeen 2, 3, 7, 8-substituted polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). See Table 8 for list of analytes and nominal reporting limits.

1.3. Department of Defense (DoD) projects require specific criteria and reporting conventions. Refer to WS-PQA-021 "DoD QSM and AFCEE QAPP Implementation".

2. SUMMARY OF METHOD

2.1. Samples containing coarse solids are prepared for extraction by grinding or homogenization. Drinking water samples are extracted with methylene chloride using separatory funnel procedures. Non drinking water type samples are filtered and then extracted with methylene chloride using separatory funnel procedures; the particulates from the water samples, soils, and other finely divided solids are extracted using a combined Soxhlet (or equivalent) extraction/Dean-Stark azeotropic distillation with toluene (Reference 7, Method 1613).

2.1.1. Internal Standards consisting of stable isotopically labeled analogs of 15 of the PCDDs and PCDFs and are added to each sample prior to extraction. Prior to cleanup and analysis, the extracts of the filtered water and the particulates are combined. (Note: Internal standards are named "Isotope Dilution Analytes" or IDA throughout this SOP.)

2.2. After extraction, $^{37}Cl_4$-labeled 2, 3, 7, 8, -TCDD is added to each extract to measure the efficiency of the cleanup process. Samples are then permeated through silica gel, acidic alumina, and activated carbon chromatography columns. High performance liquid chromatography (HPLC), basic alumina, or back extraction with sulfuric acid/water/NaOH/water can be used for further isolation of the 2, 3, 7, 8-isomers or other specific isomers or congeners.

2.3. After cleanup, the extract is concentrated to near dryness and a known amount of recovery standard is added to each extract. The recovery standard contains two $^{13}C_{12}$-labeled analogs ($^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD). Each extract is concentrated to a final volume in tetradecane. A 1-2uL aliquot of the extract is injected into the gas chromatograph/mass spectrometer. (Note: Recovery standards are called

"Internal Standards" or IS throughout the rest of this SOP.)

2.4. The analytes are separated by the GC and detected by a high resolution (≥10,000) mass spectrometer. Two exact masses (m/z's) are monitored for each analyte. The isotopically labeled compounds serve to correct for the variability of the analytical technique.

2.5. Dioxins and furans are identified by comparing GC retention times and the ion abundance ratios of the m/z's with the corresponding retention time ranges of authentic standards and the theoretical ion abundance ratios of the exact m/z's. Isomers and congeners are identified when the retention times and m/z abundance ratios agree within pre-defined limits. This is accomplished for the specific 2,3,7,8 substituted isomers by using a GC column or columns capable of resolving the 2,3,7,8-substituted isomers from other PCDD/PCDF isomers.

2.6. Quantitative analysis is performed by GC/MS using selected ion current profile (SICP) areas, in one of two ways.

2.6.1. For the fifteen 2,3,7,8-substituted isomers for which labeled analogs are available (see Table 3), the GC/MS system is calibrated and the compound concentration is determined using an isotope dilution technique. Although a labeled analog of the octa-chlorinated dibenzofuran (OCDF) is available, using high-resolution mass spectrometry, it produces an m/z that may interfere with the identification and quantitation of the unlabeled octa-chlorinated dibenzo-p-dioxin (OCDD). Therefore, this labeled analog has not been included in the calibration standards, and the unlabeled OCDF is quantitated against the labeled OCDD. Because the labeled analog of 1,2,3,7,8,9-HxCDD is used as an internal standard (i.e., not added before extraction of the sample), it cannot be used to quantitate the unlabeled compound by strict isotope dilution procedures. Therefore, the unlabeled 1,2,3,7,8,9-HxCDD is quantitated using the average of the responses of the labeled analogs of the two 2,3,7,8-substituted HxCDD's, $^{13}C_{12}$-1,2,3,4,7,8-HxCDD, and $^{13}C_{12}$-1,2,3,6,7,8-HxCDD. As a result, the concentration of the unlabeled 1,2,3,7,8,9-HxCDD is quantitated using the average recovery of the two $^{13}C_{12}$-HxCDD internal standards.

2.6.2. For non-2,3,7,8-substituted isomers, the total concentrations of all isomers within a level of chlorination (i.e., total TCDD), are determined using the average response factor from the calibration of 2,3,7,8-substituted isomers at the same level of chlorination.

2.7. The quality of the analysis is assured through reproducible calibration and testing of the extraction, cleanup, and GC/MS systems.

3. DEFINITIONS

3.1. Definitions of terms used in this SOP may be found in the glossary of the Quality Assurance Manual (QAM).

3.2. Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs): compounds (Figure 1) that contain from one to eight chlorine atoms. The seventeen 2,3,7,8-substituted PCDDs and PCDFs are shown in Table 3. The number of isomers at different chlorination levels is shown in Table 1.

3.3. Homologous series: A series of compounds in which each member differs from the next by a constant amount. The members of one level in the series are called homologs – a group of chlorinated dibenzodioxins or dibenzofurans having a specific number of chlorine atoms.

3.4. Isomer: Chemical compounds that contain the same number of atoms of the same elements, but differ in structural arrangement and properties. For example, 1,2,3,4-TCDD and 2,3,7,8-TCDD are different structural isomers.

3.5. Congener: Any isomer of any homologous series.

3.6. Internal Dilution Analyte (IDA): An IDA is a $^{13}C_{12}$-labeled analog of a congener chosen from the compounds listed in Table 3. IDA's are added to all samples including method blanks and quality control samples before extraction, and they are used to quantitate the concentration of the target analytes. Fifteen IDA's are used in this method. There is one for each of the 2,3,7,8-substituted dioxin and furan isomers (except for OCDF and 1,2,3,7,8,9-HxCDD see section 2.6.1) with the degree of chlorination ranging from four to eight. Additional IDA's may be added to act as retention time references, but they are not used for quantitation.

3.7. Isotope Dilution Analyte (IDA) Solution: A solution (isooctane or toluene) containing the fifteen IDA, which is used to spike all samples prior to extraction.

3.8. Cleanup Recovery/Surrogate Standard (SU): A $^{37}Cl_4$-2,3,7,8-TCDD analog that is added to each sample following extraction to measure the efficiency of the cleanup process.

3.9. Cleanup Recovery/Surrogate Standard Solution: A solution (isooctane or toluene) containing the cleanup recovery standard.

3.10. Internal Standard (IS): Two internal standards are used to determine the percent recoveries for the internal standards. The ^{13}C-1,2,3,4-TCDD is used to measure the percent recoveries of the tetra- and pentachlorinated internal standards while ^{13}C-

1,2,3,7,8,9-HxCDD is used to determine the recovery of the hexa-hepta- and octachlorinated internal standards . ^{13}C-1,2,3,7,8,9-HxCDD also acts as a retention time reference for the unlabeled analog present in sample extracts. They are added to the final sample extract before HRGC/HRMS instrument analysis.

3.11. Internal Standard Solution: A solution (tetradecane, toluene, or isooctane) containing the two recovery standards, which is added to the final sample extract before the HRGC/HRMS analysis.

3.12. DB-5 Column Performance Standard Mixture (DB5 CPSM)(See Table 6): A tetradecane solution containing a mixture of selected PCDD/PCDF standards including the first and last eluting compounds from each homologous series (a window defining mixture), which is used to demonstrate continued acceptable performance of the DB-5 capillary column (i.e., ≤25% valley separation of 2,3,7,8-TCDD from other TCDD isomers) and to define the homologous PCDD/PCDF retention time windows.

3.13. (NOTE: The CPSM contains the second to the last eluting HxCDD isomer [1,2,3,4,6,7-HxCDD], however, the IDA Solution [present in all calibration standards and samples] does contain the last eluting HxCDD [1,2,3,7,8,9-HxCDD])

3.14. DB-225 Column Performance Standard Mixture (DB-225 CPSM)(See Table 6): A tetradecane solution containing a mixture of selected TCDF isomers used to demonstrate continued acceptable performance of the DB-225 capillary column (i.e., ≤25% valley separation of 2,3,7,8-TCDF from other TCDF isomers).

3.15. Performance Evaluation Materials (PEM's): Representative sample portions containing known amounts of certain unlabeled PCDD/PCDF congeners (in particular the ones having a 2,3,7,8-substitution pattern). Representative interferences may be present. PEMs may be obtained from the EPA EMSL-LV or other sources and submitted to potential contract laboratories, which must analyze these and obtain acceptable results before being awarded a contract for sample analyses (see IFB Pre-Award Bid Confirmations). PEMs may also be included as unspecified ("blind") quality control (QC) samples in any sample batch submitted to a laboratory for analysis.

3.16. Signal to Noise Ratio (S/N): The ratio of the mass spectrometer response of a GC peak to the background noise signal.

3.17. Tuning (Mass Resolution Check): Standard method used to demonstrate a static resolving power of 10,000 minimum (10 percent valley definition).

3.18. Method Calibration Limits: For a given sample size, a final extract volume, and the lowest and highest concentration calibration solutions, the lower and upper calibration limits delineate the region of quantification for which the HRGC/HRMS system was calibrated with standard.

3.19. Matrix Spike Fortification Solution (also known as the Native Spike Solution): Solution used to prepare the laboratory control sample (LCS), matrix spike (MS), and matrix spike duplicate (SD) samples. It contains all unlabeled analytes listed in Table 3.

3.20. PFK: Perfluorokerosene; used to calibrate the exact m/z scale in the HRMS.

3.21. Estimated Detection Limit (EDL): The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background noise level.

3.22. Estimated Maximum Possible Concentration (EMPC): The calculated concentration of a signal having the same retention time as a PCDD/PCDF congener, but which does not meet the other qualitative identification criteria defined in the method.

3.23. Lower Calibration Limit (LCL): The level at which the entire analytical system must give a recognizable signal and acceptable calibration. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

4. INTERFERENCES

4.1. Solvents, reagents, glassware and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Where possible, reagents are cleaned by extraction or solvent rinse.

4.2. Proper cleaning of glassware is extremely important because glassware may not only contaminate the samples, but may also remove the analytes of interest by absorption on the glassware surface.

4.2.1. Glassware is rinsed with solvent and washed with a detergent solution as soon after use as practical. Sonication of glassware containing a detergent solution for approximately 30 seconds may aid in cleaning. Glassware with removable parts, particularly separatory funnels with Teflon stopcocks, must be disassembled prior to detergent washing.

4.2.2. After detergent washing, glassware is immediately rinsed with tap water or DI water, then with acetone, then with toluene. The toluene rinse is followed by hexane, and then methylene chloride.

4.2.3. Do not bake reusable glassware in an oven as a routine part of cleaning. Baking may be warranted after particularly dirty samples are encountered, but should be minimized, as repeated baking of glassware may cause active sites on the glass surface that will irreversibly absorb PCDDs/PCDFs.

4.2.4. Immediately prior to use, Soxhlet (or equivalent) extraction glassware is pre-extracted with toluene for approximately 4 hours (1 hour for Soxtherm extraction glassware) (See Method 1613A, Section 11.2.3). Separatory funnels are rinsed sequentially with acetone, toluene, hexane and methylene chloride.

4.3. All materials used in the analysis shall be demonstrated to be free from interferences by running reference blanks initially and with each sample set (samples started through the extraction process on a given 12-hour shift, to a maximum of 20 samples).

4.3.1. The reference matrix blank must simulate, as closely as possible, the sample matrix under test. Reagent water is used to simulate water samples; playground sand, white quartz sand, or sodium sulfate can be used to simulate soils; filter paper or Soxhlet extraction thimbles are used to simulate paper and similar materials; and other materials can be used to simulate other matrices.

4.4. Interferences co-extracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled. Interfering compounds may be present at concentrations several orders of magnitude higher than the PCDDs and PCDFs. The most frequently encountered interferences are: chlorinated-biphenyls; methoxy biphenyls; hydroxy biphenyl ethers; benzyl phenyl ethers; polynuclear aromatics; and pesticides. Because very low levels of PCDDs and PCDFs are measured by this method, the elimination of interferences is essential. The cleanup steps given in WS-IDP-0007 can be used to reduce or eliminate these interferences and thereby permit reliable determination of the PCDDs and PCDFs at the levels shown in Table 8.

4.4.1. If South Carolina samples show diphenyl ethers at levels that could contribute to positive furan hits, a clean-up to remove them must be performed.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the reponsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbant shoes are a minimum. All work must be stopped in the event of a known or potential compromise to the health or safety of an associate. The situation must be reported immediately to a supervisor, the EH&S Staff, or a senior manager.

5.1. Specific Safety Concerns or Requirements

5.1.1. The effluents of sample splitters for the gas chromatograph and roughing pumps on the HRGC/HRMS system are passed through either a column of

activated charcoal or be bubbled through a trap containing oil or high-boiling alcohol.

5.1.2. Eye protection that satisfies ANSI Z87.1, laboratory coat, and chemically resistant gloves must be worn while samples, standards, solvents, and reagents are being handled. Latex and vinyl gloves provide no protection against most of the organic solvents used in this method. Nitrile or similar gloves must be used. Latex gloves may be used for methanol.

5.1.3. Exposure to chemicals must be maintained as low as reasonably achievable; therefore all samples must be opened, transferred and prepared in a fume hood. Solvent and waste containers will be kept closed unless transfers are being made.

5.1.4. Laboratory procedures such as repetitive use of pipettes, repetitive transferring of extracts and manipulation of filled separatory funnels and other glassware represent a significant potential for repetitive motion or other ergonomic injuries. Laboratory associates performing these procedures are in the best position to realize when they are at risk for these types of injuries. Whenever a situation is found in which an employee is performing the same repetitive motion, the employee shall immediately bring this to the attention of their supervisor, manager, or the EH&S staff. The task will be analyzed to determine a better means of accomplishing it.

5.2. Primary Materials Used

5.2.1. The following is a list of the materials used in this method, which have a serious or significant hazard rating.

5.2.2. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	**Hazards**	**Exposure Limit (2)**	**Signs and symptoms of exposure**
Tetradecane	Irritant	None established	Inhalation of vapors may cause difficulty breathing, headache, intoxication and central nervous system damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

6.1. Preventive and routine maintenance is described in Section 11.7 of this SOP.

6.2. High-Resolution Gas Chromatograph/High-Resolution Mass Spectrometer/Data System (HRGC/HRMS/DS).

6.2.1. Gas Chromatograph: HP 6890 GC, or equivalent.

6.2.1.1. The GC must be equipped for temperature programming.

6.2.1.2. All required accessories must be available, such as syringes, gases, and capillary columns.

6.2.1.3. The GC injection port must be designed for capillary columns.

- The use of splitless injection techniques is recommended. The use of a moving needle injection port is also acceptable.

6.2.1.4. When using the method described in this protocol, a 2-µL injection volume is used consistently (i.e., the injection volumes for all extracts, blanks, calibration solutions and the performance check samples are 2 µL).

- 1 µL injections are allowed; however, laboratories are encouraged to remain consistent throughout the analyses by using the same injection volume at all times on a given HRGC/HRMS/DS.

6.2.2. Gas Chromatograph/Mass Spectrometer (GC/MS) Interface

6.2.2.1. The GC/MS interface components should withstand 350° C.

6.2.2.2. The interface must be designed so that the separation of 2,3,7,8-TCDD from the other TCDD isomers achieved in the gas chromatographic column is not appreciably degraded.

6.2.2.3. Cold spots or active surfaces (adsorption sites) in the GC/MS interface can cause peak tailing and peak broadening.

6.2.2.4. It is recommended that the GC column be fitted directly into the mass spectrometer ion source without being exposed to the ionizing electron beam.

6.2.2.5. Graphite ferrules should be avoided in the injection port because they may adsorb the PCDDs and PCDFs. Vespel® or equivalent ferrules are recommended.

6.2.3. Mass Spectrometer

6.2.3.1. The static resolving power of the instrument must be maintained at a minimum of 10,000 (10 percent valley).

6.2.3.2. The mass spectrometer must be operated in a selected ion monitoring (SIM) mode with a total cycle time (including the voltage reset time) of one second or less.

6.2.4. Data System

6.2.4.1. A dedicated data system is employed to control the rapid multiple ion monitoring process and to acquire the data.

6.2.4.2. Quantification data (peak areas or peak heights) and SIM traces (displays of intensities of each ion signal being monitored including the lock-mass ion as a function of time) must be acquired during the analyses and stored.

6.2.4.3. Quantifications may be reported based upon computer-generated peak areas or upon measured peak heights (chart recording).

6.2.4.4. The data system must be capable of acquiring data for a minimum of 10 ions in a single scan.

6.2.4.5. The data system is capable of switching to different sets of ions (descriptors) at specified times during an HRGC/HRMS acquisition.

6.2.4.6. The data system is able to provide hard copies of individual ion chromatograms for selected gas chromatographic time intervals.

6.2.4.7. The data system is also able to acquire mass-spectral peak profiles and provide hard copies of peak profiles to demonstrate the required resolving power.

6.2.4.8. The data system permits the measurement of noise on the base line.

6.2.4.9. Capable of collecting, recording and storing MS data. The VG70 and Autospec Ultima systems utilize Opus version 3.6 software and the Autospec Premiere system utilizes MassLynx version 4.1 software for collecting the data, and Chrom Version 2.2x to process the data.

6.3. GC Column

6.2.1 In order to have an isomer-specific determination for 2,3,7,8-TCDD and to allow the detection of OCDD/OCDF within a reasonable time interval in one HRGC/HRMS analysis, the 60-m DB-5 fused-silica capillary column is recommended.

6.2.2 At the beginning of each 12-hour period during which samples are analyzed and after tuning, acceptable compound separation on the GC column must be demonstrated through the analysis of a column performance check solution.

7. REAGENTS AND STANDARDS

7.1. Solvents and Standards:

7.1.1. High-purity, distilled-in-glass or highest available purity: Tetradecane.

7.1.2. Standards are purchased as solutions or mixtures with certification of their purity, concentration, and authenticity, or prepared from materials of known purity and composition.

7.1.2.1. If the chemical purity is 98% or greater, the weight may be used without correction to compute the concentration of the standard.

7.1.2.2. When not being used, standards can be stored in the dark at room temperature or refrigerated in screw-capped vials with fluoropolymer-lined or Teflon ® - lined caps.

7.1.2.3. A mark is placed on the vial at the level of the solution so that solvent loss by evaporation can be detected. If solvent loss has occurred, the solution should be replaced.

7.1.3. Sealed ampules may be used until the manufacturer's expiration date is exceeded.

7.1.3.1. If no expiration date is provided, then the expiration date will be 10 years from the date the ampule is opened.

7.1.3.2. The solvent level should be monitored prior to each use to assure there has been no concentration of the standard over time.

7.1.4. All calibration, daily isotope dilution analytes, daily internal standards, surrogates, and daily native analyte spiking solutions are stable for one year from preparation.

7.1.4.1. After 1 year, solutions may be re-verified. The re-verified solution may be used for an additional year, or until there is evidence of compound degradation or concentration.

7.1.4.2. The re-verification must be performed using an unexpired, not previously re-verified solution from a second lot or second vendor.

7.2. Stock Solutions

7.2.1. Preparation – Prepare in nonane or equivalent solvent per the steps below or purchase as dilute solutions (Cambridge Isotope Laboratories, Cambridge, MA, or equivalent). Observe standard safety precautions.

7.2.2. Dissolve an appropriate amount of assayed reference material in solvent. For example, weigh 1 to 2mg of 2,3,7,8-TCDD to three significant numbers in a 10mL vial with Teflon ® - lined cap.

7.2.3. Stock standard solutions should be checked for signs of degradation prior to the preparation of calibration or performance test standards. Reference standards that can be used to determine the accuracy of calibration standards are available from Cambridge Isotope Laboratories and may be available from other vendors.

7.2.4. Secondary standard – Using stock solutions prepare secondary standard solutions if necessary which can be further diluted the spiking standard solutions (see below).

7.3. Precision and Recovery Standard (PAR) – Also known as the Matrix Spike or Native Spike solution. Contains all the 2,3,7,8-substituted unlabeled analytes listed in Table 4. Prepare using the appropriate standards made in section 7.5 to yield a spiking solution with a concentration of 4.0ng/ml for the tetra- CDDs/CDFs, 20ng/ml for the penta-, hexa-, and hepta- CDDs/CDFs, and 40ng/ml for the octa- CDD/CDF.

7.3.1. This is prepared by the dioxin Hi-Res department.

7.4. Sample Fortification Solution (Isotope Dilution Analyte) – Also known as the Daily Isotope Dilution Analyte. From stock solutions or purchased mixtures, prepare this solution in isooctane (or toluene) to contain the fifteen isotope dilution analytes at the nominal concentrations that are listed in Table 4.

7.4.1. This is prepared by the dioxin Hi-Res department.

7.5. Internal Standard Solution – This solution contains the two internal standards ($^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD). This solution is preferably prepared in tetradecane. See Table 4 for nominal concentrations.

7.6. Surrogate Standard Solution (CRS) – Prepare $^{37}Cl_4$-2,3,7,8-TCDD at the concentration shown in Table 4, in isooctane (or toluene).

7.6.1. This is prepared by the dioxin Hi-Res department.

7.7. Calibration Standards (CS1 through CS6)

7.7.1. High-Resolution Concentration Calibration Solutions (Table 5) – Combine the spiking solutions in sections 7.4 through 7.6 to produce the five tetradecane calibration solutions listed in Table 5. These solutions permit the relative response to be measured as a function of concentration.

7.7.1.1. The CS4 (midpoint) standard is routinely used for calibration verification (Note: any other calibration point within the lower or upper calibration solution may be used for calibration verification).

7.7.1.2. Store the calibration solutions in appropriate containers and at room temperature in the dark.

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1. The sample collection, shipping, handling, and chain-of-custody procedures are not described in this document. Sample collection personnel will, to the extent possible, homogenize samples in the field before filling the sample containers. This should minimize or eliminate the necessity for sample homogenization in the laboratory.

8.2. Samples are collected in amber glass containers following conventional sampling practices (Method 1613). Freely flowing aqueous samples are collected in refrigeration bottles using automatic sampling equipment. Solid samples are collected as grab samples using wide mouth jars.

8.3. Samples are stored at 0-4ºC in the dark from the time of collection until extraction (fish tissues must be stored at - 20°C).

8.3.1. A measurement of residual chlorine is performed using Standard Methods 4500-Cl B, C, D, E, F, or G. The residual chlorine will be checked at the laboratory for all aqueous samples. If residual chlorine is present in aqueous samples, the sampler or analyst adds 80mg of sodium thiosulfate per liter of water.

8.4. Sample extraction is performed within 365 days of sampling. Sample analysis is performed within forty (40) days of extraction.

9. QUALITY CONTROL

9.1. Batches are defined at the sample preparation step. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the QC program document (WS-PQA-0003) for further details of the batch definition.

9.1.1. The quality control batch is a set of up to 20 samples of the same matrix processed using the same procedure and reagents within the same time period. The quality control batch must contain a laboratory control sample (LCS) and a method blank (MB). Laboratory generated QC samples (MB, LCS, MS/MSD) do not count toward the maximum 20 samples in a batch. Field QC samples are included in the batch count. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. If insufficient sample is available for an MS/MSD and batch specific precision is required, an LCSD may be substituted. In the event that multiple MS/MSDs are run with a batch due to client requirements, the additional MS/MSDs do not count toward the maximum 20 samples in a batch.

9.2. One method blank must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. For aqueous samples, the method blank is an aliquot of laboratory reagent water. Use Ottawa sand as the method laboratory matrix when solids are extracted. Use a mixture of Ottawa sand and canola oil as the matrix when tissues are extracted. Take the method blank through all steps detailed in the analytical procedure. The method blank is processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a non-conformance memo (NCM), then implemented when target analytes are detected in the method blank above the reporting limit or when surrogate or IDA recoveries are outside of the control limits. Re-extraction of the blank, other batch QC, and the affected samples are required when the method blank is deemed unacceptable. See policy WS-PQA-0003 for specific acceptance criteria.

9.2.1. The method blank must not contain any analyte at or above the reporting limit, or at or above 10% of the measured concentration of that analyte in the associated samples, whichever is higher.

9.2.2. If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be taken in consultation with the client.

9.2.3. Projects performed under the auspices of the DoD QSM or AFCEE must meet DoD-specific criteria for method blanks. Results are acceptable if the blank

contamination is less than ½ of the reporting limit for each analyte, or less than 1/10 of the regulatory limit, or less than 1/10 of the sample result for the same analyte, whichever is greater. If the method blank does not meet the acceptance criteria, the source of contamination must be investigated and measures taken to correct, minimize or eliminate the problem. If contamination remains, the contaminated samples should be re-prepared and reanalyzed with a new MB and batch-specific QC samples.

9.2.4. If method blank contamination is present, check solvents, reagents, fortification solutions, apparatus and glassware to locate and eliminate the source of contamination before any further samples are extracted and analyzed.

9.2.4.1. OCDD is a ubiquitous laboratory contaminant.

9.2.4.2. A method blank and the associated samples are deemed acceptable if the OCDD concentration is less than 5 times the specified reporting limit.

9.2.4.3. If the OCDD is greater than 5 times the specified limit, flag data appropriately.

9.2.4.4. The analyst is expected to investigate and eliminate potential sources of systematic contamination.

9.2.4.5. If a target analyte is detected in the blank but the associated samples are ND (not detected), then the data may be reported, unless otherwise directed by the client. Note the action in the narrative.

9.2.4.6. If a target analyte is detected in the blank, but the concentration of the contaminant in the samples is greater than 10 times the blank concentration, then the data may be reported, unless otherwise directed by the client. Note the action in the narrative.

9.2.4.7. Method blank contamination of non-target analytes (i.e., non-2,3,7,8-substituted isomers) does not require corrective action, but a non-conformance memo is generated explaining the contamination and impact on sample data. “Totals” concentrations are not flagged to reflect blank contamination because totals are considered estimated values.

9.2.4.8. If the method blank is contaminated with any 2,3,7,8-substituted target analyte above the lower calibration limit (other than the exception noted above for OCDD), and the associated sample

contains a positive result for that same analyte above the LCL and less than 10 times the blank concentration. Re-extraction of the associated sample is required, unless otherwise stipulated by the client, where the occurrence shall be documented in the non-conformance memo.

9.2.5. If new batches of reagents or solvents contain interfering contaminants, purify or discard them.

9.3. A Laboratory Control Sample (LCS) must be extracted with every process batch of similar matrix, not to exceed twenty (20) environmental samples. The LCS is an aliquot of laboratory matrix (e.g. water, Ottawa sand, sodium sulfate, etc.) spiked prior to extraction with analytes of known identity and concentration. The LCS must be processed in the same manner and at the same time as the associated samples.

9.3.1. Corrective actions must be documented on a Non-Conformance memo, then implemented when recoveries of any spiked analyte is outside control limits provided on the LIMS or by the client. Limits for Method 1613B are defined by the method, and are listed in Table 9.

9.3.2. Re-extraction of the blank, other batch QC and all associated samples are required if the LCS is deemed unacceptable.

9.3.2.1. Control charts are evaluated per WS-PQA-0003 to assure these limits are met.

9.3.3. A LCS is deemed acceptable if control analytes are above control limits and the associated samples are non detect, unless otherwise specified by the client. Note any actions in the narrative.

9.3.4. For drinking water samples for the State of Arizona, a second LCS spiked at the method reporting limit must be prepared. For clarity it will be named the Laboratory Fortified Blank (LFB). One LFB must be prepared for each day drinking water samples are extracted for the State of Arizona. All compounds in the LFB must have a recovery between 50-150%.

9.4. The assessment of matrix effects on method performance, as required by NELAP, is met in Method 1613, as in all isotope dilution techniques, with the use of isotopically labeled compounds.

9.4.1. These isotopically labeled compounds are analogs of target analytes and are spiked into each sample. Therefore, matrix effects on method performance can be judged by the recovery of these analogs. Sample analysis acceptance is controlled by the performance of these analogs in each sample.

9.4.2. A Matrix Spike/Matrix Spike Duplicate (MS/MSD or MS/SD) pair is extracted at the client's request only and is not required by Method 1613B. An MS/MSD pair are aliquots of a selected field sample spiked with analytes of known identity and concentration. The MS/MSD are also spiked prior to extraction with the same $^{13}C_{12}$-labeled IDA as the method blank, laboratory control sample, and field samples. The MS/MSD pair shall be processed in the same manner and at the same time as the associated samples.

9.4.2.1. The results obtained from the MS and MSD samples (percent recovery and concentrations of 2,3,7,8-substituted PCDDs/PCDFs) shall agree within 50 percent relative difference. Report all results, flag any outliers, and file a non-conformance memo for any outliers. Re-extraction is not required when a MS/MSD pair fail to meet one or more QC criteria.

9.5. An Instrument Blank must be evaluated after calibration standards are injected and before sample analysis may begin. This may be accomplished by analysis of a method blank. If a method blank is not available, an instrument blank must be analyzed.

9.5.1. An instrument blanks consists of solvent (isooctane, toluene, or tetradecane). It is evaluated by inspection for contamination that may affect sample analysis.

9.6. Isotope Dilution Analyte recoveries are flagged if they are outside the recovery goals. Quantitation by isotope dilution generally precludes any adverse effect on data quality due to isotope dilution analyte recoveries being outside QC limits as long as the signal-to-noise is greater than 10:1.

9.6.1. Evaluate data quality for usability, flag and submit a non-conformance memo for any analytes outside of the recovery criteria, and report if data is deemed not adversely effected.

9.6.2. Re-extraction of samples should be performed if signal-to-noise for any isotope dilution analyte is less than 10:1 or if isotope dilution analyte recoveries fall below 10%.

9.6.2.1. Re-extraction may be necessary under other circumstances when data quality has been determined to be adversely affected.

9.7. Duplicates – Upon client request, duplicates may be processed. A duplicate injection of a sample extract may be performed at the clients request to display instrument precision. The results of the laboratory duplicates (percent recovery and concentrations of 2,3,7,8-substituted PCDD/PCDF compounds) should agree within 50 percent relative difference. Report all results and flag any outliers, re-extraction is not required when RPD limits are not met.

9.8. Field Blanks – Each batch of samples may contain a field blank sample of nominally uncontaminated soil, sediment or water that is to be processed for analysis. Treat this sample as all others.

9.9. Rinsate Samples – In addition to the field blank, a batch of samples may include a rinsate, which is a portion of the solvent (usually trichloroethylene) that was used to rinse sampling equipment. The rinsate is analyzed to assure that the samples were not contaminated by the sampling equipment. The rinsate sample must be processed like a regular sample.

9.10. Recommended Corrective Actions and Troubleshooting Steps

9.10.1. Verify satisfactory instrument performance.

9.10.2. If possible, verify that no error was made while weighing the sample portions.

9.10.3. Review the analytical procedures with the performing laboratory personnel.

10. CALIBRATION AND STANDARDIZATION

10.1. For details of the calculations used to generate the regression equations, and how to use the factors generated by them, refer to SOP CA-Q-S-005 “Calibration Curves (General)”.

10.2. Two types of calibration procedures are required.

10.2.1. One type***, initial calibration***, is required before any samples are analyzed and is required intermittently throughout sample analysis as indicated by the results of the continuing calibration procedures described below.

10.2.2. The other type, ***continuing calibration***, consists of analyzing the column performance check solution and a calibration solution (typically CS3). No samples are to be analyzed until acceptable calibration is demonstrated in sections 10.6 and 10.7.

10.3. The following GC operating conditions are typically used:

DB-5 Column
Injector temp: 280ºC
Interface temp: 280 ºC
Initial temp and time: 190 ºC, 1 min
Temp program: 190-240ºC at 4 ºC/min
240ºC for 16 min
240-320 ºC at 20 ºC/min
320 ºC for 10 min

DB-225 Column
Injector temp: 240ºC
Interface temp: 240ºC
Initial temp and time: 190ºC, 1 min
Temp program: 190-240ºC at 3.5ºC/min
240ºC for 20 min

10.3.1. For South Carolina samples, the retention time of ^{13}C-1,2,3,4-TCDD must exceed 25 minutes on the DB-5 column and 15 minutes on the DB-225 column.

Method 1613 suggests the following as a temperature program that can be used to meet these criteria:

DB-5 Column
Injector temp: 270ºC
Interface temp: 290 ºC
Initial temp and time: 200 ºC, 2 min
Temp program: 200-220ºC at 5 ºC/min
220ºC for 16 min
220-235 ºC at 5 ºC/min
235ºC for 7 min
235-330°C at 5°C/min

NOTE: All portions of the column, which connect the GC to the ion source, remain at the interface temperature specified above during analysis, to preclude condensation of less volatile compounds.

10.4. Mass spectrometer (MS) resolution - tune the mass spectrometer to achieve a minimum resolving power of 10,000 (at 10 percent of peak height) at m/z 304.9824 (PFK). Other masses monitored but not required by the method are as follows:

Function 1: *[292.98245], [318.97925], [330.97925], [342.97925], [354.97925], [366.97925], [380.97604], [392.97604], [404.97604], [416.97604]*

Function 2: *[330.97925], [342.97925], [354.97925], [366.97925], [380.97604], [392.97604], [404.97604], [416.97604]*

Function 3: *[366.97925], [380.97604], [392.97604], [404.97604], [416.97604], [430.97284], [442.97284], [454.97284]*

Function 4: *[404.97604], [416.97604], [430.97284], [442.97284], [454.97284], [466.97284], [480.96967]*

Function 5: *[430.97284], [442.97284], [454.97284], [466.97284], [480.96967], [492.96967], [504.96967], [516.96967]*

While in peak examine mode, print the peak profile display for all functions required, demonstrating that this minimum resolution criterion has been met.

10.4.1. Operate the mass spectrometer in mass drift correction mode.

10.4.1.1. A lock-mass ion from the reference compound PFK (perflourokerosene) is used to correct for mass drift in each group of masses (function) in the mass spectrometer experiment.

10.4.1.2. Excessive variations of the lock-mass can indicate the presence of coeluting interferences, which may significantly reduce the sensitivity of the mass spectrometer.

10.4.1.3. Re-extraction of a smaller aliquot or dilution of the original extract may be required to reduce these interferences to an acceptable level.

NOTE: Excessive PFK may cause elevated noise levels and a dirty ion source.

For the following injections, use the GC conditions specified in section 10.2 above.

10.4.2. Monitor each group (function) of masses (see Table 10) in succession as a function of retention time to ensure that all PCDDs and PCDFs are detected.

10.4.2.1. Inject 1-2 µL of concentrated sample extract (containing recovery standards) or standard solution using spitless injection.

10.4.2.2. Start GC isothermal hold and temperature program immediately upon injection.

10.4.2.3. Start MS data collection after the solvent peak has eluted.

10.4.2.4. At the end of the temperature program, (after the octachloro-dibenzodioxin and dibenzofuran have eluted), return the GC to the initial temperature for analysis of the next sample or standard.

10.5. Retention time windows

10.5.1. Analyze a 1-2 µL of the window defining mixture (WDM) to demonstrate that the GC/MS experiment is monitoring the masses for each PCDD and PCDF chlorination level from the retention time of the first eluting isomer until that of the last eluter.

10.5.2. Isomer specificity; Analyze the isomer specificity test standard (the CPSM).

10.5.2.1. This standard solution has been combined with the window defining mixture so that both parameters can be checked with a single GC/MS injection.

10.5.2.2. Compute the percent valley between the GC peaks that elute most closely to 2,3,7,8-TCDD and TCDF on their respective columns.

10.5.2.3. Verify that the height of the valley between the most closely eluted isomers and the 2,3,7,8-isomers does not exceed 25 percent of the height of the latter.

- If this criterion is not met, GC maintenance will likely be necessary.

10.5.2.4. **NOTE**: The CPSM/WDM is required prior to sample analysis, but need not be acquired prior to the ICAL and is not provided as part of the ICAL standards package.

10.6. Initial Calibration

10.6.1. A five-point calibration curve encompassing the concentration range is used for each compound to be determined (see Table 5).

10.6.2. To calibrate the analytical system, inject a 1-2 µL aliquot of each of the 6 calibration standards (CS-1 to CS-6; Table 5). (CS-1 ultra low level is optional)

10.6.3. Print hardcopies of the mass chromatograms (masses listed in Table 9 and 13).

10.6.4. Verify that the signal-to-noise ratio (S/N) is greater than or equal to 10 for all PCDD/PCDF ions.

10.6.4.1. Generally the unlabeled TCDD/TCDF ions for solution CS-1 and CS-2 are the ones for which meeting this requirement can be difficult.

10.6.4.2. Reducing the level of PFK being bled into the source and attempting to retune the mass spectrometer for better sensitivity are two measures which often remedy low signal-to-noise ratio.

- For Arizona samples, the level of PFK metered into the HRMS during analysis should be adjusted so that the amplitude of the most intense selected lock-mass m/z signal (regardless of the descriptor number) does not exceed 10% of the full-scale deflection for a given set of detector parameters.

10.6.5. Compute ion abundance ratios for the two ions monitored for each labeled compound and analyte; verify that these are within the limits given in Table 2.

10.6.6. Calculate the relative response factor (RRF) of each unlabeled compound vs. its isotope dilution analyte, and of each isotope dilution analyte vs. its internal standard (Table 10).

10.6.6.1. Compute the mean RRF, standard deviation and percent compound.

10.6.6.2. If the relative standard deviation exceeds 20 percent for any native compound, or 30 percent for any labeled compound, the mean RRF may not be used.

- The complete calibration curve for that compound may be used over the five point range in place of the mean RRF.

10.6.7. A relative response factor is calculated for each unlabeled PCDD/PCDF vs. its 13C-labeled analogue standard using the area responses of both the primary and secondary ions (specified in Table 9). These relative response factors are calculated as follows:

$$RRF = \frac{(A_{s1} + A_{s2})\, C_{IDA}}{(A_{IDA1} + A_{IDA2})\, C_s}$$

Where:

A_{s1} and A_{s2} are the areas of the primary and secondary ions for the compound to be calibrated (NOTE: only one ion is used for 37Cl4-2, 3 ,7, 8-TCDD).

A_{IDA1} and A_{IDA2} are the area of the primary and secondary ions for the isotope dilution analyte (or internal standard when a surrogate or cleanup recovery standard is being calibrated).

C_{IDA} is the concentration of the isotope dilution analyte (or internal standard when an surrogate or cleanup recovery standard is being calibrated).

C_S is the concentration of the compound to be calibrated

10.7. Continuing Calibration:

At the beginning of each 12-hour shift during which samples are to be analyzed, GC/MS system performance and calibration are verified for all unlabeled and labeled compounds.

10.7.1. MS Resolution - A static resolving power of at least 10,000 (10 percent valley definition) must be demonstrated at appropriate masses before any analysis is performed.

10.7.1.1. Static resolving power checks are performed at the beginning and ending of each analytical sequence.

- An analytical sequence is defined as from the time the instrument run is started until it is stopped.
- Due to software limitations, an MS Resolution Check cannot be performed during an analytical sequence.
- An analytical sequence may include one or more 12 hour periods during which samples are acquired.

Note: The exceptions to Section 10.6.1.3 are samples for the state of Arizona. These samples must have the MS Resolution Check done at the beginning and the end of each 12 hour period.

10.7.1.2. The MS Resolution Checks brackets all samples from the initial MS Resolution Check, during which time no instrument parameters are changed. Static mass resolving power checks must be performed at the beinniing and end of each 12 hour run.

10.7.2. Analyze the CPSM/WDM mixture at the beginning of each 12-hour period to ensure that the retention time window and isomer specificity criteria are met.

10.7.2.1. This mixture can be analyzed either immediately before or immediately after the calibration verification standard.

10.7.2.2. In either case, inject an instrument blank or method blank (see Section 9.3 above) prior to analyzing samples. Note that the CPSM/WDM does not define the beginning of a 12-hour sample acquisition period. The 12-hour sample acquisition period begins with the calibration verification standard (see below).

10.7.3. The CS-4 calibration standard ("VER Standard," Table 5) is analyzed and quantitated using the relative response factors calculated from the initial calibration.

10.7.4. The calculated concentration of each unlabeled and labeled compound is compared to the range given in the Table 9. If all of the following criteria are met, calibration has been verified:

10.7.4.1. Ion abundance ratios for all PCDDs and PCDFs are within the limits given in Table 2.

10.7.4.2. The peaks representing each unlabeled and labeled compound, calculated using averaged relative response factors (RRFs) from the initial calibration curve, is within the limits specified in Table 9.

10.7.4.3. If any of these criteria are not met, try retuning the mass spectrometer and reinjecting the VER Standard.

10.7.4.4. If each peak's S/N ratio does not meet 10:1, the instrument sensitivity is inadequate and needs attention. Note: filament replacement may solve this issue, otherwise, replacing the ion source with a clean one will probably be necessary.

10.7.4.5. If, after two or more injections, sensitivity of the mass spectrometer is adequate but the concentrations found in the VER Standard continue to fall outside the limits stated in Table 9, the initial calibration should be repeated, if no additional problem with the instrument can be found.

10.7.4.6. As a standard practice to increase efficiency, samples may have been analyzed before the Continuing Calibration Standard (CCV) has been checked.

10.7.4.7. If any CCV criteria or CPSM criteria is not met, review the sample data for usability. If there is no adverse impact to data quality, document using an NCM, and the data may be reported otherwise reinject. Perform corrective action before the next analytical sequence.

10.8. Retention times and GC resolution – The relative retention times (RRT) of unlabeled and labeled PCDDs and PCDFs should be within the limits specified in Table 8. In addition the absolute retention times of $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$- 1,2,3,7,8,9-HxCDD internal standards must be within +/- 15 seconds of the relative retention time obtained during calibration.

11. PROCEDURE

11.1. HRGC/HRMS analysis

11.1.1. Analyze the sample extracts under the same instrument operating conditions

used to perform the instrument calibration.

11.1.2. Record the analysis information in the instrument logbook. Peer review of each analytical sequence is required and must be documented with date and initials. Document and verify each of the following in the instrument logbook: Data File ID, Sample #, Sample ID, Final Volume, Method/Matrix, Sample Size, Units.

11.2. Ongoing precision and recovery – Analyze the extract of the diluted precision and recovery standard (PAR), known as the LCS. Calculate the concentration of each unlabeled and labeled PCDD and PCDF and compare it with the limits for ongoing accuracy in Table 9.

11.2.1. If all compounds meet acceptable criteria, system performance is acceptable. If, however, any individual concentration falls outside the range given, the associated sample set should be evaluated to determine whether there is adverse impact to data quality.

11.2.1.1. If data quality has been unaffected (for example, an LCS unlabeled analyte has a high percent recovery, but all associated samples are ND) anomalize using an NCM, and report the data.

11.2.1.2. If it is determined that data quality has been adversely affected (for example, in the LCS an unlabeled analyte has a high recovery and the associated samples are positive) re-extract the adversely affected samples.

11.2.2. LCS (OPR) samples (method blanks, spiked with unlabeled PCDDs and PCDFs) are run at the rate of one for every 20 samples extracted from a given matrix, or one per daily extraction batch of a given matrix. The LCS is usually prepared at a mid-level concentration. For drinking water samples a second LCS is prepared at the reporting limit concentration. To differentiate it this LCS is called the Laboratory Fortified Blank (LFB). One LFB is prepared for each day drinking water samples are extracted. All compounds in the LFB must have a recovery between 50-150%.

11.2.3. Results that fall within the OPR specifications in Table 9 are entered in the ongoing precision and recovery database for each compound in each matrix.

11.2.3.1. Update QC charts to form a graphical representation of continuing laboratory performance.

11.2.4. Blank – Method Blank may be analyzed either after the CCV or after the solvent blank following CCV.

11.2.4.1. For South Carolina samples, any positive result in the method blank greater than 1/3 the reporting limit will be reported.

11.3. Qualitative identification: For a GC peak to be identified as a PCDD or PCDF (either an unlabeled or a labeled compound), it must meet all of the criteria below.

11.3.1. The signals for the two m/z's being monitored (See Table 10) must be present and must maximize within ± 2 seconds of each other.

11.3.2. The signal-to-noise (S/N) ratio of both the m/z's must be greater than or equal to 2.5 for a sample extract, and greater than or equal to 10 for a calibration standard.

11.3.3. The ratio of the integrated areas of the two exact m/z's monitored shall be within the specified limits (See Table 2) or within ±10% of the ratio in the midpoint (CS3) calibration.

11.3.4. The relative retention time (RRT) of the peaks for a 2,3,7,8-substituted PCDD or PCDF must be within the RRT limits (See Table 8). The retention time of peaks representing non 2,3,7,8-substituted PCDDs/PCDFs must be within the retention time windows established by the window defining mixture injected before sample analysis.

11.3.5. Confirmatory analysis—Any sample in which 2, 3, 7, 8-TCDF is identified above the lower calibration limit must be confirmed on a DB-225 column, SP-2331, or equivalent GC column.

11.3.5.1. The operating conditions may be adjusted to optimize the analysis on the second GC column.

11.3.5.2. The GC/MS must meet the mass resolution and calibration specifications in Section 10.

11.3.6. No signal shall be observed in the corresponding PCDPE ion channel having a S/N ratio greater than 2.5 at the retention time of any presumptive PCDF.

11.3.6.1. Chemical interference, rather than an interfering PCDPE may cause a signal to be observed at the m/z of the corresponding DPE.

11.3.6.2. A professional analytical judgement is necessary to determine whether a particular unlabelled analyte peak should be deleted from the "total", or the 2,3,7,8 substituted set to a detection limit because of possible DPE interference.

11.3.6.3. Additionally, whether the peak in question should be qualified as a positive by a reporting flag ("JA"), or whether the peak should be counted as a positive with no qualification because no applicable interference is present.

11.4. Analysis of complex samples.

11.4.1. Some samples contain high levels (>10 ng/L; >1000 ng/kg) of the compounds of interest, interfering compounds, and/or polymeric materials. In the case of high levels of one or more analytes (such that the concentration in the extract exceeds the upper calibration limit and/or causes saturation of the MS detector), the extract is diluted with tetradecane to bring the concentration (s) of the analyte (s) in question below the limit of the detector and into the calibration range if possible.

11.4.2. If high levels of coextracted interfering compounds are a problem, a smaller aliquot of the sample is extracted and analyzed. As noted above, complex dilution may be required. The client will be contacted to determine whether or not they will require this procedure.

11.4.3. For isotope dilution analyte recoveries outside the recommended recovery range the data should be evaluated for adverse impact. If no significant adverse impact was observed the data should be reported and an NCM filed.

11.4.3.1. For samples that may or are adversely impacted an additional aliquot of the original extract or diluted extract should be analyzed.

- If the recoveries are still outside of the range for the re-injected extract and it is determined that significant adverse impact to data quality has occurred, the sample(s) may be re-extracted, or reprocessed from an archive portion if available.
- A smaller aliquot should be used for the re-extraction unless it is suspected that the recovery problem is not matrix related.
- If the re-extracted sample(s) still does not meet the limits for labeled isotope dilution analyte recovery, the data is evaluated for adverse impact and a NCM filed.
- All recoveries outside of method criteria will be flagged. The best quality data is reported from one of the two extractions unless the client requests that both sets of data be reported.

11.4.4. Optional procedure for use in the analysis of 2,3,7,8-TCDF and/or 2,3,7,8-TCDD only.

11.4.4.1. 2,3,7,8-TCDD and/or 2,3,7,8-TCDF can either be analyzed by using the procedures above, but the sample spiking solution can be

modified to include only the labeled and unlabeled analytes of interest. This can reduce the cost of the spiking standards used. If this procedure is used, the spiking mixes can be QC'd against the existing "full-list" calibration curve.

11.4.4.2. The spiking solutions, including stock and secondary standards, are modified such that only the unlabeled and labeled 2,3,7,8-TCDD and 2,3,7,8-TCDF analytes are added, including the ^{37}Cl-2,3,7,8-TCDD (Cleanup Recovery Standard or Surrogate) and ^{13}C-1,2,3,4-TCDD (Internal Standard).

11.4.4.3. The silica column/alumina column cleanup (as described in WS-IDP-0007) may be optimized for TCDD and TCDF.

11.4.4.4. Carbon Column (as described in WS-IDP-0007) may be optimized for TCDD and TCDF.

11.4.4.5. The temperature program may be modified to optimize the GC run for separation of the TCDD and CDF isomers, and to shorten the run as appropriate.

11.4.4.6. All aspects of calibration and quantitation apply when they refer to the Tetra analytes and isotope dilution analytes only.

11.5. Data review

11.5.1. The analyst who performs the initial data calculations must initial and date the front quantitation summary of the raw data for each sample (the CCVs or ICALs have separate specific checklists) to document that they have performed the qualitative and quantitative analysis on the sample/QC data.

11.5.2. When an entire project lot or batch is completed, a checklist representing the entire data package is completed. All manual integrations must be documented according the Manual Integration SOP, S-Q-004.

11.5.3. A second analyst must verify all qualitative peak identifications.

11.5.3.1. If discrepancies are found, the data should be returned to the analyst who performed the initial peak identification for resolution.

11.5.3.2. Any changes made directly by the reviewing analyst must be dated and initialed by the reviewing analyst.

11.5.4. All hand calculations and data entry into calculation programs, databases, or spreadsheets must be checked by a second analyst at a frequency of 100

percent.

11.5.4.1. If discrepancies are found, the data should be returned to the analyst who performed the initial calculation.

11.5.4.2. Any changes made directly by the reviewing analyst must be dated and initialed by the reviewing analyst.

11.5.5. Both the analyst who performed the initial qualitative and quantitative analysis and the analyst who performed the second level review must check all items on the data review checklist.

11.6. Common observations with "real world" sample data analysis:

11.6.1. If an ion ratio is outside ratio identification limits, but within the retention time window, the analyst, using professional judgement based on historical data or other samples within the sample lot, identify the peak in question as positive with an estimated concentration based on the theoretical ratio. The OpusQuan software will automatically adjust the ion areas to reflect the theoretical ion ratio based on the ion peak with the smallest area and then quantitate an estimated concentration. The "Q" flag is used which states that the peak has been positively identified but the concentration is estimated. (Note: non 2,3,7,8 substituted totals peaks are not qualified)

11.6.1.1. The first eluting PeCDD isomer often has a chemical interference in the m/z 357.8516 ion causing the ion ratio to be outside the ratio identification window for PeCDDs.

- If this peak is the only positive PeCDD identified for "total" PeCDD, the detection limit is elevated to reflect the estimated concentration and the total is "ND" at this value.
- If there are other positive PeCDDs within the window, the isomer will be "Q" flagged as estimated on the totals summary sheet, and included in the "total" concentration. (Note that "totals" are always considered estimated and are not flagged on the final result sheet.) No NCM is required.

11.6.1.2. The 1,2,3,4,6,7,8-HpCDF isomer often has a chemical interference with the m/z 407.7818 ion that causes the ion ratio with m/z 410 to be outside the method limits.

- Often, re-integration of the m/z 407.7818 ion is possible, but if this is not possible, qualify positive values for the 1,2,3,4,6,7,8-HpCDF isomer as "positively identified, but estimated quantitation" using the "Q" qualifier because the quantitation is based on the theoretical ion ratio. A NCM observation is filed.

11.6.2. The following 2,3,7,8-substituted target analytes often require re-integration due to closely eluting non-2,3,7,8-substituted isomers on the DB-5 column. In all cases, the ^{13}C-labeled analog should be used to determine where the split between the isomers should occur.

11.6.2.1. 2,3,7,8-TCDD elutes just after the 1,2,3,7/1,2,3,8-TCDD elutes. Even though the DB-5 column is isomer specific for 2,3,7,8-TCDD, the software often integrates these isomers together when the 2,3,7,8-TCDD concentration is much less that that of the other isomer pair.

11.6.2.2. 1,2,3,4,7,8-HxCDF elutes just after the 1,2,3,4,6,7-HxCDF isomer; 2,3,4,6,7,8-HxCDF elutes just after the 1,2,3,6,8,9-HxCDF isomer, and 1,2,3,7,8,9-HxCDF elutes just prior to the 1,2,3,4,8,9-HxCDF isomer.

11.6.2.3. 1,2,3,7,8,9-HxCDD elutes just after the 1,2,3,4,6,7-HxCDD isomer.

11.6.3. Biological samples often exhibit a typical Diphenyl Ether pattern, while Incineration Ash samples often exhibit chemical interference in the DPE traces that does not contribute ions to the native furans.

11.7. Recommended Preventative Maintenance

As Needed Maintenance:
Full Bake-Out.
Change oil in rotary pump.
Change oil in diffusion pump. Replace o-rings.
Solvent rinse the flight tube.
Clean the first field free region.
Check detector voltages.
Clean and dust connectors, etc on the outside of the instrument.
Check the vacuum: ~5 x. 10^{-7} MBAR on both analyzer ion gauges, and ~5 x 10^{-6} MBAR on the source, with no helium flowing.
Check isolation valve for leaks, correct if needed.
Check for thermal trip by taking the magnet to maximum current, and verify that the coolant flow is acceptable.
Replace septum.
Clean injector port.
Cut off front portion of capillary columns. Replace column if this fails to restore column performance or when column performance (e.g. peak tailing, poor resolution, high backgrounds, etc.) indicates it is required.
Replace injection port liner when front portion of capillary column is removed.
Clean Source, including all ceramics and lenses - the source cleaning is indicated by a variety of symptoms including inability of the analyst to tune the instrument to specifications, poor response, and high background contamination.
Replace filaments when performance indicates need for replacement.

Daily Maintenance:
Check resolution sensitivity. Check stability. Check for sufficient gas supply. Check for correct column flow and/or inlet pressure. Check temperatures of injector, detector. Verify temperature programs. Check inlets, septa. Check baseline level. Check values of lens voltages, electron multiplier, and relative abundance and mass assignments of the calibration compounds. Inspect chromatogram to verify symmetrical peak shape and adequate resolution between closely eluting peaks.

12. CALCULATIONS/DATA REDUCTION

12.1. Isotope dilution: By adding a known amount of a labeled compound to every sample prior to extraction, correction for recovery of the unlabeled compound can be determined. The correction for the unlabeled compound can be made because the unlabeled compound and its labeled analog exhibit similar effects upon extraction, cleanups, concentration, and gas chromatography mass spectrometry. Relative response factors (RRF) values are used in conjunction with calibration data described in Section 10 to determine concentration directly, using the following equation:

$$C_n = \frac{(A_{n1} + A_{n2}) \times C_{IS}}{(A_{IS1} + A_{IS2}) \times RRF_n \times Vol}$$

Where:

C_n is the concentration of the unlabeled compound in the extract.

A_n is the area of the native in the lighter mass (1) and heavier mass (2).

C_{IDA} is the concentration of the isotope dilution analyte.

RRF_n is the relative response factor from the calibration curve for that compound.

Vol is the sample size used for the extraction and/or cleanups (in milliliters, liters, grams, or extract.

12.1.1. Reporting conventions are as follows:

12.1.1.1. Aqueous results in pg/L (parts per quadrillion);

12.1.1.2. Solid results (soils, sediment, filter cake, compost, waste, etc) in pg/g or ng/kg (parts per trillion);

- Solid samples may be reported on a dry weight basis by reporting and correcting for percent solids.

12.1.1.3. Extracts or filters in pg/sample or pg/extract (parts per quadrillion).

12.1.1.4. Tissue sample results in pg/g or ng/kg of wet tissue, not on the basis of the lipid content of the sample. Report the percent lipid content if requested.

12.1.2. Because of a potential interference, the labeled analog of OCDF is not added to the sample. Therefore, this unlabeled analyte is quantitated against the labeled OCDD. As a result, the concentration of unlabeled OCDF is corrected by the recovery of the labeled OCDD.

12.1.2.1. In instances where OCDD and OCDF behave differently during sample extraction, concentration, and cleanup procedures, a decrease in the accuracy of OCDF may result. However, given the low toxicity of this compound relative to other dioxins and furans, the potential decrease in accuracy is not considered significant.

12.1.3. Because the labeled analog of 1,2,3,7, 8, 9-HxCDD is used as an internal standard (i.e. not added before extraction of the sample), it cannot be used to quantitate the unlabeled compound by strict isotope dilution procedures.

12.1.3.1. The unlabeled 1,2,3,7,8,9-HxCDD is quantitated using the averages of the responses of the labeled analogs of the other two 2,3,7,8-substituted HxCDD's, 1, 2, 3, 4, 7, 8-HxCDD and 1, 2, 3, 6, 7, 8-HxCDD. As a result, the concentration of the unlabeled 1, 2, 3, 7, 8, 9-HxCDD is corrected for by the average recovery of the other two HxCDD IDA.

12.1.4. Any peaks representing non-2, 3,7,8-substituted dioxins or furans are quantitated using an average of the response factors from all of the 2,3,7,8-isomers in the same level of chlorination.

12.1.5. Report results at or above the minimum level (also known as the Lower Calibration Limit – See Table 5).

12.1.6. Report results below the minimum level as not detected. Some clients or regulatory agencies require sample/analyte specific estimated detection limits. If these are required, there is a three-tiered approach to reporting and detection limits.

12.1.6.1. In the absence of target analytes, a sample specific estimated detection limit (EDL) is calculated based on signal-to-noise (S/N) ratios at the retention time of the target analyte.

- The target analyte is then reported as "not detected" at the EDL.

12.1.6.2. When target analytes meet method identification criteria and are free of interferences, they are reported as unqualified positives down to the lowest calibration standard concentration (the LCL, See Table 5).

- Below the lower calibration limit, qualitatively confirmed analytes are reported as "estimated" down to the project detection limit. The default is the EDL but that can change based on specific project requirements.
- To denote the less certain quantitation the value is "J" flagged as estimated.

12.1.6.3. The TDL is a value set by the lab at which there is no significant chance of a false positive (usually set at ½ the LCL value).

- If there is a peak below the TDL, a detection limit based on the ion peaks is calculated and the target analyte is reported as "not detected" at the calculated detection limit.
- Second column confirmation will be performed only for 2,3,7,8-TCDF positives greater than the lower calibration limit (Note: "Totals" peaks, i.e. non-2,3,7,8-substituted isomers are not considered target analytes, but are identified using the above criteria. "Totals" concentrations are always considered estimated and are never flagged.)

12.1.7. If the concentration of any target analyte exceeds the upper calibration range of the initial calibration curve, but does not saturate the instrument detector, the analyte is qualified by the "E" flag and an NCM is submitted. ("Totals" concentrations are always considered as estimates and are not flagged.)

12.1.7.1. Historical data indicates that for the isotope dilution method, dilution and re-injection will not produce significantly different results from those reported with the "E" qualifier.

12.1.7.2. Clients may request dilution and re-injection to bring target compounds within the calibration range. (Note: dilution of an extract to bring target compounds within range also dilutes the isotope dilution analytes which may adversely impact the data).

12.1.8. When target analyte peaks <u>saturate the detector</u>, TestAmerica Sacramento will provide one dilution to bring the response below the saturation level and/or the upper calibration level as part of the initial analysis cost.

12.1.8.1. Additional dilutions or re-extraction at a smaller sample aliquot will be performed at client request only. (Note: Complex dilution is one where the pre-spiked isotope dilution anaytes are diluted out and

must be re-added to the extract. The sample analyte concentrations are then calculated using an internal standard method and all results from this dilution are therefore estimated.)

12.1.9. Results for samples that required dilution may be reported from more than one injection. For example, some analyte results may be reported from the original injection, while others are taken from the dilution.

12.1.9.1. Isomers reported from a dilution shall be qualified with a "D" qualifier, or narrated if all or most of the congeners are reported from the dilution analysis. (Note: Dilution will not always eliminate the "E" flag qualifier.)

12.1.10. The total concentration in each level of chlorination is the sum of the concentrations of all isomers identified in that level greater than the target detection limit, including any non-2,3,7,8-substituted isomers, which elute within the CPSM window.

12.1.10.1. The total concentration is calculated by the OpusQuan software as follows: The total area of 2,3,7,8-substituted isomers is subtracted from the total area of all isomers to get a non-2,3,7,8 substituted total area. A non-2,3,7,8-total concentration is then calculated using the average RRF value. The 2,3,7,8-substituted isomer concentrations are added to the non-2,3,7,8-total concentration to get a "actual" total for all isomers.

12.1.11. Results are reported to two significant figures. For aqueous samples, the units are pg/L. For solid samples (soils, sludges, sediments, etc) the units are pg/g.

12.2. Isotope Dilution Analyte : Compute the concentrations of the ^{13}C-labeled analogs and the ^{37}Cl-labeled Surrogate in the extract using the response factors determined from calibration curve and the following equation:

$$C_{IDA} = \frac{(A_{IDA1} + A_{IDA2}) \times Q_{IS}}{(A_{IS1} + A_{IS2}) \times RRF_{IDA}}$$

Where:

C_{IDA} is the concentration of the isotope dilution analytein the extract (pg/g, pg/L)

A_{IDA} the area of the isotope dilution analyte in the lighter mass (1) and the heavier mass (2).

A_{IS} is the area of the internal standard in the lighter mass (1) and heavier mass (2).

Q_{IS} is the amount of internal standard spiked.

RRF_{IDA} is the response of the isotope dilution analyte relative to the response of the internal standard in the initial calibration curve.

12.3. Calculate the isotope dilution analyte percent recovery using the following equation:

$$\%\,\mathrm{Recovery} = \frac{CIDA}{Amount\,Spiked} \times 100$$

(Note: There is only one m/z for the ^{37}Cl-labeled standard.)

13. METHOD PERFORMANCE

13.1. Method Detection Limit

Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in QA Policy #: CA-Q-S-006 and WS-QA-0006. MDLs are available in the Quality Assurance department.

13.2. The group/team leader has the responsibility to ensure that this procedure is performed by an associate, who has been properly trained in its use and has the required experience.

13.3. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QC files.

13.4. The laboratory operates a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of capability (IDOC), analysis of samples spiked with compounds to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance.

13.4.1. The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision by this method. This ability is established by generating four laboratory control samples that meet recovery criteria. For each alternative sample matrix, four aliquots of the alternative reference matrix are used.

13.5. The laboratory must make a one time initial demonstration of capability for each individual method. Demonstrations of capability for both solid and aqueous matrices are required. This requires analysis of QC check samples containing all of the standard analytes for the method.

13.5.1. Four aliquots of the QC check samples are analyzed using the same procedure used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid-level calibration.

13.5.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria in Table 9.

13.5.3. If any analyte does not meet the acceptance criteria, then the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.5.4. In recognition of advances that are occurring in analytical technology, and to allow the analyst to overcome sample matrix interferences, the analyst is permitted certain options to improve separations or lower costs of measurements. These options include alternate extraction, concentration, cleanup procedures, and changes in columns and detectors. Unique changes are to be documented using a non-conformance memo. Permanent modifications or additions should be documented using an addendum to this SOP.

14. POLLUTION CONTROL

It is TestAmerica policy to evaluate each method and look for opportunities to minimize waste generated (i.e. examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.1. Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards that must be discarded.

15. WASTE MANAGEMENT

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to WS-EHS-0001. The following waste streams are produced when this method is carried out.

15.1. Autovials contaminated with methylene chloride, toluene, tetradecane and other solvents. As the autovials are removed from the instrument after analysis, they are stored in vial files in the instrument lab for at least ninety days, depending on client requirements. After at least ninety days, the vial files are transferred to the waste disposal area where they are drummed and shipped as PCB waste after no more than 90 days.

16. REFERENCES/CROSS-REFERNCES

16.1. EPA Method 1613, Revision A, October 1990.

16.2. EPA Method 1613, Revision B, October 1994.

16.3. Federal Register, 40 CFR Part 136, Guidelines Establishing Test Procedures for the Analysis of Pollutants; EPA Method 1613, Final Rule, 10/1994, NTIS PB95-104774.

17. METHOD MODIFICATIONS

17.1. Deviations from referenced method:

17.1.1. Section 10.2.4 of Method 1613 reads "The absolute retention time of ^{13}C-1,2,3,4-TCDD shall exceed 25.0 minutes on the DB-5 column, and the retention time of ^{13}C-1,2,3,4-TCDD shall exceed 15.0 minutes on the DB-225 column; otherwise the GC temperature program shall be adjusted and this test repeated until the above-stated minimum retention time criteria are met." Our retention time on both columns deviate from the above method, but using section 1.5 of Method 1613 "the analyst is permitted to modify the method to lower the cost of measurements, provided that all performance criteria in this method are met," we have modified the GC program to provide a shorter run time while still meeting method performance criteria thus lowering the cost of analysis.

17.1.2. Section 10.2.1.2 of Method 1613 reads "The lock-mass for each group of m/z's shall be monitored and shall not vary by more than $\pm$20% throughout its respective retention time window." Data is evaluated on a sample by sample basis to establish whether the lock-mass deviations have adversely affected data quality. "Totals" are always considered estimated values, so lock-mass dips effecting a non-2,3,7,8-substituted isomer may be considered inconsequential. If a target 2,3,7,8-substituted isomer is adversely effected by a lock-mass deviation the sample may be diluted and re-injected or re-injected on a different instrument.

17.1.3. Section 10.1.2.1 of Method 1613 reads "The level of PFK metered into the HRMS during analysis should be adjusted so that the amplitude of the most intense selected lock-mass m/z signal (regardless of the descriptor number)

does not exceed 10% of the full-scale deflection for a given set of detector parameters." The qualifier "should" indicates that action is suggested but not required (see Section 24.0 of Method 1613). The exception to this is state of Arizona drinking water samples. For Arizona drinking water samples, following section 10.1.2.1 is required.

17.1.4. Section 17.6.1.4.2 of Method 1613 reads "Blanks – report results above one-third the method limit." We report blanks using the same criteria as that used for samples.

17.1.5. Section 17.6.2 of Method 1613 reads "Results for the PCDDs/PCDFs in samples that have been diluted are reported at the least dilute level at which the areas at the quantitation m/z's are within the calibration range." Data quality is always taken into account. Every effort is made to accommodate this method suggestion, but exceptions may occur when actual data results are analyzed.

17.1.6. Section 18.3 of Method 1613 reads "Chlorodiphenyl Ethers – If chromatographic peaks are detected at the retention time of any PCDDs/PCDFs in any of the m/z channels being monitored for the chlordiphenyl ethers, cleanup procedures must be employed until these interferences are removed." Chlorodiphenyl Ethers (DPE) peaks will only interfere with PCDFs, so references to PCDDs are not applicable. PCDF data is analyzed to determine whether DPE interference is present. If DPE peaks are present at –2 to +2 seconds from the retention time of a peak in a PCDF trace, that peak is eliminated from the "total" concentration when there are other positive PCDFs present without DPE interference. Otherwise, these DPE interference peaks are taken into consideration when determining a "total" detection limit.

18. ATTACHMENTS

18.1. Tables or figures referenced in body of SOP.

18.1.1. Compound Structure

18.1.2. Table 1 - Isomers of Chlorinated Dioxins and Furans

18.1.3. Table 2 - Theoretical Ion Abundance Ratios and QC Limits

18.1.4. Table 3 - The Seventeen 2,3,7,8-Substituted PCDD and PCDF Congeners

18.1.5. Table 4 – Concentration of Stock and Spiking Solutions

18.1.6. Table 5 - Concentrations of Calibration Solutions

18.1.7. Table 6 – GC Retention Time Window Defining Test

18.1.8. Table 7 - List of CDDs/CDFs Determined by ID/IS/HRGC/HRMS

18.1.9. Table 8 – Retention Time Reference, Relative Retention Time

18.1.10. Table 9 – Acceptance Criteria for Performance Test

18.1.11. Table 9.1 – Acceptance Criteria for Performance Test (Tetras-Only Analysis)

18.1.12. Table 10 – Descriptors, Exact m/z's

19. REVISON HISTORY

19.1. WS-ID-0007, Revision 3.7, Effective 02/07/2014

19.1.1. Renamed Internal Standards (as per the method) to Isotope Dilution Analytes (as per our LIMS) to clarify for personnel.

19.1.2. Renamed Recovery Standards (as per the method) to Internal Standards (as per the LIMS) to clarify for personnel.

19.1.3. Renamed Cleanup Recovery Standards (as per the method) to Surrogate Standards (as per the LIMS) to clarify for personnel.

19.1.4. Editorial Revisions

19.1.5. The revision history prior to 2010 has been removed, and is available in earlier versions of this SOP.

19.2. WS-ID-0007, Revision 3.6, Effective 05/15/2012

19.2.1. Revised Table 10 to reflect correct mass/charge ratios and elemental composition of analytes.

19.2.2. Editorial revisions.

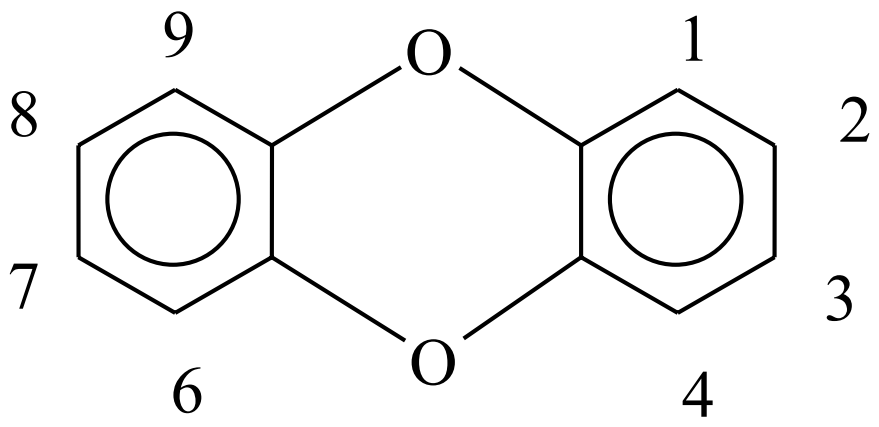
19.3. WS-ID-0007, Revision 3.5, Effective 04/15/2011

19.3.1. Section 11.2.4: Changed to - "Method Blank may be analyzed either after the CCV or after the solvent blank following CCV.

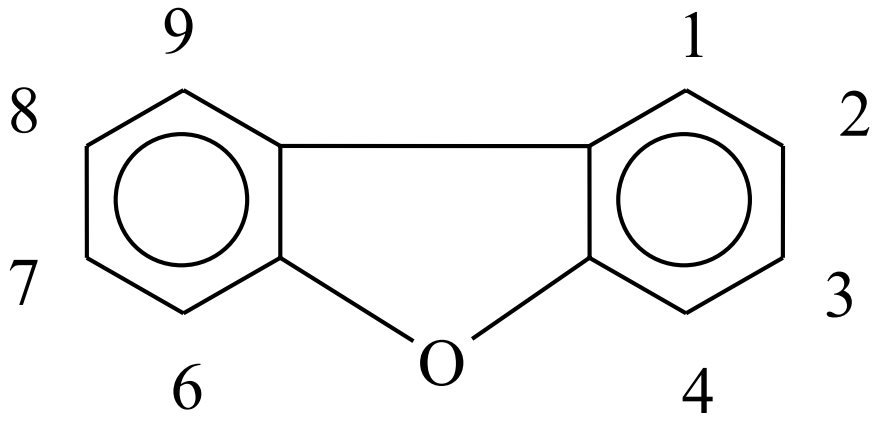
19.3.2. Deleted Section 17.1.4.

19.3.3. Editorial changes.

Figure 1
Structure of Dibenzodioxin and Dibenzofuran



Dibenzodioxin



Dibenzofuran

Table 1: Isomers of Chlorinated Dioxins and Furans as a Function of the Number of Chlorine Atoms

# of Chlorine Atoms	# of Dioxin Isomers	# of 2,3,7,8 Isomers	# of Furan Isomers	# of 2,3,7,8 Isomers
1	2	---	4	---
2	10	---	16	---
3	14	---	28	---
4	22	1	38	1
5	14	1	28	2
6	10	3	16	4
7	2	1	4	2
8	1	1	1	1
Total	**75**	**7**	**135**	**10**

Table 2: Theoretical Ion Abundance Ratios and QC Limits

# of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits(1)	
			Lower	Upper
4(2)	M / M+2	0.77	0.65	0.89
5	M+2 / M+4	1.55	1.32	1.78
6	M+2 / M+4	1.24	1.05	1.43
6(3)	M / M+2	0.51	0.43	0.59
7(4)	M / M+2	0.44	0.37	0.51
7	M+2 / M+4	1.04	0.88	1.20
8	M+2 / M+4	0.89	0.76	1.02

(1) QC limits represent 15% windows around the theoretical ion abundance ratios.
(2) Does not apply to $^{37}Cl_4$-2,3,7,8-TCDD (Cleanup Recovery Standard).
(3) Used for $^{13}C_{12}$-HxCDF only.
(4) Used for $^{13}C_{12}$-HpCDF only.

Table 3: The Seventeen 2,3,7,8-Substituted PCDD and PCDF Congeners

PCDD	PCDF
2,3,7,8-TCDD(*)	2,3,7,8-TCDF(*)
1,2,3,7,8-PeCDD(*)	1,2,3,7,8-PeCDF(*)
1,2,3,6,7,8-HxCDD(*)	2,3,4,7,8-PeCDF(*)
1,2,3,4,7,8-HxCDD(*)	1,2,3,6,7,8-HxCDF(*)
1,2,3,7,8,9-HxCDD(+)	1,2,3,7,8,9-HxCDF(*)
1,2,3,4,6,7,8-HpCDD(*)	1,2,3,4,7,8-HxCDF(*)
1,2,3,4,5,6,7,8-OCDD(*)	2,3,4,6,7,8-HxCDF(*)
	1,2,3,4,6,7,8-HpCDF(*)
	1,2,3,4,7,8,9-HpCDF(*)
	1,2,3,4,5,6,7,8-OCDF

(*)The 13C-labeled analog is used as an internal standard.
(+)The 13C-labeled analog is used as a recovery standard.

Table 4: Concentration of Stock and Spiking Solutions Containing CDDS/CDDFs and Labeled Compounds

Analyte	Type	Labeled Compound Stock Solution (ng/mL=pg/µL)	Labeled Compound Spiking Solution[a] (ng/mL=pg/µL)	PAR Stock Solution (ng/mL=pg/µL)	PAR Spiking Solution[b] (ng/mL=pg/µL)
Isotope Dilution Standards					
$^{13}C_{12}$-2,3,7,8-TCDD	IS	100	2	--	--
$^{13}C_{12}$-1,2,3,7,8-PeCDD	IS	100	2	--	--
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	IS	100	2	--	--
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	IS	100	2	--	--
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	IS	100	2	--	--
$^{13}C_{12}$-OCDD	IS	100	4	--	--
$^{13}C_{12}$-2,3,7,8-TCDF	IS	100	2	--	--
$^{13}C_{12}$-1,2,3,7,8-PeCDF	IS	100	2	--	--
$^{13}C_{12}$-2,3,4,7,8-PeCDF	IS	100	2	--	--
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	IS	100	2	--	--
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	IS	100	2	--	--
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	IS	100	2	--	--
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	IS	100	2	--	--
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	IS	100	2	--	--
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	IS	100	2	--	--
Internal Standards					
$^{13}C_{12}$-1,2,3,4-TCDD	RS	200	100[d]	--	--
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	RS	200	100[d]	--	--
Surrogate Standard					
$^{37}Cl_4$-2,3,7,8-TCDD	CRS	200	0.8[c]	--	--
Native Standard					
2,3,7,8-TCDD	NS	--	--	40	4
1,2,3,7,8-PeCDD	NS	--	--	200	20
1,2,3,4,7,8-HxCDD	NS	--	--	200	20
1,2,3,6,7,8-HxCDD	NS	--	--	200	20
1,2,3,7,8,9-HxCDD	NS	--	--	200	20
1,2,3,4,6,7,8-HpCDD	NS	--	--	200	20
OCDD	NS	--	--	400	40
2,3,7,8-TCDF	NS	--	--	40	4
1,2,3,7,8-PeCDF	NS	--	--	200	20
2,3,4,7,8-PeCDF	NS	--	--	200	20
1,2,3,4,7,8-HxCDF	NS	--	--	200	20
1,2,3,6,7,8-HxCDF	NS	--	--	200	20
2,3,4,6,7,8-HxCDF	NS	--	--	200	20
1,2,3,7,8,9-HxCDF	NS	--	--	200	20
1,2,3,4,6,7,8-HpCDF	NS	--	--	200	20
1,2,3,4,7,8,9-HpCDF	NS	--	--	200	20
OCDF	NS	--	--	400	40

(a) typical spike amount is 1.0mL
(b) typical spike amount is 50µL
(c) typical spike amount is 1.0mL
(d) typical spike amount is 20µL

Table 5: Concentration of CDD's/CDF's in Calibration and Calibration Verification Solutions

Compound	Concentration (ng/mL)				
	CS2	CS3	CS4	CS5	CS6
Native CDDs and CDFs					
2,3,7,8-TCDD	0.5	2	10	40	200
2,3,7,8-TCDF	0.5	2	10	40	200
1,2,3,7,8-PeCDD	2.5	10	50	200	1000
1,2,3,7,8-PeCDF	2.5	10	50	200	1000
2,3,4,7,8-PeCDF	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDD	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDD	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDD	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDF	2.5	10	50	200	1000
2,3,4,6,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDD	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDF	2.5	10	50	200	1000
1,2,3,4,7,8,9-HpCDF	2.5	10	50	200	1000
OCDD	5.0	20	100	400	2000
OCDF	5.0	20	100	400	2000
Labeled CDDs and CDFs					
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	100	100	100	100
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	100	100	100	100
$^{13}C_{12}$-OCDD	200	200	200	200	200
Surrogate Standard/ FS					
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	2	10	40	200
Internal Standards					
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

Table 6: GC Retention Time Window Defining Test and Isomer Specificity Test Solution

DB-5 column GC retention-time window defining solution		
CDD/CDF	**First Eluter**	**Last Eluter**
TCDF	1,3,6,8-	1,2,8,9-
TCDD	1,3,6,8-	1,2,8,9-
PeCDF	1,3,4,6,8-	1,2,3,8,9-
PeCDD	1,2,4,7,9-	1,2,3,8,9-
HxCDF	1,2,3,4,6,8-	1,2,3,4,8,9-
HxCDD	1,2,4,6,7,9-	1,2,3,4,6,7-[(a)]
HpCDF	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-
HpCDD	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-
DB-5 Column TCDD Specificity Test Standard[(b)]		
	1,2,3,7+1,2,3,8-TCDD 2,3,7,8-TCDD 1,2,3,9-TCDD 1,2,3,4-TCDD	
DB-225 Column TCDF Isomer Specificity Test Standard[(c)]		
	2,3,4,7-TCDF 2,3,7,8-TCDF 1,2,3,9-TCDF	

(a) The 1,2,3,4,6,7-HxCDD isomer is not the last eluting isomer. 1,2,4,7,8,9-HxCDD is the last eluting HxCDD isomer and is present in the internal standard solution.
(b) Column performance criteria is met on the DB-5 column when the percent valleys between the 2,3,7,8-TCDD analyte and the closest eluting analytes are ≤25%.
(c) Column performance criteria is met on the DB-225 column when the percent valleys between the 2,3,7,8-TCDF analyte and the closest eluting analytes are ≤25%.

Table 7: Chlorinated Dibenzo-p-Dioxins and Furans Determined by Isotope Dilution and Internal Standard High Resolution Gas Chromatography (HRGC)/High Resolution Mass Spectrometry (HRMS)

CDDs/CDFs (1)	CAS registry	Labeled analog	CAS registry
2,3,7,8-TCDD	1746-01-6	$^{13}C_{12}$-2,3,7,8-TCDD	76523-40-5
		$^{37}Cl_4$-2,3,7,8-TCDD	85508-50-5
Total TCDD	41903-57-5		
2,3,7,8-TCDF	51207-31-9	$^{13}C_{12}$-2,3,7,8-TCDF	89059-46-1
Total TCDF	55722-27-5		
1,2,3,7,8-PeCDD	40321-76-4	$^{13}C_{12}$-1,2,3,7,8-PeCDD	109719-79-1
Total PeCDD	36088-22-9		
1,2,3,7,8-PeCDF	57117-41-6	$^{13}C_{12}$-1,2,3,7,8-PeCDF	109719-77-9
2,3,4,7,8-PeCDF	57117-31-4	$^{13}C_{12}$-2,3,4,7,8-PeCDF	116843-02-8
Total PeCDF	30402-15-4		
1,2,3,4,7,8-HxCDD	39227-28-6	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	109719-80-4
1,2,3,6,7,8-HxCDD	57653-85-7	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	109719-81-5
1,2,3,7,8,9-HxCDD	19408-74-3	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	109719-82-6
Total HxCDD	34465-46-8		
1,2,3,4,7,8-HxCDF	70648-26-9	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	114423-98-2
1,2,3,6,7,8-HxCDF	57117-44-9	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	116843-03-9
1,2,3,7,8,9-HxCDF	72918-21-9	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	116843-04-0
2,3,4,6,7,8-HxCDF	60851-34-5	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	116843-05-1
Total HxCDF	55684-94-1		
1,2,3,4,6,7,8-HpCDD	35822-46-9	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	109719-83-7
Total HpCDD	37871-00-4		
1,2,3,4,6,7,8-HpCDF	67562-39-4	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	109719-84-8
1,2,3,4,7,8,9-HpCDF	55673-89-7	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	109719-94-0
Total HpCDF			
OCDD	3268-87-9	$^{13}C_{12}$-OCDD	114423-97-1
OCDF	39001-02-0	Not Used	

(1) Chlorinated dibenzo-p-dioxins and chlorinated dibenzofurans

TCDD = Tetrachlorodibenzo-p-dioxins
TCDF = Tetrachlorodibenzofurans
PeCDD = Pentachlorodibenzo-p-dioxins
PeCDF = Pentachlorodibenzofurans
HxCDD = Hexachlorodibenzo-p-dioxins
HxCDF = Hexachlorodibenzofurans
HpCDD = Heptaachlorodibenzo-p-dioxins
HpCDF = Heptachlorodibenzofurans
OCDD = Octachlorodibenzo-p-dioxins
OCDF = Octachlorodibenzofurans

Table 8: Retention Time References, Quantitation References, Relative Retention Times, and Minimum Levels for PCDDs and PCDFs.

			Minimum Level (1)		
CDD/CDF	**Retention Time and Quantiation Reference**	**Relative Retention Time**	**Water (pg/L=ppq)**	**Solid (ng/kg=ppt)**	**Extract (pg/µL=ppb)**
Compounds using $^{13}C_{12}$-1,2,3,4-TCDD as the Injection Internal Standard (Recovery Standard)					
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF	0.999-1.003	10	1	0.5
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD	0.999-1.002	10	1	0.5
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF	0.999-1.002	50	5	2.5
2,3,4,7,8-PeCDF	$^{13}C_{12}$-2,3,4,7,8-PeCDF	0.999-1.002	50	5	2.5
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD	0.999-1.002	50	5	2.5
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD	0.923-1.103	--	--	--
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.976-1.043	--	--	--
$^{37}Cl_4$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.989-1.052	--	--	--
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.000-1.425	--	--	--
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.001-1.526	--	--	--
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD	1.000-1.567	--	--	--
Compounds using $^{13}C_{12}$-1,2,3,7,8,9-HxCDD as the Injection Internal Standard (Recovery Standard)					
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	0.999-1.001	50	5	2.5
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	1.000-1.005	50	5	2.5
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	0.999-1.001	50	5	2.5
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	0.999-1.001	50	5	2.5
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	0.999-1.001	50	5	2.5
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	0.999-1.004	50	5	2.5
1,2,3,7,8,9-HxCDD	(2)	1.000-1.019	50	5	2.5
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	0.999-1.001	50	5	2.5
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	0.999-1.001	50	5	2.5
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	0.999-1.001	50	5	2.5
OCDF	$^{13}C_{12}$- OCDD	0.999-1.001	100	10	5.0
OCDD	$^{13}C_{12}$- OCDD	0.999-1.001	100	10	5.0
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3, 7,8,9-HxCDD	(3)	--	--	--
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3, 7,8,9-HxCDD	0.949-0.975	--	--	--
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3, 7,8,9-HxCDD	0.977-1.047	--	--	--
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3, 7,8,9-HxCDD	0.959-1.021	--	--	--
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3, 7,8,9-HxCDD	0.977-1.000	--	--	--
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3, 7,8,9-HxCDD	0.981-1.003	--	--	--
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3, 7,8,9-HxCDD	1.043-1.085	--	--	--
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3, 7,8,9-HxCDD	1.057-1.151	--	--	--
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3, 7,8,9-HxCDD	1.086-1.110	--	--	--
$^{13}C_{12}$- OCDD	$^{13}C_{12}$-1,2,3, 7,8,9-HxCDD	1.032-1.311	--	--	--

(1) The Minimum Level (ML) for each analyte is defined as the level at which the entire analytical system must give a recognizable signal and acceptance calibration point. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

(2) The retention time reference for 1,2,3,7,8,9-HxCDD is $^{13}C_{12}$-1,2,3,6,7,8-HxCDD, and 1,2,3,7,8,9-HxCDD is quantified using the averaged responses for $^{13}C_{12}$-1,2,3,4,7,8-HxCDD and $^{13}C_{12}$-1,2,3,6,7,8-HxCDD.

(3) Method 1613 has many typographical errors within this table. Most have been corrected. This RRT is not present in Method 1613, but the internal standard is clearly identifiable and there is no adverse impact for this error.

Table 9: Acceptance Criteria for Performance Tests (1)

CDD/CDF	Test Conc. (ng/mL = pg/µL)	IPR (2)(3)		OPR (LCS) (ng/mL = pg/µL)	VER (CC3) (ng/mL = pg/µL)
		S (ng/mL = pg/µL)	X (ng/mL = pg/µL)		
2,3,7,8-TCDD	10	2.8	8.3-12.9	6.7-15.8	7.8-12.9
2,3,7,8-TCDF	10	2.0	8.7-13.7	7.5-15.8	8.4-12.0
1,2,3,7,8-PeCDD	50	7.5	38-66	35-71	39-65
1,2,3,7,8-PeCDF	50	7.5	43-62	40-67	41-60
2,3,4,7,8-PeCDF	50	8.6	36-75	34-80	41-61
1,2,3,4,7,8-HxCDD	50	9.4	39-76	35-82	39-64
1,2,3,6,7,8-HxCDD	50	7.7	42-62	38-67	39-64
1,2,3,7,8,9-HxCDD	50	11.1	37-71	32-81	41-61
1,2,3,4,7,8-HxCDF	50	8.7	41-59	36-67	45-55
1,2,3,6,7,8-HxCDF	50	6.7	46-60	42-65	44-57
1,2,3,7,8,9-HxCDF	50	6.4	42-61	39-65	45-56
2,3,4,6,7,8-HxCDF	50	7.4	37-74	35-78	44-57
1,2,3,4,6,7,8-HpCDD	50	7.7	38-65	35-70	43-58
1,2,3,4,6,7,8-HpCDF	50	6.3	45-56	41-61	45-55
1,2,3,4,7,8,9-HpCDF	50	8.1	43-63	39-69	43-58
OCDD	100	19	89-127	78-144	79-126
OCDF	100	27	74-146	63-170	63-159
$^{13}C_{12}$-2,3,7,8-TCDD	100	37	28-134	20-175	82-121
$^{13}C_{12}$-2,3,7,8-TCDF	100	35	31-113	22-152	71-140
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	39	27-184	21-227	62-160
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	34	27-156	21-192	76-130
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	38	16-279	13-328	77-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	41	29-147	21-193	85-117
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	38	34-122	25-163	85-118
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	43	27-152	19-202	76-131
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	35	30-122	21-159	70-143
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	40	24-157	17-205	74-135
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	37	29-136	22-176	73-137
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	35	34-129	26-166	72-138
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	41	32-110	21-158	78-129
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDD	100	40	28-141	20-186	77-129
$^{13}C_{12}$- OCDD	200	95	41-276	26-397	96-415
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.6	3.9-15.4	3.7-15.8	7.9-12.7

(1) All specifications are given as concentration in the final extract, assuming a 20µL final volume.
(2) s = standard deviation of the concentraion.
(3) X = average concentration.

Table 9.1: Acceptance Criteria for Performance Tests (Tetras – Only Analysis)

CDD/CDF	Test Conc. (ng/mL = pg/µL)	IPR (2)(3)		OPR (LCS) (ng/mL = pg/µL)	VER (CC3) (ng/mL = pg/µL)
		S (ng/mL = pg/µL)	X (ng/mL = pg/µL)		
2,3,7,8-TCDD	10	2.7	8.7 – 12.4	7.3 – 14.6	8.2 – 12.3
2,3,7,8-TCDF	10	2.0	9.1 – 13.1	8.0 -14.7	8.6 - 11.6
$^{13}C_{12}$-2,3,7,8-TCDD	100	35	32 – 115	25 – 141	85 – 117
$^{13}C_{12}$-2,3,7,8-TCDF	100	34	35 – 99	26 - 126	76 - 134
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.4	4.5 – 13.4	3.7-15.8	8..3 – 12.1

Table 10: Descriptors, Exact m/z's, m/z types, and Elemental Compositions of the CDDs and CDFs

Descriptor	Exact m/z (1)	m/z Type	Elemental Composition	Substance (2)
1	292.9825	QC	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (3)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (3)
	319.8965	M	$C_{12}H_4{}^{35}Cl_4O_2$	TCDD
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD (4)
	330.9792	Lock	C_7F_{13}	PFK
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (3)
	333.9339	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD (3)
	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}ClO$	PeCDF
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCDPE
2	330.9792	QC	C_7F_{13}	PFK
	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	342.9792	Lock	C_8F_{12}	PFK
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (3)
	354.9792	Lock	C_9F_{13}	PFK
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	366.9793	QC	C_9F_{13}	PFK
	367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (3)
	369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD (3)
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCDPE
3	373.8208	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	380.9760	Lock	C_8F_{15}	PFK
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (3)
	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (3)
	389.8157	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	392.9760	Lock	C_9F_{15}	PFK
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (3)
	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD (3)
	430.9728	QC	C_9F_{17}	PFK
	445.7550	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
4	392.9760	QC	C_9F_{15}	PFK
	407.7818	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF (3)
	419.8220	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF (3)
	423.7766	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	430.9729	Lock	C_9F_{17}	PFK

Descriptor	Exact m/z (1)	m/z Type	Elemental Composition	Substance (2)
	435.8169	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (3)
	437.8140	M+4	$^{13}C_{12}H^{35}Cl_5{}^{37}CL_2O_2$	HpCDD (3)
	479.7165	M+4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCDPE
5	392.9760	QC	C_9F_{15}	PFK
	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	442.9728	Lock	$C_{10}F_{17}$	PFK
	443.7399	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M+2	$^{13}C1_2{}^{35}Cl_7{}^{37}ClO_2$	OCDD (3)
	471.7750	M+4	$^{13}C1_2{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (3)
	479.7165	M+4	$C_{12}Cl_8{}^{37}Cl_2O$	NCDPE
	513.6775	M+4	$^{13}C_{12}{}^{35}Cl_8{}^{37}Cl_2O$	DCDPE

(1) Nuclidic masses used:
H = 1.007825
O = 15.994915
C = 12.00000
^{13}C = 13.003355
^{35}Cl = 34.968853
^{37}Cl = 36.965903
F = 18.9984

(2) Nomenclature
TCDD = Tetrachlorodibenzo-p-dioxin
PeCDD = Pentachlorodibenzo-p-dioxin
HxCDD = Hexachlorodibenzo-p-dioxin
HpCDD = Heptachlorodibenzo-p-dioxin
OCDD = Octachlorodibenzo-p-dioxin
HxCDPE = Hexachlorodiphenyl ether
HpCDPE = Heptachlorodiphenyl ether
NCDPE = Nonachlorodiphenyl ether
OCDPE = Octachlorodiphenyl ether
DCDPE = Decachlorodiphenyl ether
TCDF = Tetrachlorodibenzofuran
PeCDF = Pentachlorodibenzofuran
HxCDF = Hexachlorodibenzofuran
HpCDF = Heptachlorodibenzofuran
OCDF = Octachlorodibenzofuran
PFK = Perfluorokerosene

(3) Labeled compound

(4) There is only one m/z for $^{37}Cl_4$-2,3,7,8-TCDD (Cleanup Recovery Standard)

Title: PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS AND SOLID SAMPLES BY COLD VAPOR ATOMIC FLUORESCENCE

[Method: 1631E]

Approvals (Signature/Date):

Technology Specialist	Date 09/27/13	Health & Safety Coordinator	Date 09/27/13
Quality Assurance Manager	Date 09/26/13	Technical Director	Date 09/26/13

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1. SCOPE AND APPLICATION

1.1 This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS) using Method 1631E.

1.2 CVAFS analysis provides for the determination of total mercury (organic and inorganic). The oxidant, bromine monochloride has been found to give quantitative recovery with both types of compounds. Detection limits, sensitivity, and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation, and volume of sample used.

1.3 Method 1631E (hereafter abbreviated to Method 1631 in this SOP) is applicable to the preparation and analysis of mercury in ground water, surface water, effluents, and other aqueous samples. Appendix A to Method 1631 is applicable to the preparation and analysis of mercury in sediments, soils, biological media and other solid samples. All matrices require sample preparation prior to analysis.

1.5 The TestAmerica North Canton reporting limit for mercury in aqueous matrices is 0.5 ng/L by Method 1631. The reporting limit for mercury by Method 1631 in solid matrices is 1.0 ug/kg.

2. SUMMARY OF METHOD

2.1 This SOP describes a technique for the determination of mercury in solids, biological, and aqueous solutions. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor and fluorescence at 253.7 nm. For aqueous samples, a representative portion of the sample is digested and oxidized in bromine monochloride. For solid or biological samples, 1 gram of sample is digested with cold aqua regia, diluted, and further oxidized with bromine monochloride. Excess free halogens in the digestate are then reduced with hydroxylamine hydrochloride. The mercury (+2) is reduced to its elemental state with stannous chloride and purged from solution with argon in a gas / liquid separator. For Method 1631, the mercury vapor is collected on a gold trap and then thermally desorbed to the detector. The mercury vapor passes through a cell positioned in the light path of an atomic fluorescence spectrophotometer. Fluorescence is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample fluorescence to the calibration curve (fluorescence vs. concentration).

3. DEFINITIONS

3.1 Refer to the glossary in the TestAmerica North Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1 Chemical and physical interferences may be encountered when analyzing samples using this method.

4.2 Gold, silver, and iodide are known interferences. At mercury a concentration of 2.5 ng/L and at increasing iodide concentrations from 30 to 100 mg/L, test data have shown that mercury recovery will be reduced from 100 to 0 percent.

4.3 The use of a brominating digestion coupled with atomic fluorescence detection overcomes many of the chloride, sulfide, and molecular absorbance interferences. No interferences have been noted for sulfide concentrations below 24 mg/L.

4.4 Water vapor may collect in the gold traps (Method 1631), and subsequently condense in the fluorescence cell upon desorption, giving a false peak due to scattering of the excitation radiation. Condensation can be avoided by pre-drying the gold trap and by discarding those traps that tend to absorb large quantities of water.

4.5 The fluorescent intensity is strongly dependent upon the presence of molecular species in the carrier gas that can cause *quenching* of the excited atoms.

4.6 The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. All glassware is cleaned per SOP NC-QA-014. Be aware of potential sources of contamination, and take appropriate measures to minimize or avoid them. The analytical instrument and sample / standards preparation area should be protected from mercury vapor or particulates in the laboratory air. Samples, standards and blanks should only be opened in a clean area. Gloves must be powder free, and should be checked for mercury contamination. Do not use powdered nitrile gloves as they have been shown to have either low-level mercury contamination or interferences. Only clean gloves should touch the instrument and other equipment used to process blanks, standards, and samples.

5. SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2 The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used

in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Bromine Monochloride	Corrosive Poison Oxidizer	0.1 (Br) ppm TWA	May be fatal if inhaled. Causes severe eye and skin burns. Causes damage to the following organs: Lungs, mucous membranes, respiratory tract, skin, central nervous system, eyes, lens or cornea.
Potassium Bromate	Oxidizer	0.1 mg/m^3 TWA	Irritates respiratory tract. May cause coughing and shortness of breath. Causes irritation to the skin. May cause redness, itching, and pain. In the presence of liquids, it is slowly absorbed in toxic amounts. Prolonged exposure may cause burns. Causes irritation to eyes with redness, pain. May cause eye damage.

1 – Always add acid to water to prevent violent reactions.
2 – Exposure limit refers to the OSHA regulatory exposure limit.

5.3 Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and cleanup techniques before working with mercury. Since mercury vapor is toxic, precaution must be taken to avoid its inhalation, ingestion, or absorption through skin. All lines should be checked for leakage, and the mercury vapor must be vented into a hood or passed through a mercury–absorbing media such as a carbon filter.

5.4 Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.5 Exposure to hazardous chemicals must be maintained **as low as reasonably achievable.** All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.6 All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica North Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and to a laboratory supervisor.

5.7 Do not look directly into the beam of the Hg lamp. The UV light these lamps radiate is harmful to the eyes.

5.8 Cylinders of compressed gas must be handled with caution in accordance with local regulations. It is recommended that, wherever possible, cylinders are located outside the laboratory and the gas led to the instrument through approved lines.

5.9 The CVAFS apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1 Atomic Fluorescence Spectrophotometer equipped with:

6.1.1 Fluorescence Cell with quartz ends. Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide accurate measurements. Any

scratches or fingerprints can alter the absorption of UV radiation.

6.1.2 Mercury specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL)

6.1.3 Peristaltic pump

6.1.4 Flowmeter

6.1.5 Recorder or printer

6.1.6 Gas /Liquid separator

6.1.7 Drying devices: Nafion Dryer (used for all methods), soda lime trap (Method 1631)

6.1.8 Gold traps (2): Quartz tube containing gold-coated sand

6.1.9 Hotblock maintaining a temperature of 50-110°C

6.2 Sample bottles, 40 mL borosilicate glass VOC vials, QEC or equivalent, < 0.5 ng/L contamination when used for Method 1631 samples. In actual practice, should contribute less than 0.1 ng/L to facilitate meeting method blank criteria. Unless tested by the manufacturer for cleanliness and accuracy, 12 vials from each lot must be gravimetrically tested at the 40 mL point. Cleanliness is assessed by adding 0.2 mL BrCl (Section 7.15). Store the test vials at room temperature for at least 12 hours and analyze as samples. All vial results must be less than the reporting limit.

6.3 Argon gas supply, high purity, or equivalent: A gold trap may be used in-line to further purify the argon.

6.4 Bubbling apparatus consisting of:

6.4.1 Tygon tubing

6.4.2 Teflon Tee fittings

6.5 Calibrated automatic pipettes

6.6 Disposable cups or tubes, low mercury content

6.7 Starch / iodide paper or equivalent

6.8 0.45 um filtering apparatus

7. REAGENTS AND STANDARDS

7.1 Reagent water must be produced by a US Filter PureLab Plus deionized water system or equivalent. Reagent water must be free of mercury and interferences as demonstrated through the analysis of reagent and method blanks.

7.2 Stock (10 mg/L) mercury standards (in 5-10% HNO_3) are purchased. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year, and must be replaced sooner if verification from an independent source indicates a problem.

7.3 Intermediate mercury standard (10 µg/L): Fill a 100 mL volumetric flask about half full with reagent water. Add 0.5 mL of BrCl solution (Section 7.15). Add 0.10 mL of the stock mercury standard (Section 7.2) and dilute to 100 mL with reagent water. The intermediate mercury standard should be replaced every nine months.

7.4. Working mercury standard (1 µg/L): Fill a 40 mL vial about half full with reagent water. Add 0.2 mL of BrCl solution (Section 7.15). Add 4.0 mL of the intermediate mercury standard (Section 7.3) and dilute to 40 mL with reagent water. The working mercury standard should be replaced every three months. Additional information can be found in SOP NC-QA-017.

7.5. The calibration standards listed in Table I must be prepared fresh from the working standard (Section 7.4) by transferring 0, 0.02, 0.04, 0.08, 0.2, 0.4, and 1.0 mL of a mercury standard into 40 mL vials and diluting to volume with reagent water. For Method 1631, use the working standard (Section 7.4). BrCl (Section 7.15) and $NH_2OH{\bullet}HCl$ (Section 7.12) reagent solutions are also added.

Note: Alternate approaches to standard preparation may be taken and alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained. For example, some automated mercury systems may not require 40 mL of standard and therefore smaller volumes may be generated to reduce waste generation.

7.6. The initial calibration verification standard (QCS) must be made from a different manufacturer or lot than that of the calibration standards.

7.7. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed with all reagents that are used for sample preparation.

7.8. Hydrochloric acid (HCl), concentrated, trace metal grade, and ultra trace mercury

grade.

Note: Ultra trace mercury HCl (when commercially available) should be used to prepare the bromine monochloride solution. Trace metal grade HCl may be used to prepare the stannous chloride and 2% HCl rinse solutions provided that these solutions are purged with argon prior to use.

7.9. Autosampler rinse solution (2%): 400 mL trace metal grade HC1 diluted to 20 L reagent water. Purge overnight with argon.

7.10. Stannous Chloride Solution Concentrate: Add 500 g of $SnCl_2 \bullet 2H_2O$ to 2.4 L trace metals concentrated hydrochloric acid. Allow the $SnCl_2 \bullet 2H_2O$ to completely dissolve. ACS Reagent grade suitable for mercury determination (< 1 ppb) recommended.

7.11. Stannous Chloride Working Solution: Fill a 2.5 L glass bottle (HCl leached) with 2.25 L of reagent water. Add sufficient stannous chloride concentrate (Section 7.10) to bring the total volume to 2.5 L. This produces a reductant solution that is 10% HCl and 2% $SnCl_2 \bullet 2H_2O$. Purge with argon (0.5 L/min) for at least 24 hours. Analyze a reagent blank with this solution prior to analysis of samples (Section 9.7).

7.12. Hydroxylamine Hydrochloride Solution: Dissolve 300 g of $NH_2OH \bullet HCl$ in reagent water. Dilute to 1 L. Add 1 mL of stannous chloride solution working solution and purge with argon (0.5 L/min) for at least 24 hours. Analyze a reagent blank made with this solution prior to analysis of samples (Section 9.7).

7.13. Potassium Bromide KBr reagent grade, low mercury content is desirable. This dry reagent may be baked at 250°C for at least 8 hours to volatilize trace Hg(0) contamination.

7.14. Potassium Bromate.$KBrO_3$, reagent grade, low mercury content is desirable. This dry reagent may be baked at 250°C for at least 8 hours to volatilize trace Hg (0) contamination.

7.15. Bromine monochloride preservative/oxidizing solution: In a ventilation hood, add 5.4 g KBr to 500 mL of ultra trace (low mercury) HCl. Allow the salt to dissolve. Slowly add 7.6 g $KBrO_3$. Halogen fumes will be emitted during this step. Adequate ventilation is essential to protect analyst safety. Analyze a reagent blank with this solution prior to analysis of samples (Section 9.7).

Note: Prior to placing a new lot of BrCl into production, spike 1 mL into a blank and LCS and analyze. If recovery is < 80%, re-prep the BrCl reagent. If it fails again, the reagent lot is not approved for use.

7.16. Nitric acid, concentrated, trace metal grade

7.17.Sulfuric Acid, concentrated, trace metal grade

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Preservation Holding Time

8.1.1. Holding time from time of collection is extended to 28 days when the sample is preserved with HCl or the oxidation step is performed in the sample bottle used for collection. Preservation/oxidation is verified by the persistence of the yellow color of the BrCl. Additional BrCl must be added if the preservative/oxidizer is consumed. Record any additional BrCl used (see Section 11.2.5). Samples to be analyzed for dissolved Hg must be transferred to the filtering apparatus within 48 hours of collection, then preserved as above. Once preserved, holding time is 90 days from sample collection to analysis.

8.1.2. Solid and biological sample holding time for Hg is one year from collection to digestion and preservation. The holding time for digested and preserved solid samples is 90 days from sample preparation.

8.2. Collection and Storage

8.2.1. The clean hands/dirty hands procedure should be followed for collection. Standard sampling kits include environmental sample kit (2 x 40mL vials), MS/MSD kit (4 x 40mL vials), field blank kit (2 empty + 2 DI-filled 40mL vials), and trip blank kit (2 DI-filled 40mL vials). Alternative client-specified configurations of sample kits may be provided. Samples are stored in a mercury-clean area.

8.2.2. Solid samples may be stored in fluoropolymer or borosilicate glass or polyethylene bags.

8.2.3. Tissue samples may be shipped to the laboratory frozen or chilled at 0-4 degrees C, and may be processed and stored in one of the following ways:

8.2.3.1 Tissue that arrive frozen, should be keep frozen until time for homogenization. Thaw, homogenize, and then refreeze the tissue in a glass container. Subsampling can occur immediately after homogenization before the refreeze or at a later date with another thaw/refreeze cycle.

8.2.3.2 Tissue that arrive cold (0-4 ºC) but not frozen can be homogenized within 24 hours and frozen in glass jar. Subsampling can occur immediately after homogenization before the freeze or at a later date with another thaw/refreeze cycle.

8.2.3.3 Tissues that arrive cold (0-4 ºC) but not frozen can be frozen upon

receipt and kept frozen until time for homogenization. Thaw, homogenize, and refreeze the tissue in a glass container. Subsampling could occur immediately after homogenization before the refreeze or at a later date with another thaw/refreeze cycle

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

9.2. Prior to the analysis of any analyte using Methods 1631, the following requirements must be met.

9.2.1 Method Detection Limit (MDL). An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, which have been carried through the entire analytical procedure. MDLs must be re-determined in accordance with 40 CFR Part 136 Appendix B requirements. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the TestAmerica Canton reporting limit. In addition the MDL for Method 1631 must be = 0.2 ng/L. Refer to TestAmerica Canton SOPs NC-QA-021 and CA-Q-S-006 for details on MDL analysis and criteria.

9.2.2 Initial Demonstration Study (initial precision and recovery study): This requires the analysis of four QC check samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance. The results of the initial demonstration study must be acceptable before analysis of samples may begin.

9.2.2.1 Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.2.3 Carry-Over Determination. Analyze system blanks immediately after calibration solutions containing successively larger concentrations of Hg – from this test determine the amount of Hg that will carry >0.5 ng/L of Hg into a succeeding system blank. When a sample with one half or more of this determined amount is analyzed, then a system blank or sample below the reporting limit must be demonstrated before subsequent sample can be reported. Samples with detectable Hg analyzed after the high sample but before system cleanliness is demonstrated must be re-analyzed.

9.3. Preparation Batch

9.3.1. A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike

duplicate (2 MS/MSD pairs if the batch has more than ten samples). In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.4. Sample Count.

9.4.1. Laboratory-generated QC samples (Method Blanks, LCS, and MS/MSDs) are not included in the sample count for determining the size of a preparation batch.

9.5. Method Blank (MB)

9.5.1. One MB must be processed with each preparation batch. The MB consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The MB is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The MB should not contain any analyte of interest at, or above, the reporting limit. The sample result must be a minimum of 10 times higher than the MB contamination level.

9.5.2. If there is no analyte greater than the RL in the samples associated with an unacceptable MB, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.5.3. Re-preparation and re-analysis of all samples associated with an unacceptable MB is required when reportable concentrations are determined in the samples (see exceptions noted above).

9.5.4. If the above criteria are not met and re-analysis is not possible due to limited sample quantity, then the sample data must be qualified. This anomaly must be addressed in the project narrative and the client must be notified.

9.5.5. Preparation blanks must be prepared for 0.2, 0.4, 0.6, 0.8, 1 and 2mL volumes of BrCl on each day samples are prepped. If there is a positive detection in any of these blank samples, this information must be included in the case narrative of any job containing samples that were spiked with a corresponding level of BrCl. This prep blank does not have any specific acceptance criteria.

9.6. System / Subtraction Blank

9.6.1. The system (calibration) blank consisting of all reagents used to prepare

samples and standards will be used for background subtraction and system cleanliness monitoring. Three system blanks are prepared and analyzed with the initial calibration curve (ICal). Apply the average calibration factor from the ICal to the average raw response from these three system blanks. The calculated mercury concentration must be less than the reporting limit. The standard deviation of the three blanks must be < 0.10 ng/L. The average raw response from these three blanks will be subtracted from all raw response data from all other data prior to calculating concentration factor (for cal standards) or concentrations. Subsequent system blanks are analyzed as ICB and CCB in conjunction with the ICV (QCS) and CCV (OPR). These IC and CC blanks are used to monitor the cleanliness of the instrument and are calculated in the same manner as samples and are not used for background subtraction purposes. The absolute value of the calculated mercury concentration must be less than the reporting limit.

9.7. Reagent Blank

9.7.1. Reagent blanks are used to demonstrate that the reagents used to prepare samples for Hg analyses are free from contamination. The Hg concentration in reagent blanks is determined by analyzing the reagent solutions.

9.7.2. Reagent blanks are required when the batch of reagents (bromine monochloride, hydroxylamine hydrochloride, and stannous chloride) are prepared. The amount of Hg in a reagent blank containing BrCl solution, stannous chloride solution, and hydroxylamine hydrochloride solution must be < 0.2 ng/L.

9.8. Laboratory Control Sample (LCS).

9.8.1. One aqueous LCS must be processed with each preparation batch. The LCS is a second source standard used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The LCS must be carried through the entire analytical procedure and must be a second source standard. The acceptance criterion is 77-123%. If the LCS is outside established control limits the system is out of control and corrective action must occur.

9.8.2. In the instance where the LCS recovery is greater than the maximum and the sample results are < RL, the data may be reported with qualifiers**. Such action must be addressed in the case narrative.**

9.8.3. Corrective action will be repreparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable.

9.9.Additional information on QC samples can be found in QA Policy QA-003.

9.10. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.10.1. One MS/MSD pair must be processed for each 10 samples in preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client-specific data quality objectives (DQOs) may require the use of sample duplicates in place of or in addition to MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Method 1631 requires that each matrix be spiked at a 10% frequency. Some regulatory agencies interpret each discharge or sampling point as a separate matrix. It is the client's responsibility to determine which sample(s) is to be matrix spiked each time samples are submitted for analysis. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table I (Appendix A).

9.10.2. If analyte recovery or RPD falls outside the acceptance range, corrective action will include:

9.10.2.1. If the MS/MSD fails due to the high background concentration of mercury in the parent sample, spike concentration will be adjusted accordingly, and the parent sample, MS and MSD will be reanalyzed.

9.10.3. MS/MSD results which again fall outside the control limits must be addressed in the case narrative.

9.11 Initial Calibration Verification (ICV/ICB) (QCS – Quality Control Sample)

9.11.1. Calibration accuracy is verified by analyzing a second source standard (ICV) immediately following an Initial Calibration. The ICV result must fall within 20% of the true value for that solution. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within ± the reporting limit (RL) from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected, and the instrument recalibrated (see Section 11.5.5 for required run sequence). If the cause of the ICV or ICB failure was not directly instrument related, the corrective action will include repreparation of the ICV, ICB, CCV, and CCB with the calibration curve.

9.12 Continuing Calibration Verification (CCV/CCB) (Ongoing Precision and Recovery - OPR)

9.12.1. Calibration accuracy is monitored in the analytical sequence through the analysis of a known standard at the end of the analytical sequence or every 12 hours. Additional CCVs may be analyzed as necessary. The CCV concentration must be at 5 ng/L for 1631. The CCV result must fall within 77-123% of the true value for that solution for 1631. A CCB is analyzed immediately following each CCV. (See Section 11.5.5 for required run sequence). The CCB (system blank) must fall within ± the reporting limit (RL) from zero. Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. Sample results may only be reported when bracketed by valid ICV/CCV and ICB/CCB pairs.

9.12.2. In the instance where the CCV or CCB is greater than the maximum acceptance criteria and the sample results are < RL, the data may be reported. Such action must be addressed in the case narrative.

9.13 Control Limits

9.13.1 Control limits are prescribed in method 1631E. Control limits are easily accessible via LIMS.

9.14 Method Detection Limits (MDLs) and MDL Checks

9.14.1 MDLs and MDL Checks are established by the laboratory as described in SOPs NC-QA-021 and CA-Q-S-006.

9.14.2 MDLs are easily accessible via LIMS

9.15 Nonconformance and Corrective Action

9.15.1 Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.2, except the oxidation time need does not need to be a minimum of 12 hours and can be used immediately since the mercury is already in an oxidized state in the standard.

10.2. Calibration may be performed daily (every 24 hours), but is required only when indicated by instrument and preparation QC problems. The instrument calibration date and time must be included in the raw data.

10.3. Set up the instrument with the operating parameters recommended by the manufacturer (Table II). Allow the instrument to become thermally stable before beginning calibration (approximately 1-2 hours of warm-up is required if the lamp has been turned off). The most stable results are obtained if the lamp is left on full time.

Refer to the CVAFS instrument manual for detailed setup and operation protocols.

10.4. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of six standards and three calibration blanks. One standard must be at the TestAmerica North Canton reporting limit. Analyze standards in ascending order beginning with the blanks. Refer to Section 7.5 and Table I for additional information on preparing calibration standards and calibration levels.

10.5. For DoD work, refer to SOP NC-QA-016 for specific details.

10.6 The calibration factors must have less than 15% RSD or the instrument shall be stopped and recalibrated prior to running samples. Sample results cannot be reported from a curve with an unacceptable RSD. Also, the low standard must calculate back within ±25% of the true value.

10.7 Refer to Sections 9.12 and 9.13 for calibration verification procedures, acceptance criteria, and corrective actions.

11. PROCEDURE

11.1. For DoD work, refer to SOP NC-QA-016 for specific details.

11.2. Aqueous Sample Preparation

11.2.1 All calibration and calibration verification standards (ICV, ICB, CCV, CCB) and laboratory QC samples (LCS, MB, MS, MSD) are processed with the same digestion reagents used for the field samples.

11.2.2 Open the outer sample bag and carefully dump the inner bag containing the sample bottles onto a clean bench top in the low level mercury area with a minimum of handling. Immediately discard the outer sample bag. Change gloves between each sample or work with another analyst using the clean hands/dirty hands technique.

11.2.3 Change gloves and open the remaining inner bag, remove the sample vials, label, and place in the low-level mercury prep area.

11.2.4 Remove about 2.7 mL from each sample vial. This will leave 40 mL in the bottle. Confirm by checking the meniscus and the 40mL calibration point. Set the cap back on the original vial. Repeat this process for all 40 mL vial aliquots of the sample. Transfer 1 mL of sample from a separate unpreserved "10X dilution" labeled tube and add 9 mL of reagent water. Reseal the original sample vial caps if it will be greater than three minutes before the next step is performed (Section 11.2.5).

11.2.5 Temporarily lift the cap and add 0.20 mL of BrCl (Section 7.15) to the 40 mL sample vial, reseal and mix. Store the sample vials at room temperature for

at least 12 hours.

11.2.6 Starch / iodide paper may be used to detect excess halogens (i.e., BrCl) in colored samples where the yellow color of the BrCl cannot be seen. If the yellow tint from the BrCl disappears and starch/iodine paper does not detect halogens, add an additional 0.2 mL of BrCl to the 40 mL sample vial, reseal, mix and allow to digest for another 12 hours. Repeat this iterative process until a maximum of 1 mL of BrCl has been added to the 40 mL sample vial.

11.2.7 If starch / iodide paper still does not detect halogens, add an additional 1 mL aliquot of BrCl, reseal and mix. Store the sample vials at room temperature for at least 12 hours. Record the lot number of the starch/iodide paper **and the amount of BrCl added to the sample** in the LIMS prep batch comments.

11.2.8 If the maximum (2 mL) aliquot of BrCl is added to the sample, and the yellow BrCl color persists, purge the sample and associated batch QC for 2 hours with Argon to remove potential interferences, and proceed with analysis. Record the amount of BrCl used in the LIMS prep batch comments.

11.2.9 If the 2 mL maximum was reached and the yellow BrCl color still does not persist, perform a 10x dilution on the same aliquot and resume the bromination process with iterations of BrCl as described above in sections 11.2.5-11.2.7.

11.2.10 Preparation blanks must be prepared for 0.2, 0.4, 0.6, 0.8, 1 and 2mL volumes of BrCl on each day samples are prepped. If there is a positive detection in any of these blank samples, this information must be included in the case narrative of any job containing samples that were spiked with a corresponding level of BrCl.

Note: To meet IL EPA requirements the vials may be heated at approximately 50°C for six hours. If the oxidizer has been consumed, add additional BrCl and heat for an additional six hours.

11.3 Biological Sample Preparation

11.3.1. This procedure is intended for tissue and other primarily organic matrices (excluding coal). It does, however, give quantitative recovery for Hg on finely divided geological matrices such as sediments and soils.

11.3.2 Accurately weigh 1.0 gram of sample directly into a tared digestion vessel.

Note: The use of too much organic material will consume all of the acid in the digestion, resulting in low recovery.

11.3.3 To each sample, add 3 mLs of H2SO4 and 7 mLs of HNO3. Place the digestion vessel in an acid fume hood and loosely cap with a clean marble or equivalent. For wood, paper or other dry carbohydrates that can react violently with the HNO3/H2SO4 solution, allow the sample to sit in the cold acid for at least 4 hours before heating.

11.3.4 After digesting at room temperature, place the digestion vessel in a hotblock in the hood and slowly bring to a gentle boil by incrementally increasing the plate temperature over a 1-hour period to 85-95°C. If excessive sample foaming occurs, bring to temperature more slowly. Reflux for 2-3 hours to fully oxidize remaining organic matter. The mineral portion of soil and sediment samples will not dissolve, but will be effectively leached by this digestion.

11.3.5 After the digestion is complete, allow it to cool. Add 1mL of BrCl and bring to the calibration mark on the digestion vessel with water. Shake the sample/BrCl solution to homogenize, and allow to sit at least 4 hours prior to analysis to oxidize remaining dissolved methyl Hg.

11.3.5.1 For the MB, add approximately 1 mL of reagent water in lieu of 1g of solid sample.

11.3.5.2 For the LCS, add 1.0 mL of the 10 ug/L intermediate mercury standard (Section 7.3) in lieu of 1g of solid sample.

11.3.5.3 For the MS/MSD, add 1.0 mL of the 10 ug/L intermediate mercury standard (Section 7.3) in addition to the 1g of solid sample.

11.3.6 Proceed to Section 11.4.4.

11.4 Solid Sample Preparation

11.4.1 Homogenize the sample then weigh 1 g into a 40 mL VOA vial. The VOA vial must come from a lot that has been pre-screened for Hg contamination (Section 6.2).

11.4.1.1 For the MB, add approximately 1 mL of reagent water in lieu of 1g of solid sample.

11.4.1.2 For the LCS, add 1.0 mL of the 10 ug/L intermediate mercury standard (Section 7.3) in lieu of 1g of solid sample.

11.4.1.3 For the MS/MSD, add 1.0 mL of the 10 ug/L intermediate mercury standard (Section 7.3) in addition to the 1g of solid sample.

11.4.2 In a fume hood, add 8 ml of concentrated HCl, swirl, and add 2 mL concentrated HNO_3 to the sample in the 40 mL vial. Cap and allow the sample to digest for at least 4 hours.

11.4.3 Add 1.0 ml of BrCl (Section 7.15) to the digestate, then dilute with reagent water (Section 7.1) to the 40 mL calibration point. Shake, then allow to settle until supernatant is clear. Store the sample vials at room temperature for at least 12 hours. Centrifuge or filter, if necessary.

11.4.4 For screening, transfer 50 uL of the supernatant into a "10X dilution" 10 ml culture tube and dilute to 10 mL with reagent water. For analysis, transfer 2 mL of the supernatant into a pre-screened VOA vial and dilute to the 40 mL calibration point with reagent water, add 200 uL of BrCl, then cap and shake. The "10X dilution" aliquot may be analyzed as specified in Section 11.3. The 40 mL VOA vial sample is ready for analysis and may be analyzed as specified in Section 11.4. Based on sample matrix and/or historical results, a greater dilution may be required.

11.5 Sample Screening

11.5.1 Add 0.05 mL of hydroxylamine solution (Section 7.12) and analyze the 10X screening aliquot of the sample using a single-point calibration (10 ng/L)

11.5.2 If the sample response (note that this is a 10X dilution) exceeds that of the 5 ng/L standard, then the sample concentration is beyond the normal calibration range of Method 1631. Prepare the appropriate dilution for 1631 analysis.

11.5.3 If the 10X dilution screen response is non-detect at 5 ng/L, then the sample may be analyzed without dilution, depending on the reporting limit needed by the client unless matrix interferences warrant dilution.

11.6 Sample Analysis

11.6.1 When ready to begin analysis, add 0.10 mL of hydroxylamine hydrochloride solution (Section 7.12) to the samples to reduce the excess BrCl (the BrCl has been reduced when no yellow color remains). Cap and shake. Add the hydroxylamine solution in 0.10 mL increments until the BrCl is completely reduced. Record the total volume used on the benchsheet.

Note: Spiking is done before the addition of the hydroxylamine hydrochloride reagent.

11.6.2 With instrument control parameters set to appropriate values (see Table II), load samples into autosampler. Use 40 mL vials for Method 1631.

11.6.3 Start autosampler sequence.

11.6.4 All measurements must fall within the defined calibration range to be valid. Dilute and re-analyze all samples for analytes that exceed the highest calibration standard.

11.6.5 The following analytical sequence must be used:

Instrument Calibration
ICV (QCS)
ICB
CCV (OPR)
CCB
Maximum 12 hours
CCV
CCB
Repeat sequence every 12 hours between CCV/CCB pairs as required to complete run
CCV
CCB

Refer to Quality Control Section 9 for the appropriate quality control criteria.

Notes:
Samples include the MB, LCS, MS, MSD, duplicate, field samples, and sample dilutions.

Instrument calibration need not be performed if the run QC parameters indicate that the system is in control.

11.6.6 To facilitate the early identification of QC failures and samples requiring rerun, it is strongly recommended that sample data is reviewed periodically throughout the run.

11.6.7 Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance, and troubleshooting.

11.6.8 One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo.

11.6.9 Any unauthorized deviations from this procedure must also be documented as a non-conformance with a cause and corrective action described.

11.7 Analytical Documentation

11.7.1 Record all analytical information in LIMS, including any corrective actions or modifications to the method.

11.7.2 Record all standards and reagents in the LIMS Reagents module. All standards and reagents are assigned a unique number for identification.

11.7.3 Record all sample results and associated QC in LIMS. Level I and Level II reviews are performed in LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calibration Factors are calculated according to the equation:

$$CF(x) = \left(\frac{Area(x) - Area(b)}{Conc(x)} \right)$$

Where:
CF(x) = calibration factor of standard (x)
area(x) = area of standard (x)
conc(x) = concentration of standard (x)
area(b) = average area of 3 calibration blanks

12.2. ICV percent recoveries are calculated according to the equation:

$$\%R = 100 \left(\frac{Found(ICV)}{True(ICV)} \right)$$

12.3. CCV percent recoveries are calculated according to the equation:

$$\%R = 100 \left(\frac{Found(CCV)}{True(CCV)} \right)$$

12.4. Matrix spike recoveries are calculated according to the following equation:

$$\%R = 100 \left(\frac{SSR - SR}{SA} \right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.5. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.6. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD-MS|}{\left(\frac{MSD+MS}{2}\right)}\right]$$

Where:
MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:
DU1 = Sample result
DU2 = Sample duplicate result

12.7 The final concentration for an aqueous sample is calculated as follows:

ng/L = C x D

Where:
C = Concentration (ng/L) from instrument readout
D = Instrument dilution factor

12.8 The final concentration for a solid sample is calculated as follows:

ug/kg = C x D x W x P

Where:
C = Concentration (ng/L) from instrument readout
D = Instrument dilution factor
W = Weight/volume factor = 0.040, when 1 g of sample is digested and diluted to 40 mL
P = Preparation factor = 20, when 2 mL of digestate is diluted to 40 mL

12.9 Appropriate factors must be applied to sample values if dilutions are performed.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.3.

13.2. Method performance is determined by the analysis of method blanks and laboratory control samples. The method blanks must meet the criteria in Section 9.5.

13.3. Training Qualification

The Group/Team Leader has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1 It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15.2.Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. **Acid waste-aqueous waste generated by the analysis.** Samples vials are collected and taken to the waste storage building. The vials are crushed and the liquid waste and glass are separated. The liquid waste is neutralized and released to the POTW. The glass is disposed of in the trash.

16. REFERENCES

16.1. References

16.1.1. Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, U.S. EPA, August 2002

16.1.2. Appendix to Method 1631, Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation, U.S. EPA, January 2001

16.1.3. Corporate Quality Management Plan (CQMP), current version

16.1.4. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.5. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.6. Revision History

Historical File:		Revision 1: 04/05/01		Revision 5.2: 03/11/09
		Revision 2: 08/14/01		Revision 5.3: 08/17/10
		Revision 3: 09/18/02		Revision 5.4: 12/09/11
		Revision 4: 12/16/02		Revision 5.5: 02/20/12
		Revision 5.0: 01/17/05		
		Revision 5.1: 07/28/07		

16.2 Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.2.5. Supplemental Practices for DoD Project Work, NC-QA-016

16.2.6. Standards and Reagents, NC-QA-017

16.2.7. Subsampling, NC-IP-001

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Modifications/Interpretations from Reference Method

17.1.1 Section 9.1.7 of the method requires three method blanks per analytical batch. The section also describes an analytical sequence that includes a CCV (OPR) only at the beginning and end of the sequence, and that includes no CCBs (system blanks) after calibration. This SOP requires only one method blank per preparation batch, but requires additional stability and cleanliness checks through the analysis of a CCV/CCB pair at the beginning, end and after every 12 hours during an analytical run.

17.1.2 Section 9.2.1 of the method recommends that an MDL be determined whenever a new operator begins work. At this laboratory, a new operator receives proper, documented training and must prove competence through an initial demonstration of performance that includes the successful analysis of four LCSs (see Section 9.3.2 of this SOP).

17.1.3 Section 9.4.5.1 of the method recommends that field blank analysis immediately before analyzing samples from the batch. Field blanks are analyzed as normal samples in this laboratory with no particular run order requirement.

17.1.4 Section 9.4.7 of this method recommends that 5% of the bottles in a lot be monitored. Bottle cleanliness in this laboratory is verified by the initial analysis of 5% of the bottles from three boxes of a lot of 40 mL sample vials.

17.1.5 The volume descriptions for the equation in Section 12.3.2 of the method includes subtraction of the volume of reagent used in the standards and the samples. Since the volume of reagents used in samples and standards is typically the same (or differs insignificantly in rare cases), this subtraction is not included in the determination of Hg concentration in this laboratory.

17.1.6 Interpretations and Differences from Method 1631 Appendix A

17.1.7 In the method, after digestion with aqua regia is complete, the digestate is diluted with 0.07 N BrCl for elemental carbon-containing samples. In this SOP, all samples are diluted reagent water to which 1 mL of 0.2 N BrCl has been added. This presents a BrCl concentration in the diluted digestate comparable to the concentration achieved using the method technique. Also, since it is added to all digestates (not only those known to contain elemental carbon), the analyzed digestate will always contain some BrCl, and thereby be more comparable to the calibration standards.

APPENDIX A

TABLE I

MERCURY REPORTING LIMITS, CALIBRATION STANDARD, QC STANDARD, AND SPIKING LEVELS (ng/L)

	1631E			
	Conc ng/L	**µL Std (Sec.7.4)**	**Conc ug/kg Solid**	**µL Std (Sec.7.3) Solid**
Standard Water RL	0.5			
Standard Solid RL			1.0	
Std 1 (in triplicate)	0	0		
Std 2	0.5	20		
Std 3	1	40		
Std 4	2	80		
Std 5	5	200		
Std 6	10	400		
Std 7	25	1000		
ICV (QCS)	5	200 (Sec 7.6)		
CCV (OPR)	5	200		
LCS	5	200	10	1000
MS/MSD	5	200	10	1000

TABLE II

RECOMMENDED INSTRUMENT PARAMETERS
(LEEMAN LABS HYDRA AF GOLD PLUS)

Instrument Parameter	1631
Argon flow (L/min)	0.5
Pump flow (mL/min)	10
Rinse (sec)	60
Uptake (sec)	240
Sample volume (mL)	40
Integration (sec)	0.70 (70 sec total)
Method	CVAFS with trap
Furnace 1 temp (? C)	600
Furnace 2 temp (? C)	600
Dry Time (sec)	5
Desorption time (sec)	70
Stabilize time (sec)	10

APPENDIX B

Example: TestAmerica North Canton Hg Data Review Checklist

Run Date:_____**Analyst**_____

ICAL DATE _____ **ICAL BATCH #**_____

Acceptance criteria is found in the applicable laboratory SOP or TALS. If not acceptable, generate an NCM in TALS.

Items for Review	Level I	Level II
Calibration/Instrument Run QC		
Instrument calibrated per manufacturer's instructions and at SOP specified levels (including 3 initial calibration blanks)?		
ICV/CCV analyzed ≤ 12 hours and within control limits?		
ICB/CCB analyzed ≤ 12 hours and within +/- RL?		
Sample Information		
Were sample results within calibration range?		
All reported results bracketed by acceptable QC?		
Sample analyses done within holding time?		
Preparation/Matrix QC		
Samples preserved within holding time?		
LCS done per prep batch and within QC limits?		
Method blank done per prep batch and <RL?		
MS run at required frequency (1 per 10 samples) and within limits?		
MSD or DU run at required frequency (1 per 10 samples) and RPD within SOP limits?		

Items for Review	Level I	Level II
Other		
Are all nonconformances documented appropriately?		
Current MDL data on file?		
Calculations and Transcriptions checked for error?		
All client/project specific requirements met?		
Date of analysis verified as correct?		

Reviewed by Analyst/Level I:_____

Start Date:_____ Time_____ End Date:_____ Time_____ Analytical Batch

Reviewed by Analyst/Level I:_____

Start Date:_____ Time_____ End Date:_____ Time_____ Analytical Batch

Reviewed by Peer/Sup/ Level II:_____

Start Date:_____ Time_____ End Date:_____ Time_____ Analytical Batch

Reviewed by Peer/Sup/ Level II:_____

Start Date:_____ Time_____ End Date:_____ Time_____ Analytical Batch

By signing “Reviewed by” I signify that I have evaluated the items indicated and I acknowledge responsibility for the above referenced data

APPENDIX C

TROUBLESHOOTING GUIDE

Problem	Possible Cause
Poor or No Fluorescence or Sensitivity Check Failed	Incorrect wavelength Dirty windows Window loose Etched or dirty optics Wrong lamp Bad lamp Not enough or no sample introduced Empty sample cup Incorrectly made standards Gas leak EDL power supply set on “Continuous”
Erratic Readings	Source lamp not aligned properly Lamp not prewarmed Injection tip partially clogged Contaminated reagents Contaminated glassware Drying tube saturated Bad lamp Injection tip hitting outside of tube Injection tip coated or not set properly Leak in sample tubing Power fluctuations Air bubbles in tubing
EDL Won’t Light	Lamp cable not plugged in Lamp power set at 0 Lamp is dead Power supply fuse is blown Short in cord
Standards Reading Twice or Half Normal Fluorescence or Concentration	Incorrect standard used Incorrect dilution performed Dirty cell

APPENDIX D

CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 hydrochloric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered Gloves must not be used in the mercury laboratory since the powder contains mercury, as well as other metallic analytes. Only powder free gloves should be used in the Metals Laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and discard.

APPENDIX E

PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Cold Vapor Atomic Absorption (Leeman Labs Hydra AF Gold Plus) [1]

Daily	Semi-annually	As Needed
Check argon flow	Check Hg lamp intensity	Change Hg lamp
Check pump tubing		Change liquid/gas separator
Check drain		Change Nafion dryer
Check soda lime drying tube		

APPENDIX F

INSTRUMENT SETUP FOR ANALYSIS

Hg Analysis (Leeman Labs Hydra AA Gold Plus)

SCREENING ANALYSIS

There are 3 separate screens to use **WinHgRunner**, **WinHgDatabase**, and **Rack Editor**

1. To Set Your Protocol and Dataset

   Find a previous protocol under the **WinHgDatabase** screen on the right hand side Dataset/Proto

   Use the arrow down to find a 245.7 protocol

   Save a new protocol File-**Save Protocol**- type in file name (245.7 (date) ex. 24570101) Then select the **(RN) key** (this will take you to the **WinHgRunner** screen)

   WinHgRunner – **File**-**New**- type in dataset name ((date)(letter) for ex. 0101A) type in batch name (ex. Screen)

   Need to find new protocol created in **WinHgDatabase**

2. Activate Gas and Pump

   WinHgRunner – under **Control tab** turn on Gas and pump

3. To Calibrate Curve (standards are loaded in the far left tray)

   WinHgRunner – under the **Standard tab** turn on **S1 S2 Rep1** load the 2 standards (blank and 10ppt) to begin analyzing **Stnd Auto tab**

4. To Check Calibration Curve

   WinHgDatabase – under **Cal Curve tab** (blank recommended to be below 50 counts and 10 ppt recommended to be above 600 counts) then **Accept** curve

5. Typing Labels

   Rack Editor - **File**-**New** (pick 44 rack)- type in labels under sample ID and **Save As** ((date)(letter) ex. 0101A)

   The first sample will be a 10ppt standard (using the remaining 10ppt calibration standard) and proceeding with samples

6. To Begin Analyzing Sample

WinHgRunner – under **Sample tab** - type in rack name, start cup, end cup, cups per rack (44 for screen) then to analyze select **Run Auto tab**

7. Checking Results

WinHgRunner – under **Report tab** results are shown

Each sample is analyzed at a 10x dilution.

Therefore if a result reads 2.5ppt multiply by 10 for a result of 25ppt (which would need diluted at a 2x). Any sample that reads over 25ppt should be diluted since 25ppt is your high standard.

SAMPLE ANALYSIS

There are three separate screens to use: **WinHgRunner**, **WinHgDatabase**, and **Rack Editor**

1. To Set Your Protocol and Dataset

Find a previous protocol under the **WinHgDatabase** screen on the right hand side Dataset/Proto

Use the arrow down to find a 1631 protocol

Save a new protocol File-**Save Protocol**- type in file name (1631(date) ex. 16310101) Then select the **(RN) key** (this will take you to the **WinHgRunner** screen)

WinHgRunner – **File**-**New**- type in dataset name ((date)(letter) for ex. 0101A) type in batch name (ex. Screen)

Select a new protocol created in **WinHgDatabase**

2. Activate Gas and Pump

WinHgRunner – under **Control tab** turn on Gas and Pump

3. To Calibrate Curve (standards are loaded in the far left tray; all blanks are analyzed in cup 1)

WinHgRunner – under **Standard tab** (in this step you need to run 2 blanks then the calibration curve)

First blank - Select **S1 Rep3** then analyze **Stnd Auto tab** when completed

Second blank - Select **S1 Rep2** then analyze **Stnd Auto tab** when completed

Calibration curve - Select **S1 S2 S3 S4 S5 S6 S7 Rep1** then analyze **Stnd Auto tab**

4. To Check Calibration Curve

WinHgDatabase – under **Cal Curve tab** – the following criteria should be met %RSD CF <15%, Avg. BB <0.5 and %Recovery 75-125%. If curve passes criteria – Select **Accept**

5. Check Verification Standards

Rack Editor – **File**-**New** (pick 14 rack) – type in labels under sample ID (ICV, ICB, CCV, CCB) and **Save As** ((date)(letter) ex. 0101A)

6. Analyze Verification Standards

WinHgRunner – under **Sample tab** type in rack name, start cup, end cup, cups per rack (14) then to analyze select **Run Auto**

7. Check Verification Results

WinHgRunner - under **Report tab** the results should be ICV (80-120%), CCV (77-123%) and ICB/CCV (>0.5ppt)

8. Typing Labels

Rack Editor - **File**-**New** (pick 14 rack)- type in labels under sample ID and select **Save AS** ((date)(letter) ex. 0101A)

9. Analyzing Additional Samples

WinHgRunner – under **Sample tab** type in rack name, start cup, end cup, cups per rack (14) then to analyze select **Run Auto**

10. Checking Results

WinHgRunner – **Select** Report tab

Sequence of Run:
Instrument Calibration (Step #3 and #4)
ICV (Step #5, #6, #7)
ICB
CCV
CCB
Maximum 12 hours (Step #8, #9)
CCV
CCB
Repeat sequence

PRINTING REPORTS

To print Cal curve:

WinHgDatabase – under **Cal Curve tab** select **Print Cal** to print curve

To print Report:

WinHgDatabase – under **Report tab** under format turn on report select **Generate** to print

To transfer run:

Select PRN fomat and select Generate to transfer the file to the N drive using a unique file name.

Locate the file on the N drive. Right click and send to TALS Import.

Title: Determination of Total Cyanide (CLP SOW ISM01.2)

Approval Signatures:

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1.0 Scope and Application

This SOP describes the laboratory procedure for the determination of total cyanide in samples taken from hazardous waste sites.

1.1 Analytes, Matrix(s), and Reporting Limits

This procedure may be used for a variety of matrices including: water, soil and sediment.

The contract required quantitation limit (CRQL) is 10 ug/L for water samples and 0.5 mg/Kg for soils.

2.0 Summary of Method

The cyanide as hydrocyanic acid (HCN) is released from the sample by a reflux-distillation using midi-distillation, and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined spectrophotometrically. During the spectrophotometric analysis, the cyanide is converted to cyanogen chloride (CNCl), by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The absorbance is read at a wavelength between 570 and 580 nanometers (nm).

This procedure is based on the following reference method:

- Exhibit D, Analytical Methods, USEPA CLP SOW for Inorganic Superfund Methods, ISM01.2, January 2010.

3.0 Definitions

A list of terms and definitions are provided in Appendix A.

4.0 Interferences

Sulfides adversely affect the spectrophotometric procedure. Samples should be field tested for the presence of sulfides following the procedures described in the SOW.

The presence of surfactants may cause the sample to foam during refluxing. If this occurs, the lab will add an antifoam agent.

Oxidizing agents such as chlorine decompose most of the cyanides. The samples should be field tested for the presence of oxidizing agents following the procedures described in the SOW.

High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and nitrite will form nitrous acid that will react with some organic compounds to form oximes. These oximes will decompose under test conditions to generate HCN. The interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid prior to the distillation process.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

Potassium cyanide and sodium cyanide will give off Hyrdogen Cyanide (HCN) gas if combined with strong acids. Inhalation of CN gas can cause irritation, dizziness, nausea, unconsciousness and potentially death.

5.2 Primary Materials Used

Table 2 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the MSDS. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

6.0 Equipment and Supplies

Catalog numbers listed in this SOP are subject to change at the discretion of the vendor. Analysts are cautioned to be sure equipment used meets the specification of this SOP.

6.1 Miscellaneous

- Balance – Capable of accurately weighing to the nearest 0.01 g.
- Glassware – Class A volumetric flasks and pipettes.
- Midi-reflux distillation apparatus including boiling flask condenser and absorber.
- Heating mantel or heating block as required.
- Lead Acetate Paper
- KI Starch Paper

6.2 Analytical System

- Lachat Quikchem 8000 Automated Cyanide Analyzer

7.0 <u>Reagents and Standards</u>

7.1 Reagents

Reagent Water; ASTM Type II or equivalent

Cadmium Carbonate-Powdered; reagent grade; JT Baker or equivalent

Ascorbic Acid-Crystals; reagent grade; JT Baker or equivalent

Sulfamic Acid (Powdered); JT Baker or equivalent

Midi-Distillation Reagents:

Sulfuric Acid (H_2SO_4)-Concentrated; reagent grade; JT Baker or equivalent

Sodium Hydroxide (NaOH); JT Baker or equivalent

Magnesium Chloride – Anti-foam Agent; JT Baker or equivalent

Sodium Hydroxide Solution (0.25N NaOH): Measure 200g of sodium hydroxide pellets into a 20L plastic carboy filled with reagent water. Ensure all pellets are dissolved and solution is thoroughly mixed.

Sulfamic Acid Solution; Measure 100g of sulfamic acid into a 1000mL flask filled with 800mL of reagent water, mix until dissolved and bring up to a final volume of 1000mL.

Sulfuric Acid Solution, 50% (v/v): Measure 1000 mL of reagent water into an empty glass bottle. Add a magnetic stir bar and place the bottle on a stir plate in a fume hood. While stirring carefully add 1000 mL of concentrated sulfuric acid to the reagent water in the glass bottle.

Magnesium Chloride Solution (2.5M): Weigh 510 g of $MgCl_2 \cdot 6H_2O$ into a 1L volumetric flask, and dilute to 1000 mL with reagent water.

Spectrophotometric Reagents

Barbituric Acid; Fisher or equivalent

Chloramine-T Plus; Fisher or equivalent

Hydrochloric Acid (HCl)-Concentrated (Specific Gravity 1.19); reagent grade; JT Baker or equivalent

Pyridine; JT Baker or equivalent

Sodium Phosphate, Monobasic, Monohydrate, Granular; Mallinckrodt CHEMICALS or equivalent

Chloramine-T Solution (0.014M): Dissolve 2.0 g chloramine-T plus in 500 mL of reagent water. Refrigerate until use and prepare fresh daily.

Sodium Phosphate Buffer: Add 800 mL of reagent water to a 1000 mL volumetric flask. Add 138g of $NaH_2PO_4 \cdot H_2O$ to the flask to dissolve. Once dissolved, dilute the solution to 1000 mL with reagent water. Filter the solution through a 0.45 μm filter into a vacuum flask and de-aerate the solution under vacuum for one half hour prior to use.

Color Reagent- Pyridine-barbituric acid: Weigh 150 g barbituric acid into an amber glass bottle. Add 750 mL pyridine to the bottle and mix with a stir bar on a stir plate in a fume hood. Add 150 mL of concentrated HCl mix and cool to room temperature. Dilute to 2500 mL with reagent water. Store in a refrigerator maintained at 4°C (±2).

7.2 Standards

Cyanide Stock Standard (1000 mg/L); ERA (Standardization is not necessary if purchased as a certified solution)

Cyanide Intermediate Standard Solution (10mg/L): Add 2.5mL of the stock standard solution to a 250 mL volumetric flask and bring to volume with 0.25N NaOH.

Cyanide Working Standard Solution (1.0 mg/L): Prepare fresh daily by diluting 10mL of intermediate standard solution in a 100mL volumetric flask and bring to volume with 0.25N NaOH.

ICV Solution: Obtain from USEPA or purchase a 1000 mg/L stock standard solution from a different manufacturer or lot than the solution used for calibration. Standardization is not necessary if purchased as a certified solution. ICV value cannot be equal to a point on the calibration curve, but should fall near the middle range of the calibration curve.

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection so these procedures are not included in this SOP. Listed below are laboratory recommended minimum sample size and containers.

Matrix	Sample Container	Minimum Sample Size	Preservation[2]	Holding Time[1]	Reference
Water	Polyethylene or glass containers	100 mL	pH of >12 with Sodium hydroxide Chilled to <4°C	12 Days VTSR	ISM01.2
Soil	Polyethylene or glass containers	25 g	Chilled to <4°C	12 Days VTSR	ISM01.2

[1]Holding time is determined from validated time of sample receipt (VTSR).

[2] Sample collection personnel should test samples for sulfide and oxidizing agents immediately after sample collection. The presence of sulfide may be checked with lead acetate paper. If sulfides are present, an additional sample volume (25mL) should be collected and the total volume of sample treated with powdered cadmium carbonate or lead carbonate. After the addition of treatment, field sampler should filter the sample through filter paper. If no sulfides are present, sample collection personnel should test for the presence of oxidizing agents using a strip of potassium iodide – starch test paper. If oxidizing agents are present, the sample should be treated with ascorbic acid. After which the sample is preserved with sodium hydroxide to a pH greater than 12 and cooled until distillation.

Samples are stored protected from light and refrigerated at 4°C (± 2°C) from the time of receipt until 60 days after delivery of a reconciled, data package to the client. After 60 days has elapsed, unless otherwise specified by client or regulatory program, the samples are disposed of in a manner that complies with all applicable regulations.

9.0 Quality Control

9.1 Sample QC

The laboratory prepares the following quality control samples with each batch of samples.

QC Item	Frequency	Acceptance Criteria
Method Blank (MB)	1 per digestion batch or SDG which ever is more frequent	See Table 3
Matrix Spike (MS)	1 per digestion batch or SDG per matrix	See Table 3
Sample Duplicate (SD)	1 per digestion batch or SDG per matrix	See Table 3
Post Distillation Spike (PDS)	When matrix spike fails	See Table 3

9.2 Instrument QC

The following instrument QC is performed:

QC Item	Frequency	Acceptance Criteria
Initial Calibration (ICAL)	Initial instrument setup and daily	See Section 10.2.1
Second Source Calibration Verification (ICV)	Once, after each ICAL	%R 85-115
Continuing Calibration Verification (CCV)	At the beginning and end of analytical run and every 2 hours or at a frequency of 10%, which ever is sooner	%R 85-115
Initial Calibration Blanks (ICB)	Once, after each ICV.	<CRQL
Continuing Calibration Blanks (CCB)	After every CCV and during the analytical run every 2 hours or at a frequency of 10%, which ever is sooner	<CRQL

10.0 Procedure

10.1 Instrument Operating Conditions

Set the operating conditions using the instructions provided by the manufacturer of the instrument.

10.2 Instrument Calibration

10.2.1 Initial Calibration (ICAL)

Calibrate the instrument daily, or after initial calibration (ICV) or continuing calibration (CCV) failure.

Prepare fresh calibration standards with each calibration performed using at least 5 standards and a blank (6 total). One of the calibration standards must be at or below the contract required quantitation limit (CRQL). The recommended concentrations of the calibration standards are in the table that follows.

Level	Parent Standard	Amount (mL)	Final Volume (mL)	Final Concentration (ug/L)
Blank			100	0
Level 1	CN Working (1 mg/L)	1.0	100	10
Level 2	CN Working (1 mg/L)	5.0	100	50
Level 3	CN Intermediate (10 mg/L)	1.0	100	100

Level 4	CN Intermediate (10 mg/L)	2.0	100	200
Level 5	CN Intermediate (10 mg/L)	4.0	100	400

To prepare each calibration level, add the specified volume of parent standard to a 100 mL volumetric flask that contains approximately 80 mL of reagent water then dilute to volume with 0.25N sodium hydroxide solution.

Distill and analyze the standards following the procedure that begins in Section 10.4. The data system acquires the data and prepares a standard curve by plotting the instrument response of the calibration standards against the true value concentration and using linear regression, calculates the correlation coefficient. The correlation coefficient must be greater than or equal to 0.995. If these criteria are not met, repeat the calibration.

Check the calibration equation to establish the representativeness of the data that were used to produce the calibration equation. To perform the check, re-fit the non-blank calibration data back to the calibration equation or the comparison of the calculated concentration of each of the standards against the expected concentration of the associated standard. This difference is related to the actual residual. For this calculation the Percent Difference shall be used where the above difference is further divided by the expected amount or concentration of the respective standard. If these Percent Differences for each of the standards do not fall within ±30%, then the calibration equation is not acceptable and must be corrected.

Check the y-intercept from the linear regression initial calibration equation to ensure it is not below the low standard. If the y-intercept is not below the low standard, the calibration fails. Repeat the calibration. No samples may be analyzed until this criterion is met.

10.2.2 Initial Calibration Verification (ICV)

Immediately after calibration, check the accuracy of the calibration with the ICV standard provided by the EPA. Distill and analyze the ICV following the procedure described in section 10.4.

The percent recovery of the ICV must be within 85-115%. If this criterion is not met, correct the problem, recalibrate and repeat the ICV verification.

10.2.3 Continuing Calibration Verification (CCV)

To verify accuracy of the calibration during the analytical sequence, analyze a CCV standard at the beginning of the sequence, after the last sample and at a frequency not to exceed 1 hour. The concentration of the CCV standard must be at the mid-level concentration of the calibration curve.

Prepare the CCV using the same source standard as used for initial calibration at a concentration of 200 mg/L. See the table for the preparation of calibration standards for the formulation. Distill and analyze the CCV following the procedure described in section 10.4.

The percent recovery of the CCV should be within 85-115%. If this criterion is not met, correct the problem, recalibrate, repeat the ICV verification and reanalyze all samples since the last compliant CCV.

10.2.4 Initial and Continuing Calibration Blanks (ICB/CCB)

Analyze calibration blanks immediately after every ICV and CCV during the analytical sequence. The absolute value of the ICB/CCB must be less than or equal to the CRQL. If it is not, correct the problem, recalibrate and reanalyze all samples since the last compliant calibration.

10.3 Sample Preparation (Midi-Distillation)

Test each water sample for the presence of sulfide and oxidizing agents.

Sulfide Test: Place a drop of sample on a strip of lead acetate paper. If the strip turns brown, treat the sample with powdered cadmium carbonate. Repeat this process until the strip paper does not darken. After which, filter the sample through a 0.22 um filter and take the portion for sample analysis from the filtrate.

Oxidizing Agents: Place a drop of sample on a strip of KI-starch paper. If the strip turns blue, stop work, notify the laboratory PM and wait for further instruction. The PM must contact the sample management office (SMO) for further instruction. The laboratory is not authorized to proceed with sample preparation or analysis prior to notification to SMO.

For waters, transfer 50 mL of sample into a labeled pre-washed distillation tube. Use 50 mL of reagent water for the method blank. Add 0.5 mL of the Cyanide Intermediate Standard Solution (10 mg/L) to the sample selected as the matrix spike.

For soils, measure 1 g of sample into a labeled pre-washed distillation tube. Use 1 g of sea washed sand for the method blank. Add 0.5 mL of the Cyanide Intermediate Standard Solution (10mg/L) to the sample selected as the matrix spike. Add 50 mL of reagent water to each distillation tube.

All standards are distilled in the same manner as samples. To prepare the standards for distillation, add a known volume of intermediate or working standard to a 100mL volumetric flask and adjust to final volume using 0.25N sodium hydroxide solution using the specifications provided in the following table:

Distilled Standard Preparation

Level	Parent Standard	Amount (mL)	Final Volume (mL)	Final Concentration (mg/L)
Blank	0		100	0
Level 1	CN Working (1 mg/L)	1.0	100	10
Level 2	CN Working (1 mg/L)	5.0	100	50
Level 3	CN Intermediate (10 mg/L)	1.0	100	100
Level 4	CN Intermediate (10 mg/L)	2.0	100	200
Level 5	CN Intermediate (10 mg/L)	4.0	100	400
ICV	CN Second Source (1 mg/L)	6.0	50	120
CCV	CN Intermediate (10 mg/L)	2.0	100	200

NOTE: The ICV preparation in this table provides the final concentration if the ICV is prepared from the laboratory purchased second source standard. If the ICV solution is provided by the EPA, the analyst is instructed to prepare and analyze the ICV per the instructions given by the EPA and the final concentration may vary based on the concentration of the EPA solution.

Transfer 50 mL of each prepared standard above into a labeled pre-washed distillation tube.

10.4 Midi-Distillation

Add 50 mL of 0.25N sodium hydroxide solution to the gas absorbing impinger on the distillation apparatus. Connect the distillation tube, condenser and absorber for each standard, field and QC sample. Turn the vacuum on and adjust the valves to achieve a flow rate of three bubbles per second from the impingers in each reaction vessel. After five minutes of vacuum flow has elapsed, add 2mL of the sulfamic acid solution through the inlet valve and allow samples to mix. After three minutes has elapsed, add 5 mL of a 50% (v/v) sulfuric acid solution (H2SO4) through the top inlet tube of each distillation head into the reaction vessel and mix for 5 minutes. Note: The acid volume must be sufficient to adjust the pH of the samples to below 2.0.

To each distillation tube, add 2 mL of magnesium chloride solution through the top air inlet tube of each distillation head into the reaction flask. If excessive foaming occurs, add another 2 mL of magnesium chloride solution or dilute and re-distill the sample.

Turn on the heating block and heat the solution to boiling (~123-125°C). Reflux for 1½ hours. After this time period has elapsed, turn off the heat block and continue the vacuum flow for an additional 15 minutes to cool the tubes. After the tubes have cooled, close off the vacuum at the gang valve and remove the absorber.

Analyze the distillates immediately or seal and store them at 4°C until analysis. The distilled solutions must be analyzed within the 12-day holding time.

10.5 Analysis - Semi-Automated Spectrophotometric Determination

Bring the samples, standards and the preparation blank to room temperature prior to analysis.

Set up the Lachat analyzer following the manufacturer instructions. Fill the reagent containers and connect them to the instrument. Initiate the start sequence and allow the instrument to warm up.

Prepare a post distillation spike on the same sample that was used for the matrix spike. To prepare the post-distillation spike, transfer 0.2 mL of Cyanide Working Standard Solution (1.0mg/L) and 9.8 mL of parent sample to a volumetric flask.

NOTE: For initial analysis, the concentration of the post distillation spike standard is equivalent to 2X the CRQL. If the matrix spike recovery is outside control limits, the unspiked sample result does not exceed four times the concentration of spike added and if the indigenous level in the unspiked sample is higher than 2X the CRQL, then the post-distillation spike must be repeated with a spike concentration equivalent to 2X the indigenous level in the unspiked sample.

On the PC connected to the instrument select the autosampler template and enter the sample Ids in the order of analysis. Place the samples, calibration blanks, calibration standards, and performance check standards in the position on the autosampler rack that corresponds to their assigned position in the autosampler template. Place the autosampler rack in the autosampler tray and initiate the software macro to begin analysis.

Analytical Sequence

An example analytical sequence that includes initial calibration (ICAL) is provided below.

Injection Number	Lab Description
1	Calibration Blank
2	10 Calibration Standard
3	50 Calibration Standard
4	100 Calibration Standard
5	200 Calibration Standard
6	400 Calibration Standard
7	ICV
8	ICB
9	CCV
10	PBW/S
11	CCB
12-20	Samples
21	CCV
22	CCB

NOTE: In addition to the beginning and end of the analytical sequence, analyze a CCV throughout the analytical sequence at a frequency not to exceed 1 hour.

The autoanalyzer uses a pyridine-barbaturic acid solution for color development. The solution upon reaction with cyanide (as cyanogen chloride, CNCl) produces a deep magenta color. After color development, the autoanalyzer measures the absorbance at 578nm and calculates the concentration of cyanide using the equations given in Section 11.0.

After analysis is complete, review the results against the established acceptance criteria and perform corrective action, as needed.

Dilute and reanalyze any samples that exceed the linear range and perform post digestion spikes as necessary.

11.0 Calculations / Data Reduction

11.1 Calculations

Unless otherwise noted all calculations are performed by the Lachat Autoanalyzer data processing software and the TALS LIMS system.

Aqueous Sample Concentration

$$C_{(ug/L)} = \frac{\mu g}{L_{dist}} * \frac{V_{dist}}{V_{samp}}$$

Where:
$\mu g/L_{dist}$ = Lachat result adjusted for dilution factor

V_{dist} = distillate volume
V_{samp} = sample volume

Soil Sample Concentration

$$C_{(mg/Kg\ \ drywt.)} = \frac{\mu g}{L_{dist}} * \frac{V_{dist}}{g_{samp}} * \frac{100}{\%\ \ solids}$$

Where:
$\mu g/L_{dist}$ = Lachat result adjusted for dilution factor
V_{dist} = distillate volume
g_{samp} = initial sample weight
% Solids = percent solids determination

11.2 Data Review

11.2.1 Primary Review

Evaluate the results of the instrument performance check samples and field and QC samples against the established acceptance criteria. If criteria are not met, perform corrective action. If any data is reported outside criteria, initiate a nonconformance memo (NCM).

Upload the data into TALS. Enter the worksheet and batch information in the TALS batch. Set results to primary and secondary as appropriate, check QC linkages then set the TALS batch to first level review.

11.2.2 Secondary Review

Review project documents such as the Project Plan (PP), Project Memo or any other document/process used to communicate project requirements to ensure those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Verify that the acceptance criteria for the calibration and QC items listed in Table 1 were met. If the results do not fall within the established limits verify the recommended corrective actions were performed. If not, initiate corrective actions and/or verify an NCM was created to document the criteria exception. Verify analytical results are qualified accordingly and the TALS batch information is complete. Set samples to 2nd level review.

Run the LIMS QC Checker, investigate and correct any problems found. Run and review the deliverable. Fix any problems found then set the method chain to lab complete.

11.2.3 Data Reporting

The report format, application of data qualifiers and creation of the data deliverable is performed by the LIMS using the formatter set by the project manager during log-in. The LIMS formatter for CLP SOW is designed to match the reporting specifications given in the CLP SOW.

Records of electronic and hardcopy data are maintained as described in laboratory SOP BR-QA-014.

12.0 Method Performance

A Method Detection Limit (MDL) must be determined on each instrument used for analysis for each matrix and non-prepared analyses prior to initial use of the method and annually thereafter.

Refer to laboratory SOP BR-QA-005 for the laboratory's procedure for method detection limit studies.

10.2 Demonstration of Capabilities (DOC)

Perform a method demonstration of capability at initial set-up and when time there is a significant change in instrumentation or procedure.

Each analyst that performs the analytical procedure must complete an initial demonstration of capability (IDOC) prior to independent analysis of client samples. Each analyst must demonstrate on-going proficiency (ODOC) annually thereafter. DOC procedures are further described in the laboratory's quality system manual (QAM) and in the laboratory SOP for employee training.

10.3 Training Requirements

Any employee that performs any portion of the procedure described in this SOP must have documentation in their employee training file that they have read this version of this SOP.

Instrument analysts, prior to independent analysis of client samples, must also have documentation of demonstration of initial proficiency (IDOC) and annual on-going proficiency (ODOC) in their employee training files.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability).

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to BR-EH-001 *Hazardous Waste*. The following waste streams are produced when this method is carried out.

- Aqueous Alkaline Waste – Satellite Container: 5 Gallon Polyethylene Container

15.0 References / Cross-References

- Exhibit D, Analytical Methods, USEPA CLP SOW for Inorganics Superfund Methods, ISM01.2, January 2010.

- Laboratory SOP BR-QA -019 *Data Review*
- Laboratory SOP BR-QA-011 *Procedures for Employee Training & Demonstration of Proficiency.*
- Laboratory SOP BR-QA-014 *Laboratory Records*
- Laboratory SOP BR-QA-002 *Standard Preparation*
- Laboratory SOP BR-QA-005 *Determination of LOD, LOQ & RL*.
- Laboratory SOP BR-EH-001 *Hazardous Waste*
- Laboratory Quality Assurance Manual (QAM)
- Corporate Environmental Health and Safety Manual (CW-E-M-001)
- ion

16.0 Method Modifications

Not Applicable.

17.0 Attachments

- Table 1: Primary Materials Used
- Appendix A: Terms and Definitions

18.0 Revision History

Revision 0 is the first version of this SOP.

Table 1: Primary Materials Used

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Potassium Cyanide	Poison Corrosive	5 Mg/M3 TWA as CN	**This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death.** Corrosive to the respiratory tract. May cause headache, weakness, dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heart beat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage.
Pyridine	Flammable Irritant	5 ppm-TWA	Inhalation causes severe irritation to the respiratory tract. Symptoms of overexposure include headache, dizziness, nausea, and shortness of breath. Causes severe irritation possibly burns, to the skin. Symptoms include redness and severe pain. Absorption through the skin may occur, resulting in toxic effects similar to inhalation. May act as a photosensitizer. Vapors cause eye irritation. Splashes cause severe irritation, possible corneal burns and eye damage.
Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of Sodium Hydroxide dust will cause irritation of the nasal and respiratory system.
Silver Nitrate	Corrosive Poison	0.01 mg/m3 (TWA)	This is a corrosive, poisonous material. It will cause burns to any area of contact and is harmful if inhaled. Ingestion may cause death. Contact with other material may cause fire.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Appendix B: List of Definitions

Analyte: The element or ion an analysis seeks to determine; the element of interest.

Analytical Sequence: The actual instrumental analysis of the samples from the time of instrument calibration through the analysis of the final CCV or CCB.

Background Correction: A technique to compensate for variable background contribution to the instrument signal in the determination of trace elements.

Batch: A group of samples prepared at the same time in the same location using the same method.

Blank: An analytical sample designed to assess specific sources of contamination.

Calibration: The establishment of an analytical curve based on the absorbance, emission intensity, or other measured characteristic of known standards.

Calibration Blank: A blank solution containing all of the reagents and in the same concentration as those used in the analytical sample preparation.

Calibration Standards: A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve).

Continuing Calibration Verification (CCV): A single parameter or multi- parameter standard solution prepared by the analyst and used to verify the stability of the instrument calibration with time, and the instrument performance during the analysis of samples.

Contract Required Quantitation Limit (CRQL): Minimum level of quantitation acceptable under the contract Statement of Work (SOW).

Control Limits: A range within which specified measurement results must fall to be compliant. Control limits may be mandatory, requiring corrective action if exceeded, or advisory, requiring that noncompliant data be flagged.

Dissolved Metals: Analyte elements in a water/aqueous sample which will pass through a 0.45 micrometer (µm) filter.

Dry Weight: The weight of a sample based on percent solids. The weight after drying in an oven.

Duplicate: A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

Holding Time: The elapsed time expressed in days from the date of receipt of the sample by the Contractor until the date of its analysis.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations; used to define the quantitative response, linearity, and dynamic range of the instrument to target analytes.

I**nitial Calibration Verification (ICV):** Solution(s) prepared from stock standard solutions, metals or salts obtained from a source separate from that utilized to prepare the calibration standards. The ICV is used to verify the concentration of the calibration standards and the adequacy of the instrument calibration.

Interference Check Sample: A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interfluent correction factors.

Interferents: Substances which affect the analysis for the element of interest.

Laboratory Control Sample (LCS): A control sample of known composition.

Linear Range, Linear Dynamic Range: The concentration range over which the instrument response remains linear.

Matrix: The predominant material of which the sample to be analyzed is composed.

Matrix Effect: In general, the effect of particular matrix constituents.

Matrix Spike: Aliquot of a sample (water/aqueous or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

Method Detection Limit (MDL): The concentration of a target parameter that, when a sample is processed through the complete method, produces a signal with 99 percent probability that it is different from the blank. For 7 replicates of the sample, the mean value must be 3.14s above the blank, where “s” is the standard deviation of the 7 replicates.

Percent Difference (%D): The difference between the two values divided by one of the values.

Percent Solids (%S): The proportion of solid in a soil sample determined by drying an aliquot of the sample.

Preparation Blank: An analytical control that contains reagent water and reagents, which is carried through the entire preparation and analytical procedure.

Relative Percent Difference (RPD): The relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero.

Sample: A portion of material to be analyzed that is contained in single or multiple containers and identified by a unique sample number.

Sensitivity: The slope of the analytical curve (i.e., functional relationship between instrument response and concentration).

Serial Dilution: The dilution of a sample by a factor of five. When corrected by the dilution factor, the diluted sample must agree with the original undiluted sample within specified limits. Serial dilution may reflect the influence of interferents.

Stock Solution: A standard solution which can be diluted to derive other standards.

Target Analyte List (TAL): A list of Inorganic Analytes (metals and cyanide) as designated in Exhibit C.

Validated Time Of Sample Receipt (VTSR): The date on which a sample is received at the Contractor's facility, as recorded on the shipper's delivery receipt and Sample Traffic Report/Chain of Custody Record.

Title: Total Organic Carbon
Lloyd Kahn Method

Approval Signatures:

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1.0 Scope and Application

This SOP describes the laboratory procedure for the determination of total organic carbon (TOC) in soil and solid materials.

1.1 Analytes, Matrix(s), and Reporting Limits

This procedure may be used to determine total organic carbon in soil and solid materials. This procedure may not be amenable to oily matrices.

The routine reporting limit is 1000 mg/kg based on an initial sample weight of 10 mg.

2.0 Summary of Method

10 mg of sample is transferred to a tin capsule, treated with phosphoric acid and dried in an oven at a temperature 105℃ for 30 minutes to one hour t o separate the organic carbon from inorganic carbonates and bicarbonates. The sample is analyzed on an instrument where it is pyrolyzed in an inductive type furnace. The carbon is converted to carbon dioxide and measured by a differential thermal conductivity detector.

This procedure is based on the following reference documents:

- EPA Region II Document Determination of Total Organic Carbon in Sediment, July 27, 1998, authored by Lloyd Kahn, Quality Assurance Specialist.

If the laboratory's SOP has been modified from the above referenced document, a list of modifications is provided in Section 15.0 of this SOP.

3.0 Definitions

A list of general laboratory terms and definitions are provided in Appendix A.

4.0 Interferences

Volatile organics in the sediments may be lost in the de-carbonation step resulting in a low bias.

Maintaining the sample at 4°C, analyzing the sample within the specified holding time, and analyzing the wet sample, may minimize bacterial decomposition and volatilization of the organic compounds.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

None

5.2 Primary Materials Used

Table 1 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the SDS. The table does not include all materials used in the procedure. A complete list of materials used can be found in section 7.0. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS. Any questions regarding the safe handling of these materials should be directed to the laboratory's Environmental Health and Safety Coordinator.

6.0 Equipment and Supplies

- Drying Oven: Capable of maintaining a temperature of 105 ±2℃.
- Carlo Erba Elemental Analyzer Model EA1108 and Model NA 1500 or equivalent.
- Costech Elemental Analyzer: Model 4010 or equivalent.
- Analytical Balance: Capable of weighing to the nearest 0.001mg.
- Aluminum Weigh Boats.
- Tweezers
- 5mm X 9mm tin capsules
- Quartz Columns: Costech Analytical or equivalent.
- Quartz wool: for segregating and containing column materials
- Copper Wire, Reduced: Costech Analytical or equivalent.
- Tungsten on Alumina: Costech Analytical or equivalent.
- High Temperature Gloves
- Clear Plastic Sample Trays: Costech Analytical or equivalent.
- 100ul Hamilton syringe or similar

7.0 Reagents and Standards

7.1 Reagents

- Reagent water
- Phosphoric Acid, Concentrated: Reagent Grade, J.T. Baker recommended.

Phosphoric Acid Solution (1:19): Add approximately 100 mL of reagent water to a 200 mL volumetric flask. Add 18.34 g of concentrated phosphoric acid to the volumetric flask then adjust to volume with reagent water. Mix the solution well then transfer the solution to a 250 mL polyethylene bottle. Assign an expiration date of six months from date made and store the solution at room temperature.

7.2 Standards

- Potassium Hydrogen Phthalate (KHP) (Primary Standard Grade) Used to calibrate the instrument. 47.05% Carbon by weight

- Laboratory Control Samples (LCS) Material, Organic Material of known Carbon percentage: Purchased from LECO Corporation.

1% Carbon KHP Solution (10,000 mg Carbon/L): Add 50 mL of reagent water to a 100 mL volumetric flask. Add 2.128 g of KHP and dissolve completely. Adjust to final volume with reagent water. To mix the solution, cap the flask and invert. Allow the air bubble to reach the top of the flask. Repeat 9 times. Assign an expiration of 6 months from the date prepared and store at room temperature.

0.1% Carbon KHP Solution (1000mg Carbon/L): Add approximately 25 mL of reagent water to a 50 mL volumetric flask. Add 5 mL of 1 % Carbon KHP solution to the flask and adjust to final volume with reagent water. To mix the solution, cap the flask and invert. Allow the air bubble to reach the top of the flask. Repeat 9 times. Assign an expiration date of 6 months from the date prepared so long as the parent solution does not expire sooner, in which case use the earliest expiration date. Store the solution at room temperature.

0.01% Carbon KHP Solution (100mg Carbon/L): Add approximately 25 mL of reagent water to a 50 mL volumetric flask. Add 0.5 mL of 1% Carbon KHP Solution and adjust to final volume with reagent water. To mix the solution, cap the flask and invert. Allow the air bubble to reach the top of the flask. Repeat 9 times. Assign an expiration date of 6 months from the date prepared so long as the parent solution does not expire sooner, in which case use the earliest expiration date. Store the solution at room temperature.

Note: Alternatively a 10,000mg/L TOC standard may be purchased from a reputable vendor (Spex Certiprep, SCP Science or ERA) and diluted appropriately to prepare the intermediate solutions above.

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection so sampling procedures are not included in this SOP. Sampling requirements may be found in the published reference method. Listed below are the recommended minimum sample size, preservation and holding time requirements:

Matrix	Sample Container	Minimum Sample Size	Preservation	Holding Time	Reference
Solids	Amber glass	10 g	Chilled to ≤ 4℃	14 Days	Lloyd Kahn Method

Holding time is calculated from date of sample collection.

Unless otherwise specified by client or regulatory program, after analysis, samples and extracts are retained for a minimum of 30 days after provision of the project report and then disposed of in accordance with applicable regulations.

9.0 Quality Control

9.1 Sample QC

The following QC samples are analyzed with each batch:

QC Item	Frequency	Acceptance Criteria
Method Blank (MB)	1 in 20 or fewer samples	< RL
Laboratory Control Sample (LCS)	1 in 20 or fewer samples	%R (75-125)
Sample Quadruplicate	Client request; Prepare LCS in Quadruplicate if sample is not specified.	SD (≤ 3 X SD of annual P&A study)
Matrix Spike	Client request	%R (75-125)
Duplicate/Matrix Spike Duplicate	Client request	RPD 20%

If a sample quadruplicate is not designated by the PM analyze the LCS in quadruplicate as a measure of method precision.

9.2 Instrument QC

The laboratory analyzes the following instrument check standards:

QC Item	Frequency	Acceptance Criteria
Initial Calibration (ICAL)	Initial Method Set-Up, after combustion chamber is changed (approx. every 200 drops)	Correlation coefficient must be >0.995
Initial Calibration Verification (ICV)	Following Calibration	%R (75-125)
Calibration Verification (CCV)	Every 20 drops and at the end of the analytical sequence	%R (75-125)
Calibration Blank (CCB)	After every CCV	<RL

10.0 Procedure

10.1 Calibration

Analyze a calibration curve each time the combustion column is changed. Change the column after 200 drops or when you experience QC recovery issues, odd peak shapes or baseline issues. The column change procedure is provided in Appendix B.

The recommended formulations for each calibration level are provided in the following table:

Calibration Standards	1.0% C KHP uL	0.1% C KHP uL	0.01%C KHP uL	% Carbon KHP	Carbon (mg)	mg/Kg of Carbon (10mg sample)
Level 1	0	0	0	47.05	0	0
Level 2	0	0	100	47.05	0.010	1000
Level 3	0	40	0	47.05	0.040	4000
Level 4	25	0	0	47.05	0.25	25000
Level 5	50	0	0	47.05	0.500	50000
Level 6	75	0	0	47.05	1.000	75000

Using a volumetric Hamilton or similar syringe, measure the specified volume of standard into a tin capsule. Dry the calibration levels completely by placing in the oven at 105°C for 60 minutes. Fold the capsules. Proceed to Section 10.6 for analysis instructions.

The instrument software system plots peak area against mg of Carbon and calculates a correlation coefficient using standard linear regression. The correlation coefficient (r) must be $\geq$ 0.995 for the calibration to be considered acceptable. If it is not, repeat the calibration prior to analysis.

10.2 Troubleshooting

- Calibration passes at > 0.995 correlation, but LCS fails abnormally low: Re-calibrate.
- Large peak before Carbon peak; Indicates leak in system, perform leak test, isolate and repair leak.
- Carbon peak “maxes out” at instrument 1200mv (peak has flat top): Reanalyze sample at lower weight.
- No peaks on any chromatograms, no results: Gases to instrument may be off. Turn on all gasses at valve manifold.
- Autosampler will not work at all: Gasses to instrument may be off. Turn on all gasses at valve manifold.
- Carry over; Clean autosampler slide, if persists reduce sample mass. Note sample carryover in NCM. Oily samples may not be amenable to this test.
- Single chromatogram shows results at bottom of page, but no peak or baseline in chromatogram window: Re-print single chromatogram.
- Some or all chromatograms show carbon peak at same retention time as CCV, but peak is not identified as carbon, or is identified as another element: Retention time shifted. Adjust retention time in calibration window, and reprint chromatograms.
- Upon recalibration, peaks are not being identified as carbon: In calibration window, general tab, adjust retention time to match peaks. Starting at level 1, “Open Standard”, open level1 curve pt. in calibration directory, click “Add Peak” button, click on peak itself. Increase level #, opening standard for each curve pt and add each peak. Carbon Tab should have all five calibration points on curve, if done correctly.

- Peaks in chromatograms identified as carbon, but all results in summary table below chromatogram are zero: Current calibration not associated with run when started. Open current calibration, copy first two columns for all points (5 rows) in small table in general tab. Then, open calibration that was associated with run (should be empty) and paste into table in calibration tab. Reprint all chromatograms on run.
- Software crashes during analysis: Boot up software normally. Chromatograms already printed/analyzed are ok, but, sample that was analyzing during shutdown is lost. Restart table at next sample by un-checking "run" box for samples already run and sample that was lost.
- Autosampler error causes few samples to remain in autosampler tray after run has finished: Identify samples that got stuck. Create a new run and analyze stuck samples (with initial weights) with bracketing QC. No PBS/LCS needed.
- Autosampler error causes many sequential samples to remain in autosampler tray after run has finished (usually end of run): Add rows onto existing table. Identify samples that did not get analyzed and repeat Ids and weights into added rows. Restart table. All analyzed samples' status should be blue (analyzed), added rows should be green (not analyzed yet).

10.3 Sample Preparation

Homogenize the sample using the procedure described in Section 5.5.1 or 5.5.2 of SOP BR-QA-020.

NOTE: The determination of percent moisture is performed following the procedures of SOP BR-WC-006. The determination is not part of this test and may be performed by a different analyst.

Using tweezers place a tin capsule on the analytical balance and tare the balance. Unless a different sample weight is specified by the PM, measure 10 mg of well mixed sample into the capsule. Record the actual sample weight used on sample preparation log. Remove the capsule from the balance and place into one of the aluminum holding trays.

To prepare the duplicate sample; weigh an addition tin capsule of the parent sample as above.

To prepare the Matrix spike sample, weigh an additional tin of the parent sample as above. Spike 35uL of 1% KHP solution directly into the tin.

NOTE: The PM may specify use of a lesser sample mass when there is project history to indicate high levels of carbon present in the samples.

Check method comments for the jobs included in the batch and for any sample designated as a sample quadruplicate prepare four separate tins for this sample using the above procedure.

To prepare the method blank place an empty tin capsules into an aluminum holding tray.

To prepare the LCS weigh ~9 mg of the LECO LCS material into the tin capsules and set in an aluminum holding tray. Prepare the LCS in quadruplicate if a sample has not been specified.

Add two drops of 1:19 phosphoric acid to each tin capsule and note if sample effervesces. Continue adding acid drop-wise until effervescence stops or the tin is half full. If effervescence

did not subside notify the project manager for guidance and initiate a nonconformance report. Place the aluminum trays into a drying oven set to a temperature of 105ºC for 60 minutes or until all samples appear dry.
Using tweezers pinch the top of each tin capsule closed and compress the capsule around the material inside. Work carefully so as not to tear the capsule, but crush it down to the smallest size. Set the prepared samples in line in a clear plastic sample tray for storage, or place directly into an autosampler tray leaving positions open for the CCV and calibration blanks.

10.4 Preparation of the ICV, CCV and Blanks

For each ICV weigh ~9-11 mg of the LECO LCS material into a tin capsule.

For each CCV, transfer 35uL of 1% KHP to a tin capsule. Dry the capsules in a drying oven at 105 ^{o}C for 30-60 minutes or until dry. Fold the capsule and compress down to the smallest size possible. Prepare enough CCVs to ensure a CCV frequency of every 20 drops and at the beginning and end of the analytical sequence. Use a folded empty tin for each calibration blank.

10.5 Software Set-up and Analysis of a Curve

If a there is not a valid curve or the valid curve is not listed in the software, create a calibration curve in the analytical software. Enter the standard type, level, and mg of KHP used for each calibration level. Enter each sample ID and their respective weights into the instrument software, enter a weight of 10 mg for the method blank and calibration blanks and save the sample table. Enter the weight for the LCS. Add the tin capsules to the autosampler tray in sequence and set the tray into the autosampler carriage.

An example analytical sequence that includes ICAL is as follows:

Initial Calibration (calibration blank and 5 calibration standards)
ICV
ICB
CCV
CCB
MB
LCS
Samples
CCV
CCB
Samples
CCV
CCB

Click the “start” icon to begin the analysis.

11.0 Calculations / Data Reduction

11.1 Calculations

The instrument software calculates TOC in wet weight using the area response from the calibration curve and sample mass used. The determination of TOC in dry weight is performed by the laboratory’s LIMS system.

See Appendix C for equations for percent recovery and relative percent difference.

11.2 Data Review

11.2.1 Primary Data Review

Enter the results of the quadruplicate analysis into the EXCEL spreadsheet designated for this purpose. Compare the standard deviation derived from the quadruplicate sample against the standard deviation from the annual P&A study. If the SD of the sample quadruplicate is greater than 3 times the SD of the annual study, initiate a nonconformance memo and notify the PM to determine if further action is necessary.

Upload the instrument data to the laboratory information system (LIMS) "TALS". Evaluate the sequence against the acceptance criteria given in Table 2. Perform the recommended corrective action as necessary. If corrective action is not taken or is not successful, initiate a nonconformance memo (NCM) to document the situation. Set the Batch to 1st level reviewed.

Assemble supporting documents including the quad sample calculation spreadsheet and forward to secondary review staff.

11.2.2 Secondary Data Review

Spot-check the analytical results. Verify that acceptance criteria were met and if the results do not fall within the established limits verify the recommended corrective actions were performed. If corrective action was not taken or is unsuccessful, ensure the situation is documented with a nonconformance memo (NCM) and ensure data is qualified accordingly.

Set the batch to second level review. Scan and attach copies of supporting documentation such as; run logs, raw data and quad sample spreadsheet to the batch. Set the job to lab complete, review the form set, correct any problems then forward supporting documentation to report management.

11.2.3 Data Reporting

The report format, application of data qualifiers and creation of the data deliverable is performed by the LIMS using the formatter set by the project manager during log-in.

Retain, manage and archive electronic and hardcopy data as specified in laboratory SOP BR-QA-014 Laboratory Records.

12.0 Method Performance

12.1 Detection Limit (DL), Limit of Detection (LOD) and Limit of Quantitation (LOQ)

Establish a DL, LOD and LOQ for the method. Verify the LOQ at initial method set up following the procedures specified in laboratory SOP BR-QA-005. Verify the LOD and LOQ at the frequency established for the method using the procedures specified in same SOP. The frequency of LOD and LOQ verification depends on the strictest frequency of the regulatory program for which the method supports. The frequency requirement is documented in a spreadsheet maintained by the QA Department.

12.2 Annual Precision and Accuracy Study

Perform a precision and accuracy study annually by analyzing 15 replicates of a representative sample. Create a control chart of the results, calculate the standard deviation and generate an upper and lower limit at 3X the standard deviation. Use the results of the annual study for evaluation of the quadruplicate sample included in each batch.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to BR-EH-001 *Hazardous Waste*.

The following waste streams are produced when this method is carried out.

- Caustic waste – 2.5 L glass satellite container.
- Acidic Waste - 2.5L glass satellite container

The satellite containers are labeled "Hazardous Waste" along with the type of waste category generated. Authorized personnel routinely transfer the contents of the satellite containers to the hazardous waste storage room for future disposal in accordance with Federal, State and Local regulations.

15.0 References / Cross-References

- EPA Region II Document Determination of Total Organic Carbon in Sediment, July 27, 1998, authored by Lloyd Kahn, Quality Assurance Specialist.
- Corporate SOP CW-E-M-001 Corporate Environmental Health and Safety Manual
- Laboratory SOP BR-QA-005, Procedures for the Determination of Limits of Detection (LOD), Limits of Quantitation (LOQ) and Reporting Limits (RL).
- Laboratory SOP BR-QA-011 Employee Training
- Laboratory SOP BR-EH-011 Hazardous Waste
- Laboratory SOP BR-QA-014 Laboratory Records
- Laboratory Quality Assurance Manual (QAM)

16.0 Method Modifications

The laboratory procedure is modified from the reference method as follows:

Modification Number	Method Reference	Modification
1	TOC by Lloyd Kahn	The Laboratory uses 1:19 (w/w) phosphoric acid to decarbonize the sample and dries the sample in an oven at 105°C
2	NA	The laboratory determines the % solids by drying in an oven at 105°C per SOP BR-WC-006.
3	TOC by Lloyd Kahn	P&A studies are performed annually on a representative sample to determine 3 times the method standard deviation (SD). In the event a sample is not specified by the PM the LCS is run in quadruplicate.

17.0 Attachments

- Table 1: Primary Materials Used
- Table 2: QC Summary & Recommended Corrective Action
- Appendix A: Terms and Definitions
- Appendix B: Column change procedure
- Appendix C: Equations

18.0 Revision History

BR-WC-008, Revision 14.0

- Title Page: Updated signature approvals and copyright date
- Updated MSDS to SDS
- All Sections: Replaced acetanilide and sulphanilimide standards with KHP solutions.
- Section 7 & 9: Updated SOP to include calibration standards in CIPA.
- Section 10: Updated ICV, LCS and CCV preparation to reflect bench practice and meet DoD criteria. Added troubleshooting information.

BR-WC-008, Revision 13.0:

All sections of this SOP were revised such that the laboratory procedure matches the cited reference method except for the modifications listed in Section 15.0. This SOP is considered a complete re-write from prior versions.

Table 1: Primary Materials Used

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Phosphoric Acid	Corrosive	1 Mg/M3 TWA	Inhalation is not an expected hazard unless misted or heated to high temperatures. May cause redness, pain, and severe skin burns. May cause redness, pain, blurred vision, eye burns, and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Table 2: QC Summary, Frequency, Acceptance Criteria and Recommended Corrective Action (TOC Lloyd Kahn)

QC Item	Frequency	Acceptance Criteria	Recommended Corrective Action[1]
ICAL	Following each column change and when CCV failure indicates calibration may no longer be valid.	correlation coefficient ≥ 0.995	Standards check, re-calibration
CCV	Every 20 drops and at the end of the analytical run	%R (75-125)	Re-prepare and reanalyze samples not bracketed by passing standard. If CCV fails high, and TOC is not detected in any of the bracketed samples, the samples without TOC may be reported without reanalysis.
CCB	Following each CCV	< RL	Re-prepare and reanalyze batch.
Method Blank (MB)	Once per batch of 20 samples	< RL	Re-prepare and reanalyze batch.
LCS	Once per batch of 20 samples.	%R (75-125)	Re-prepare and reanalyze batch.
Sample Quadruplicate	Client request. If no quad specified for any jobs included in the batch analyze the LCS in quadruplicate.	SD ≤ 3X annual P&A SD	If sample quad, notify PM. If LCS quad, reanalyze the entire batch.

[1]*The recommended corrective action may include some or all of the items listed in this column. The corrective action taken may be dependent on project data quality objectives and/or analyst judgment but must be sufficient to ensure that results will be valid. If corrective action is not taken or is not successful, data must be flagged with appropriate qualifiers.*

Appendix A: Terms and Definitions

Batch: environmental samples, which are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria.

Calibration: the establishment of an analytical curve based on the absorbance, emission intensity or other measured characteristic of known standard.

Calibration Standards: a series of known standard solutions used to calibrate the instrument response with respect to analyte concentration.

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample.

Appendix B: Column Change Procedure:

Turn off the helium and oxygen supplies to the instrument.

Dial the left furnace temperature to a reading of 052 (this equates to 520˚C). Wait until the temperature drops below 600˚C to remove the column.

Remove the panel covering the furnace and unscrew the autosampler connection from the top of the column.

Unscrew the fitting at the bottom of the column and remove.

Lift the column up and out of the furnace using high temperature gloves.

CAUTION: The column will still be 500-600˚C. Do not touch the center portion of the column. Place the spent column in the metal can designated for this purpose.

Lay a new quartz column on the bench top, measure and mark off for the following:

- One inch up from the bottom and add a ½ inch plug of quartz wool. Note: pack the quartz wool tightly enough for it to stay in place.
- Pour in 2 ½ inches of copper wire
- Pack another ½ inch quartz wool plug on top of the copper
- Pour in 3 inches of tungsten
- Pack a final ½ inch quartz wool plug on top of the tungsten

Place the new column into the furnace and reconnect the top and bottom fittings. Snug these up, but don't over tighten.
Replace the panel covering the furnace, dial the furnace temperature back to 102 (this equates to

1020˚C), and turn the helium and oxygen supplies back on.

When the instrument comes up to operating temperature, it is ready to calibrate.

Appendix C: Equations

Percent Recovery (%R) LCS and CCVs

$$\%R = \frac{SR}{SA} \times 100\%$$

Where:
SR= Sample Result
SA=Concentration of Spike Added

Relative Percent Difference (%RPD)

$$\%RPD = \frac{|D_1 - D_2|}{\frac{D_1 + D_2}{2}} \times 100$$

Where:
D1 = Sample result
D2 = Duplicate Result

Title: Analytical Method for Trace Volatiles
[CLP SOW SOMO1.2]

Approvals (Signature/Date):

William S. Cicero — 12/27/07 Laboratory Director	Name — 12/27/07 Current Department Manager
Kirstin L. McCracken — 12/27/07 Quality Assurance Manager	Bryce E. Stearns — 12/27/07 Technical Director
Bryce E. Stearns — 12/27/07 Interim Health & Safety Coordinator	

This cover page documents management approval for the following changes to this SOP:

- **This SOP has been renamed and was previously identified as SOP No. LM-MV-SOMO1.2 – VOA Trace.**
- **Any reference within this document to Severn Trent Laboratories, Inc. or STL, should be understood to refer to TestAmerica Laboratories, Inc. (formerly known as Severn Trent Laboratories, Inc.)**
- **The effective date of this SOP has been changed to January 1, 2008.**

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STANDARD OPERATING PROCEDURE
TestAmerica BURLINGTON

ANALYTICAL METHOD FOR TRACE VOLATILES
CLP SOW SOM01.2

Applicable Matrix: Water

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1.0 SCOPE AND APPLICATION

1.1 This SOP describes the laboratory procedure for the analysis of water samples containing trace concentrations of volatile organic compounds listed in Section 18.0, Table 1. This procedure is specific to the USEPA Contract Laboratory Program (CLP) Statement of Work (SOW) SOM01.2. This method was established by the EPA to analyze for samples collected from drinking water and well/groundwater type sources around Superfund sites.

1.2 This SOP also describes the optional CLP SOW procedure for analysis of compounds using Selected Ion Monitoring (SIM). SIM analysis is specific to target compounds, , 1,2-dibromoethane, and 1,2-dibromo-3-chloropropane.

1.3 The EPA has identified and published in the SOW the following problems associated with some compounds analyzed by this method:

- Chloromethane, vinyl chloride, bromomethane, and chloroethane can display peak broadening if the compounds are not delivered to the GC column in a tight band.
- Acetone, hexanone, 2-butanone, and 4-methyl-2-pentanone have poor purge efficiencies.
- 1,1,1-Trichloroethane and all the dichloroethanes can dehydrohalogenate during storage or analysis.
- Chloromethane can be lost if the purge flow is to fast.
- Bromoform is one of the compounds most likely to be adversely affected by cold spots and/or active sites in the transfer lines. Response of its quantitation ion (m/z 173) is directly affected by the tuning of the GC/MS to meet the instrument performance criteria for 4-bromofluorobenzene at ions m/z 174/176. Increasing the m/z 174/176 ratio may improve bromoform response.
- Due to the lower quantitation limits required by this method, extra caution must be exercised when identifying compounds.

2.0 SUMMARY OF METHOD

2.1 The laboratory performs a full scan analysis using the trace method first. If the SIM compounds are detected at or above the CRQL during the full scan analysis, then SIM analysis should not be performed.

Deuterated monitoring compounds (DMCs) and internal standards (ISTD) are added to each samples and the entire vial is placed in the instrument autosampler. An inert gas is bubbled through a 25 mL aliquot of sample that is placed in a purge and trap chamber maintained at ambient temperature. The purgeable compounds are transferred from the aqueous phase to the vapor phase and swept through a sorbent column where the purgeables are trapped. After purging is complete, the sorbent column is heated and

back flushed with the inert gas and the purgeables are desorbed onto a GC column. The GC is temperature programmed to separate the purgeable compounds that are then detected with a mass spectrometer.

3.0 DEFINITIONS

3.1 See Appendix C for a complete list of definitions.

4.0 INTERFERENCES

4.1 Method interference may be caused by impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory method and instrument blanks. The use of non-Polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

4.2 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during storage and handling. Therefore samples analyzed by this procedure must be stored separately from other laboratory samples and standards and must be analyzed in a room demonstrated to be free from contaminates.

4.3 Contamination by carryover can occur whenever high level and low level samples are sequentially analyzed. To reduce carryover, the purging device and sampling syringe must be rinsed with reagent water between sample analyses. For samples containing large amounts of water-soluble materials, suspended solids, high-boiling compounds, or high purgeable levels, it may be necessary to wash out the purging device with a detergent solution between analyses, rinse it with distilled water, and then dry it in an oven at 105°C. The trap and other parts of the system are also subjected to contamination; therefore, frequent bake out and purging of the entire system may be required.

4.4 The volatile laboratory and preparation area should be completely free of solvents except for methanol.

5.0 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.2 Specific Safety Concerns or Requirements

The toxicity or carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Use reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water.

Safety glasses, gloves and protective clothing must be worn.

5.3 The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform, and vinyl chloride.

5.4 Primary Materials Used

Table 2, Section 18.0 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the Material Safety Data Sheet (MSDS). The table does not include all materials used in the procedure. A complete list of materials used can be found in Section 7.0. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Any questions regarding the safe handling of these materials should be directed to the laboratory's Environmental Health and Safety Coordinator.

6.0 EQUIPMENT AND SUPPLIES

6.1 44mL Borosilicate glass VOA Vials, Teflon-lined septa, QEC or equivalent.

6.2 Syringes: 10 µL-2.5 mL, Hamilton Gastight® or equivalent.

6.3 2 and 4 mL Borosilicate glass vials with Mininert® screw-cap on/off valves, Restek or equivalent.

6.4 Autosampler - EST Centurion or Archon.

6.5 Purge and Trap Device – EST- ENCON, Tekmar- LCS 2000 or Velocity XPT.

Trap Specifications - 25 to 30cm x 2.5mm ID minimum, Supelco VOCARB 3000 (K-type trap), or equivalent.

6.6 GC System - Hewlett Packard 5890 or 6890.

GC Columns - J&W DB624 75m x 0.53mm x 3.0 µm film (jet separator configuration), or DB-624 30m x 0.25mm x 1.4um film for capillary direct configuration

6.7 MS System - Mass Spectrometer: Hewlett-Packard 5971 and 5973.

The MS system must be capable of producing an averaged mass spectrum for the instrument performance check solution that meets the acceptance criteria given in Table 3, Section 18.0.

6.8 Data System

Data Acquisition - ChemStation Version B.01.00

Data Reporting - Target Version 3.5

7.0 REAGENTS AND STANDARDS

7.1 Reagents

Methanol (CH_3OH), purge & trap quality – OmniSolv high purity solvent or equivalent.

VOA-Free Reagent Water: Boil water that has been filtered through the laboratory Milli Q Plus ™ filtration system for one hour then purge with helium for a minimum of one hour.

7.2 Standards

Prepare working standard solutions from stock standard solutions purchased from commercial vendors. See Appendix B for the recommended formulation for the preparation of the following standard solutions. Assign an expiration date to the prepared solutions as specified in the following section. Store the stock standards and primary working standard solutions, except the instrument performance check solution, protected from light at a temperature of –10°C to –20°C. Store the instrument performance check solution (BFB) protected from light at a temperature of 4°C (±2°C). Individual prepared calibration standards may be held for up to 24 hours after time of preparation if they are stored in Teflon sealed screw-cap vials with zero headspace at 4°C (±2°C) and protected from light. Store all standards separately from samples and other chemical materials.

Instrument Performance Check Solution (BFB): The instrument performance check solution consists of 4-Bromofluorobenzene in methanol. Prepare the solution in a volumetric flask using the formulation specified in Appendix B. Assign an expiration date of 6 months from date made unless the expiration date of any parent component is sooner, in which case use the earliest expiration date. For ease of use, aliquots of the prepared standard may be transferred to 2 mL borosilicate glass vials equipped with a Mininert® valve.

SOM Trace Calibration Mix: The trace calibration mix contains the target and DMC compounds listed in Table 1 in methanol. Prepare the calibration mix in a 4 mL borosilicate glass vial with Mininert® valve and assign an expiration date of one month from date made unless the expiration date of any parent component is sooner, in which case use the earliest expiration date. Use the calibration mix to prepare the individual calibration standards and the opening and closing CCV standard.

SOM Internal Standard Spike Mix (ISTD): The ISTD contains 1,4-dichlorobenzene-d_4, chlorobenzene-d_5, and 1,4-difluorobenzene in methanol. Prepare the ISTD in a 4 mL borosilicate glass vial with Mininert® valve. Assign an expiration date of one month from date made unless the expiration date of any parent component is sooner, in which case use the earliest expiration date. Add the ISTD solution to all calibration standards,

blanks, and samples at a final concentration of 5.0 μg/L for Trace analysis and 0.50 μg/L for SIM analysis.

DMC Mix: The DMC MIX contains all compounds listed in Table 4 in methanol. Prepare the DMC MIX in a borosilicate 2 mL glass vial with Mininert® valve. Assign an expiration date of one month from date made unless the expiration date of any parent component is sooner, in which case use the earliest expiration date. Add the DMC MIX to all blanks and samples at a concentration of 5.0 μg/L for each non-ketone DMCs, 50 ug/L for ketone DMCs, (for SIM 0.50 μg/L for each DMCs).

Matrix Spike Mix (MS): The MS contains compounds listed in Table 5 in methanol. Prepare the MS in a 4 mL borosilicate glass vial with Mininert® valve. Assign an expiration date of one month from date made unless the expiration date of any parent component is sooner, in which case use the earliest expiration date. Add the MS spike to each MS/MSD samples at a concentration of 5.0 μg/L.

Initial Calibration and Continuing Calibration Verification (CCV) Standards: The initial calibration standards are prepared in 44 mL VOA vials using the trace calibration mix and VOA-free reagent water. Prepare five initial calibration standards containing all of the target compounds and DMCs at the following concentrations: all non-Ketone targets and associated DMCs at 0.5, 1.0, 5.0, 10, and 20 μg/L; all ketones and associated DMCs at 5.0, 10, 50, 100, and 200 μg/L;. Note that the m plus p-Xylene isomers total 0.50, 1.0, 5.0, 10, and 20 μg/L. Add ISTD to each calibration point at a concentration of 5.0 μg/L. See Appendix A for a table that summarizes the preparation information.

If analysis by the SIM technique is required, prepare calibration standards for 1,2-dibromoethane and 1,2-dibromo-3-chloropropane and their associated DMCs at concentrations of 0.050, 0.10, 0.50, 1.0 and 2.0 μg/L. Add ISTD to each calibration point at a concentration of 0.50 μg/L. See Appendix A for a table that summarizes the preparation information.

Prepare the opening and closing CCV for both trace and SIM analysis at the concentration of the mid-point calibration standard (CAL Level 3) in 44 mL borosilicate glass vials. See Appendix A for a table that summarizes the preparation information.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 Sample Collection

The laboratory does not perform sample collection thus these procedures are not applicable to this SOP. The sample collection procedure should be in accordance with the Analytical Method for the Analysis of Trace Concentrations of Volatile Organic Compounds, Exhibit D, USEPA Contract Laboratory Program Statement of Work for Organic Analysis, SOM01.2. The laboratory will provide at client request, pre-certified, pre-preserved sample collection containers, which may be shipped directly to the sampling site.

8.2 Sample Storage & Retention Requirements

Store samples that are assigned to an SDG together in the same refrigerator maintained at a temperature of 4°C (±2) with a laboratory-prepared aqueous storage blank that will be subsequently analyzed to assess for potential contamination that could occur during laboratory storage.

To prepare the storage blank, on receipt of the first samples from a Sample Delivery Group (SDG), fill two 44 mL screw cap VOA vials with VOA-free water and place the storage blanks with the with samples from the associated SDG in a refrigerator dedicated to the storage of VOA vials and maintained at a temperature of 4ºC (±2).

Unless otherwise specified by the laboratory Project Manager, hold the samples and subsequent extracts from the time of receipt until 30 days after delivery of a complete, reconciled data package. After 30 days, dispose of any unused portions of the samples in a manner that complies with applicable regulations.

8.3 Contract Required Holding Times

The contract required holding time for analysis of water samples is 10 days from Validated Time of Sample Receipt (VTSR).

9.0 QUALITY CONTROL

9.1 Blanks

A method blank, storage blank and instrument blank(s) are prepared and analyzed to determine the level of contamination that may be associated with sample processing and analysis (method blank), sample storage (storage blank) or carryover from analysis of a previous sample (instrument blank).

The frequency requirements for analysis and criteria are summarized as follows:

Method Blank: A method blank is analyzed at least once in every 12 hour time period on each instrument used for analysis. See Section 10.2 for a definition of the 12-hour time period. The method blank must be analyzed after the CCV and before analysis of any samples or storage blanks. If samples are analyzed in the same sequence as initial calibration, the method blank must be analyzed immediately after the calibration.

Storage Blank: The storage blank is analyzed after all samples in the SDG have been analyzed.

Instrument Blank: Instrument blanks are analyzed when necessary, to prevent carryover or to clean the instrument after the analysis of samples with high target or TIC concentrations.

Blank Acceptance Criteria:

1) Each blank must be analyzed on a GC/MS system that has met criteria for the instrument performance check and initial and continuing calibration.

2) The recovery of the DMCs in the blanks must meet the acceptance recovery criteria found in Table 4, Section 18.0.

3) The percent area response change for each of the internal standards must be within the inclusive range of 60 to 140 percent of its response in the most recent continuing calibration standard analysis.

4) The retention time shift for each of the internal standards must be within ±0.33 minutes of its retention time in the most recent continuing calibration standard analysis.

5) The concentration of each target compound in the method blank and storage blank must be less than the CRQL except for methylene chloride, acetone, and 2-butanone which must be less than 2 times the CRQL. The concentration of each target compound in the instrument blank must be less than the CRQL.

6) Additionally the CLP SOW requires that the concentration of non-target compounds in all blanks must be less than 2.0 ug/L. However the laboratory has found that the DMC stock standard solution commercially available contains non-target compounds, or contaminates, at concentrations exceeding the maximum allowed concentration of 2 ug/L. Until the laboratory is able to obtain a DMC stock standard solution that is free of contaminates, the laboratory identifies the non-target compounds in blanks as unknown TICs and flags with a “X” qualifier in the data package. The laboratory may also use the “X” qualifier to identify siloxanes (column bleed) found in the blank.

Any method blank that does not meet criteria must be reanalyzed along with all associated samples. Any instrument blank that does not meet criteria requires reanalysis of the samples following the instrument blank that have any target compounds detected above the CRQL. Any storage blank that does not meet criteria must be reanalyzed. If the storage blank contains target compounds above the CRQL, reanalyze to determine if the contamination occurred during storage or if the problem occurred during the analysis. If upon reanalysis, the storage blank meets criteria, then only the results of reanalysis are reported. If after reanalysis, the storage blank still does not meet criteria, the problem is documented in the case narrative along with corrective or preventive actions taken to prevent recurrence.

9.2 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

MS/MSD are performed when requested by the client. MS/MSD are processed and analyzed in the same manner as field samples and at the same concentration as the most concentrated aliquot from which the parent sample analysis is reported. MS/MSD may not be diluted to get either the spiked or non-spiked analytes within calibration range. Additionally, MS/MSD must not be performed on field, trip or rinsate blank samples.

Acceptance Criteria for MS/MSD Analysis

1) Each MS/MSD must be analyzed on a GC/MS system that has met criteria for the instrument performance check and initial and continuing calibration.

2) Each MS/MSD must be analyzed within the contract holding time.

3) The RT shift for each internal standard in the MS/MSD must be within ±0.33 minutes of the retention times for the internal standards found in the most recent CCV analysis.

4) The accuracy and precision of the MS/MSD should be within the limits given in Table 5, Section 18.0. These control limits are advisory and no further action is required unless it is determined that the frequency of failure is indicative of a systematic problem requiring investigation.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Instrument Operation Conditions

Purge and Trap Conditions
Configure the purge and trap using the following conditions. Parameters may be optimized as long as the same conditions are used for all standards, samples, and blanks.

Purge Gas: UHP Helium
Purge Flow: ~40 mL/min
Purge Temperature: Ambient
Purge Time: 11.5 min
Dry Purge Time: 0.5 min
Desorb Preheat Temperature: 250°C
Desorb Temperature: 260°C
Desorb Time 4.0 min
Bake Temperature 270°C
Bake Time 2.5 min
P&T Transfer Line Temperature: 110 °C
P&T Valve Temperature: 110 °C

GC Conditions
The following conditions are recommended and may be optimized as long as the same conditions are used for all standards, samples, and blanks.

Injection Port:	150°C
Jet Separator:	180°C
MS Transfer Line:	250°C

Temperature Program
Jet Separator:
40°C for 4.4 minutes
12.5°C/min to 165°C
30°C/min to 220°C for 4.47 minutes

Capillary Direct:
9 °C/min to100°C
35°C/min to 240°C

Mass Spectrometer Conditions
Electron Energy: 70 eV nominal
Mass Range: 35-300 amu
Ionization Mode: Electron Impact (EI)
Scan Time: >1 scan/sec

10.2 Instrument Performance Check (BFB)

Check the mass calibration of the system at the beginning of each 12-hour period during which samples or standards are analyzed with a BFB tune standard, except for SIM analysis, which does not require analysis of the instrument performance check standard. The injection time of the acceptable BFB starts the 12-hour analysis window. Within this time period, the analysis of all calibration standards, blanks, and samples must occur. All subsequent standards, samples and QC items associated with a BFB analysis must use the same GC/MS conditions used to acquire the BFB, with the exception of the temperature program. If the closing CCV standard for an analytical sequence meets the acceptance criteria of an opening CCV (see Table 6), then another 12-hour analytical period may begin without the injection of a BFB performance check sample. The new 12-hour analytical period starts at the moment of injection of the passing closing CCV.

To perform the instrument performance check, prepare the 25 ug/mL instrument performance check solution (BFB) and inject 2 uL of BFB standard onto the instrument system to yield an on-column concentration of 50 ug/mL and acquire the data.

The data system acquires the data such that three scans (the peak apex and the scans immediately preceding and following the apex) are acquired and averaged. The data system performs background subtraction using a single scan no more than 20 scans prior to the peak apex but no part of the BFB peak is background subtracted.

Check the results of the BFB analysis against the ion abundance criteria specified in Table 3, Section 18.0. The criteria must be met prior to further analysis. If criteria are not met, perform necessary corrective actions and repeat the instrument performance check. Criteria for the BFB must be met prior to subsequent analysis.

10.3 Initial Calibration

After successful analysis of the instrument performance check standard, calibrate the

instrument with a minimum of five concentration levels. Each calibration level must include all target compounds, DMCs and internal standards. If SIM is to be performed, perform a separate calibration with a minimum of five concentration levels that include target compounds, DMCs and internal standards.

Prepare the calibration standards using the formulations specified in Appendix A. Allow the standards to warm to room temperature then load the calibration standard vials into the autosampler, begin the analytical sequence and acquire the data.

The data system calculates the relative response factor (RRF), the percent relative standard deviation (%RSD), and the mean RRF for each target and system-monitoring compound over the working range of the curve. The primary characteristic ions used for quantification are given in Table 1 along with the internal standard assignments. If interference prevents use of the primary quantification ion, the secondary ion given in Table 1 may be used. Because the m- and p-xylene isomers co-elute, a single RRF for m- and p-xylene is calculated using the area response for that peak and the appropriate concentration. Equations for these calculations can be found in Appendix. B.

The following technical acceptance criteria should be met before further analysis. If it is not, investigate the source of the problem, perform instrument maintenance and recalibrate if necessary.

- The RRF at each calibration level for each target compound should be greater than or equal to the compound's minimum acceptable response factor given in Table 6.
- The %RSD for each target compound should be less than or equal to the value given in Table 6.
- Up to 2 target compounds and DMCs may fail to meet the minimum RRF criteria and the maximum %RSD criteria and still be acceptable as long as these compounds have a minimum RRF greater than or equal to 0.010 and a %RSD of less than or equal to 40.0%.

10.4 Continuing Calibration Verification (CCV)

Each day of analysis analyze an opening CCV after the instrument performance check standard, unless when samples are analyzed in the same 12-hour window as initial calibration, in which case, an opening CCV is not required. Analyze a closing CCV after all samples and blanks have been analyzed and before the end of the 12-hour window.

The 12-hour analytical window begins at the injection time of the instrument performance check standard (BFB) except when a closing CCV meets the criteria of an opening CCV in which case, analysis of a BFB is not required and the injection time of the closing CCV initiates the new 12-hour window. In those instances where the closing CCV does not meet criteria for an opening CCV, the analysis of the BFB followed by an opening CCV is required and the 12-hour analytical window begins as the injection time of the BFB.

Prepare a calibration standard at the mid level concentration (ICAL Level 3) and analyze

the standard using the same instrument conditions as used for the initial calibration.

The data system calculates the RRF for each target and DMC using the primary characteristic ions found in Table 1 and Table 3. For the internal standards, the primary ion is used unless interference is present. If interference is evident, the secondary ion(s) is used. The data system also calculates the %D between the continuing calibration RRF and the most recent initial calibration mean RRF for each target and DMC. The equations for the above calculations can be found in Appendix B.

The opening and closing CCVs must meet the following criteria:

1) The RRF for each target compound and DMC in the opening CCV must be greater than or equal to the compound's minimum acceptable response factor given in Table 6. For closing CCVs the RRF for each compound must be at least 0.010.

2) For the opening CCV the percent difference for each target compound and DMC listed in Table 6 should be less than or equal to the value given. For the closing CCV, the percent difference of the RRF must be inclusive ±50%.

   In the opening CCV up to 2 compounds may fail the RRF and %RSD criteria listed above, but these compounds must have a minimum RRF greater than or equal to 0.010 and the %D must be less than or equal to ±40%.

3) Excluding ions present in the solvent front (carbon dioxide), no quantification ion may saturate the detector.

If the opening CCV criteria cannot be met, recalibrate the instrument. If closing criteria cannot be met, reanalyze all samples and blanks analyzed within that 12-hour window.

10.5 General System Routine Maintenance and Troubleshooting

Perform the following routine maintenance as needed:

- Clean the injection port and liner
- Change the septa
- Cut 2 to 3 inches off the column
- Fill autosampler rinse vials
- Clean mount and purge vessel
- Check purge flow

Perform the following troubleshooting steps for each specific instrument condition.

<u>BFB Failure</u>
1. Shoot a 2nd BFB.
2. If the 2nd BFB fails evaluate the GC and perform column and or injection port maintenance as needed. Shoot another BFB.
3. If GC maintenance does not work evaluate and adjust the BFB parameters until the BFB passes.

Calibration Linearity Fails Criteria
1. Evaluate the RF summary for the ICAL to determine the reason for the failure.
2. Reprep and reacquire an additional calibration point if one point is different from all others.
3. If the additional calibration point does not fix the linearity perform routine GC maintenance.
4. If GC maintenance does not work to provide passing linearity evaluate standards and reprep if necessary.
5. Retune and begin to acquire another ICAL.
6. Evaluate the failing compound using a different curve fit such as linear regression.

Calibration Fails Minimum Response
1. Evaluate the integrity of the standards and reprep if necessary.
2. Evaluate GC performance and perform routine GC maintenance if necessary.
3. Evaluate MS sensitivity and increase instrumental sensitivity through tuning of the MS.

Calibration Fails RT Drift
1. Look for a leak or a plug in the GC and repair.
2. Recheck all flows to determine if any have changed.

Opening/Closing Standard Fails Linearity
1. Reanalyze a second CCV and reevaluate.
2. If reanalyzing does not work, perform routine GC and injection port maintenance.
3. If maintenance does not fix the failure then evaluate standards and recalibrate.
4. Reanalyze any samples affected by the failure.

Opening/Closing Standard Fails RT Drift
1. Look for a leak or a plug in the GC and repair.
2. Recheck all flows to determine if any have changed.
3. Reanalyze any samples affected by the failure.

Instrument Contamination
1. Check for the source of the contamination by running blank tests.
2. Remove the source of contamination once it is isolated.
3. Reanalyze blanks to prove contamination has disappeared.

Sample RTs Drift/Sensitivity
1. Evaluate the entire window to see if it appears isolated to a particular sample or to the entire window.
2. If it is sample related, evaluate the sample matrix.
3. If it is instrumental, evaluate the GC for a leak or a plug and repair.
4. Reanalyze any affected samples.

11.0 PROCEDURE

11.1 Screen Analysis

The laboratory may screen samples prior to analysis following the procedures given in SOP LM-MV-3810 *VOA Screen Analysis*. The results of screen analysis are used to determine if the concentration of any target compound exceeds the calibration range or to determine if there is interference that may hinder quantification. Despite the screen result, the CLP SOW requires that an original undiluted analysis be made and reported for all samples.

When the laboratory suspects or has evidence of a high concentration sample for target or non-target compounds, for EPA contract work, the laboratory must contact the project administrator (SMO) for further instruction. For non-EPA contract work, the laboratory should seek approval from the client to proceed with an original diluted analysis in lieu of original undiluted analysis.

11.2 pH determination

Measure and record the pH for each water sample. If the pH measurement of the sample is >2, initiate a nonconformance report and notify the laboratory Project Manager. Do not adjust the pH of any sample.

11.3 Sample Preparation & Analysis

Allow the samples to warm to ambient temperature. Using a gas-tight syringe add a sufficient amount of the internal standard (ISTD) and DMC standards through the septa cap of each vial. Add the appropriate spike volume to each MS/MSD. See the sample preparation table in Appendix A for the volume of standard solution to add to each sample type.

To prepare the method blank and instrument blanks, fill a 44 mL vial with VOA free water and add a sufficient amount of the internal standard (ISTD) and DMC standards through the septa cap of each vial. See the sample preparation table in Appendix A for spike solution volumes.

To prepare the storage blank, allow the blank to warm to ambient temperature. Using a gas-tight syringe add a sufficient amount of the internal standard (ISTD) and DMC standards through the septa cap of each vial. See sample preparation table in Appendix A for the volume of standard solution to add to each sample type.

Place the sample vials in the autosampler. Create the data acquisition sequence table on the data system, include the necessary sample information and initiate the data collection sequence. Initiate the autosampler sequence and acquire the data.

11.4 Sample Dilutions

If the peak response for any target compound exceeds the calibration range, an approximate dilution factor should be determined and the sample re-analyzed. Use the results of the undiluted sample and/or the screen analysis to determine the dilution factor to keep the concentration of target compound(s) within the upper half of the

calibration range.

Perform the dilution by transferring the appropriate aliquot of sample into a 44 mL VOA vial and adding the appropriate amount of reagent water so that no headspace remains in the sample vial. Prepare and analyze the sample as described in the previous section.

11.5 Target Compound Identification

The data system identifies target compounds using their mass spectra and comparing the sample mass spectrum to the mass spectrum of the standard of the suspected compound. The elution of the sample component must be at the same GC relative retention time as the standard component and there must be correspondence of the sample component and standard component mass spectra.

For correspondence, the sample component RRT should compare within ±0.06 RRT of the RRT of the CCV or the mid-point of the initial calibration that was analyzed within the same 12-hour window as the sample. If interference prohibits assignment, assign the RRT by using extracted ion current profiles for the ions unique to the target compound. For comparison of mass spectra, use the mass spectra obtained for the daily calibration standard for identification purposes provided that the instrument met the acceptance criteria for the BFB.

The requirements for qualitative verification by comparison of mass spectra are as follows:

- All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must to be present in the sample spectrum.

- The relative intensities of these ions must agree within ±20% between the standard and sample spectra.

- Ions greater than 10% in the sample spectrum but not present in the standard spectrum are considered and accounted for by the analyst making the comparison.

The data system determines the concentration of target compounds by using the water sample concentration calculation found in Appendix B.

The following criteria should be met for each sample analysis:

- The sample must be acquired on an instrumentation that has met all of the GC/MS tune, calibration, and blank acceptance criteria as defined in Sections 9 and 10.

- All samples and subsequent required dilutions must be analyzed within the contract holding time.

- The area response of the internal standards of the sample must be within 60% to

140% of the response of the internal standards in the most recent opening CCV.

- The retention time shift for each of the internal standard should be within ±0.33 minutes between the sample and the most recent opening CCV.

- The percent recovery for each DMC must be within the acceptance limits found in Table 4. Up to three DMCs may fail to meet the acceptance criteria listed in Table 4.

- Excluding ions in the solvent front (carbon dioxide), no ion may saturate the detector.

- It must be demonstrated that the sample analyses are free of carryover from a previously analyzed contaminated sample whose target compound response exceeds the calibrated range.

Secondary ion quantification may only be performed when there are sample matrix related interferences with the primary ion. Calculate the RRF using the area response from the most intense secondary ion free of interferences. Document the reason in the project narrative.

If any of the system monitoring or internal standard compounds fail to meet RT or recovery acceptance criteria, investigate for error. If instrument or calculation errors are found, correct the problem and re-analyze and/or recalibrate as necessary. If it is suspected that the problem is due to matrix effect, re-analyze the sample. If the results of re-analysis are within control, submit only that analysis. Otherwise provide both sets of data using R1/RE designations for the re-analysis. A failing sample with an associated MS/MSD pair is considered confirmed if failures are consistent in all three analyses.

In those instances were the automated processing system fails to accurately integrate quantification ion EICPs due to matrix interference, co-elution, and/or baseline noise, perform manual integrations. Manually integrate the peak such that it accurately defines the peak without under or over estimation of the absolute area attributable to that component peak. Include EICP printouts that display the compound peak before and after manual integration with raw data. Generate and include the manual integration summary report identifying all samples with manual integrations and signed and dated by the primary person performing manual integrations and the secondary person reviewing all manual integrations. For additional guidance regarding Manual Integration, refer to laboratory SOP LP-LB-0006 *Manual Integration*.

11.6 Non-Target Compound Identification

Identification of non-target compounds or TICs is not possible using the SIM analysis. SIM data acquisition precludes the collection of mass information necessary for the spectral identification of non-target analytes.

For Trace analysis, perform a library search using the NIST spectral library to tentatively identify up to 30 non-target, non-alkane organic compounds of greatest apparent

concentration excluding the system monitoring and internal standards compounds. Assign tentative identification based on mass spectral interpretation.

Do not report the following:

- Substances with responses less than 10 percent of the internal standard.
- Substances that elute earlier than 30 seconds before the first purgeable compound or three minutes after the last purgeable compound.
- Carbon dioxide.
- Semivolatile compounds

TIC peaks that are suspected to be straight chain, branched, or cyclic alkanes must be searched and documentation of the search supplied in the data report. Alkanes are not considered as part of the 30 compound search described earlier. Straight-chain, branched or cyclic alkanes are automatically tabulated and reported as 'total alkanes" on the Form 1 VOA-TIC. When these alkanes are tentatively identified, the concentrations are considered estimated and reported in the project narrative as alkanes by class.

Determine the estimated concentrations for non-target compounds by the internal standard method using the same equations specified for target compounds using an assumed RRF of 1. Qualify the resulting concentrations with a "J" and "N" data flag to indicate the concentration is estimated and that there are qualitative and quantitative uncertainties associated with the result.

The following guidelines should be used for making tentative identification:

- If the library search quality match is 85% or better the peak should be reported using the identification generated by the search routine, unless the mass spectral interpretation specialist feels there is just evidence not to report that identification.
- If the library produces more than one match at or above 85%, report the highest match, or first match if they are the same, unless the mass spectral interpretation specialist feels there is just evidence not to report that identification.
- If the library produces multiple matches at or above 85% (e.g. multiple isomers of a PCB), report the highest match, or first match if they are the same, unless the mass spectral interpretation specialist feels there is just evidence not to report that identification.
- If the mass spectral interpretation specialist has just evidence to support reporting a compound with a tentative identification other than the library selection (with 85% quality match or better) detail the justification in the SDG case narrative.
- If the library search produces no matches at or above 85% quality, the mass spectral interpretation specialist should attempt (where possible) to make a tentative

identification of the compound, or its class (e.g. alcohol, chlorinated, etc). Otherwise, the compound should be reported as an "Unknown".

12.0 CALCULATIONS

See Appendix B.

13.0 DATA ASSESSMENT, CRITERIA AND CORRECTIVE ACTION

Review all samples, standards, and QC samples against the acceptance criteria provided in this SOP. Generate target reports and forms using SOM01-CLP form set and arrange the volatile data following the requirements specified in the Table 7.0. Arrange SIM data separately at the end of the volatile subsection. If the results do not fall within the criteria, perform corrective action. If corrective action is not taken, or is unsuccessful, document the situation with a nonconformance report (NCR) and qualify the data using an appropriate data qualifier. For additional guidance regarding the laboratory's protocol and required elements for each level of data review (primary, secondary, and tertiary) refer to laboratory SOP LP-QA-003 *Data Review*. Submit VOA data package to Report Management for assimilation into the hardcopy data deliverable.

14.0 METHOD PERFORMANCE

A Method Detection Limit (MDL) must be determined on each instrument used for analysis for each matrix prior to initial use of the method. The MDLs are then verified annually with an MDL Verification Check sample that is subject to the same extraction and cleanup procedures as used for field samples. Some regulatory programs may require that the MDL study be repeated annually but this is not a requirement of the CLP SOW. The procedure and acceptance criteria for MDL studies and MDL verification are given in laboratory SOP LP-QA-005 *Method Detection Limits.*

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

All waste will be disposed of in accordance with Federal, State, and Local regulations. Where reasonably feasible technological changes have been implemented to minimize the potential for pollution of the environment. Employees must abide the pollution prevention and waste management procedure described in this SOP and the policies for "Waste Management and Pollution Prevention" given in Section 13 of the Corporate Safety Manual.

15.1 Waste Streams Produced by the Method

The following waste streams are produced from this procedure:

1) Acid Preserved Water Samples & Glass Vials
   Satellite Waste Container: 5 Gallon Plastic Bucket labeled "CORROSIVE"

Transfer the waste stream(s) to the appropriate satellite waste container(s) located in your work area. Notify the Environmental Health & Safety (EHS) Coordinator when the satellite container is near full. The EHS Coordinator will make arrangements for authorized personnel to transfer the waste to the waste management room for subsequent disposal. See laboratory SOP LP-LB-001 *Hazardous Waste* for additional information regarding waste management and disposal procedures.

16.0 REVISION HISTORY

16.1 This is the first version of this SOP.

17.0 REFERENCES

17.1 Exhibit D, Analytical Methods for the Analysis of Trace Concentrations of Volatile Organic Compounds, USEPA CLP SOW for Organic Analysis, SOM01.1, May 2005.

17.2 USEPA CLP SOW Clarifications to SOM01.1, November 7, 2005 and September 26, 2006.

17.3 USEPA CLP SOW Modifications Updating SOM01.1 to SOM01.2, October 5, 2006 (Updated 02-12-2007) Amended 04-11-2006.

18.0 TABLES, DIAGRAMS & FLOWCHARTS

18.1 Table 1: Target Compound List, Internal Standard Group Assignments, CRQLs, and Quantification and Qualifier Masses
18.2 Table 2: Primary Materials Used
18.3 Table 3: BFB Criteria
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18.5 Table 5: Matrix Spike Recovery, Accuracy, and Precision Limits (Advisory)
18.6 Table 6: Calibration Criteria
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18.9 Appendix B: Equations
18.10 Appendix C: Terms and Definitions

Table 1: Target Compound List, Internal Standard Assignments, CRQLs, and Quantification Ions

Compound	ISTD Group*	Trace CRQL µg/L	SIM CRQL µg/L	MZ1**	MZ2	MZ3
Dichlorodifluoromethane	1	0.5		85	87	
Chloromethane	1	0.5		50	52	
Vinyl chloride	1	0.5		62	64	
Bromomethane	1	0.5		94	96	
Chloroethane	1	0.5		64	66	
Trichlorofluoromethane	1	0.5		101	103	
1,1-Dichloroethene	1	0.5		96	61	63
1,1,2-Trichloro-1,2,2-trifluoroethane	1	0.5		101	85	151
Acetone	1	5.0		43	58	
Carbon disulfide	1	0.5		76	78	
Methyl acetate	1	0.5		43	74	
Methylene chloride	1	0.5		84	49	86
trans-1,2-Dichloroethene	1	0.5		96	61	98
Methyl-t-butyl ether	1	0.5		73	57	43
1,1-Dichloroethane	1	0.5		63	65	83
cis-1,2-Dichloroethene	1	0.5		96	61	98
2-Butanone	1	5.0		43***	72	
Bromochloromethane	1	0.5		128	49	130
Chloroform	1	0.5		83	85	
1,1,1-Trichloroethane	2	0.5		97	99	61
Carbon tetrachloride	2	0.5		117	119	
Cyclohexane	2	0.5		56	69	84
Benzene	2	0.5		78		
1,2-Dichloroethane	1	0.5		62	98	
Trichloroethene	2	0.5		95	130	132
Methylcyclohexane	2	0.5		83	55	98
1,2-Dichloropropane	2	0.5		63	112	
Bromodichloromethane	2	0.5		83	85	127
cis-1,3-Dichloropropene	2	0.5		75	77	
4-Methyl-2-pentanone	2	5.0		43	58	100
Toluene	2	0.5		91	92	
trans-1,3-Dichloropropene	2	0.5		75	77	
1,1,2-Trichloroethane	2	0.5		97	83	85
Tetrachloroethene	2	0.5		164	166	129
2-Hexanone	2	5.0		43	58	57
Dibromochloromethane	2	0.5		129	127	
1,2-Dibromoethane	2	0.5	0.050	107	109	188
Chlorobenzene	2	0.5		112	114	77

Compound	ISTD Group*	Trace CRQL µg/L	SIM CRQL µg/L	MZ1**	MZ2	MZ3
Ethylbenzene	2	0.5		91	106	
M,p-Xylene	2	0.5		106	91	
o-Xylene	2	0.5		106	91	
Styrene	2	0.5		104	78	
Bromoform	3	0.5		173	175	254
Isopropylbenzene	2	0.5		105	120	77
1,1,2,2-Tetrachloroethane	2	0.5		83	85	131
1,3-Dichlorobenzene	3	0.5		146	111	148
1,4-Dichlorobenzene	3	0.5		146	111	148
1,2-Dichlorobenzene	3	0.5		146	111	148
1,2-Dibromo-3-chloropropane	3	0.5	0.050	75	155	157
1,2,4-Trichlorobenzene	3	0.5		180	182	145
1,2,3-Trichlorobenzene	3	0.5		180	182	145

*ISTD 1 – 1,4-Difluorobenzene
ISTD 2 – Chlorobenzene-d_5
ISTD 3 – 1,4-Dichlorobenzene-d_4
** Denotes quantification mass
***m/z 43 is used for quantitation of 2-Butanone, but m/z 72 must be present for positive identification.

Table 2: Primary Materials Used

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Table 3: BFB Criteria

Mass	Ion Abundance Criteria
50	15.0-40.0% of mass 95
75	30.0-80.0% of mass 95
95	base peak, 100% relative abundance
96	5.0-9.0% of mass 95*
173	less than 2.0% of mass 174
174	50.0-120.0% of mass 95
175	5.0-9.0% of mass 174
176	95.0-101.0% of mass 174
177	5.0-9.0% of mass 176

*****All ion abundances must be normalized to m/z 95, the nominal bas peak, even though the ion abundance of m/z 174 may be up to 120% that of m/z 95

Table 4: DMC Quantification and Qualifier Masses,
Internal Standard Group Assignment and Recovery Limits

DMC	MZ1	MZ2	MZ3	ISTD Group**	Lower Limit	Upper Limit
Vinyl chloride-d3	65	67		1	65	131
Chloroethane-d5	69	71	51	1	71	131
1,1-Dichloroethene-d2	63	98	65	1	55	104
2-Butanone-d5	46	71		1	49	155
Chloroform-d	84	86	47	1	78	121
Benzene-d6	84	82		2	77	124
1,2-Dichloroethane-d4	65	67	51	1	78	129
1,2-Dichloropropane-d6	67	65	46	2	79	124
Toluene-d8	98	100	42	2	77	121
trans-1,3-Dichloropropene-d4	79	81	42	2	73	121
2-Hexanone-d5	63	46		2	28	135
1,1,2,2-Tetrachloroethane-d2	84	86		2	73	125
1,2-Dichlorobenzene-d4	152	150		3	80	131

** ISTD 1 – 1,4-Difluorobenzene, ISTD 2 – Chlorobenzene-d_5, ISTD 3 – 1,4-Dichlorobenzene-d_4

Table 5: Matrix Spike Recovery Limits and
Accuracy and Precision Limits (Advisory)

MS Compound	Lower	Upper	RPD
1,1-Dichloroethene	61	145	0-14
Benzene	76	127	0-11
Trichloroethene	71	120	0-14
Toluene	76	125	0-13
Chlorobenzene	75	130	0-13

Table 6: Calibration Criteria

Compound	Maximum %RSD ICAL	Minimum RRF ICAL & Opening CCV	Maximum %D Opening CCV	Minimum RRF Closing CCV	Maximum %D Closing CCV
Dichlorodifluoromethane	40	0.010	40	0.010	50
Chloromethane	40	0.010	40	0.010	50
Vinyl chloride	30	0.100	30	0.010	50
Bromomethane	30	0.100	30	0.010	50
Chloroethane	40	0.010	40	0.010	50
Trichlorofluoromethane	40	0.010	40	0.010	50
1,1-Dichloroethene	30	0.100	30	0.010	50
1,1,2-Trichloro-1,2,2-trifluoroethane	40	0.010	40	0.010	50
Acetone	40	0.010	40	0.010	50
Carbon disulfide	40	0.010	40	0.010	50
Methyl acetate	40	0.010	40	0.010	50
Methylene chloride	40	0.010	40	0.010	50
trans-1,2-Dichloroethene	40	0.010	40	0.010	50
Methyl-t-butyl ether	40	0.010	40	0.010	50
1,1-Dichloroethane	30	0.200	30	0.010	50
cis-1,2-Dichloroethene	40	0.010	40	0.010	50
2-Butanone	40	0.010	40	0.010	50
Bromochloromethane	30	0.050	30	0.010	50
Chloroform	30	0.200	30	0.010	50
1,1,1-Trichloroethane	30	0.100	30	0.010	50
Carbon tetrachloride	30	0.100	30	0.010	50
Cyclohexane	40	0.010	40	0.010	50
Benzene	30	0.400	30	0.010	50
1,2-Dichloroethane	30	0.100	30	0.010	50
Trichloroethene	30	0.300	30	0.010	50
Methylcyclohexane	40	0.010	40	0.010	50
1,2-Dichloropropane	40	0.010	40	0.010	50
Bromodichloromethane	30	0.200	30	0.010	50
cis-1,3-Dichloropropene	30	0.200	30	0.010	50
4-Methyl-2-pentanone	40	0.010	40	0.010	50
Toluene	30	0.400	30	0.010	50
trans-1,3-Dichloropropene	30	0.100	30	0.010	50
1,1,2-Trichloroethane	30	0.100	30	0.010	50
Tetrachloroethene	30	0.100	30	0.010	50

Compound	Maximum %RSD ICAL	Minimum RRF ICAL & Opening CCV	Maximum %D Opening CCV	Minimum RRF Closing CCV	Maximum %D Closing CCV
2-Hexanone	40	0.010	40	0.010	50
Dibromochloromethane	30	0.100	30	0.010	50
1,2-Dibromoethane	30	0.010	40	0.010	50
Chlorobenzene	30	0.500	30	0.010	50
Ethylbenzene	30	0.100	30	0.010	50
m,p-Xylene	30	0.300	30	0.010	50
o-Xylene	30	0.300	30	0.010	50
Styrene	30	0.300	30	0.010	50
Bromoform	30	0.050	30	0.010	50
Isopropylbenzene	40	0.010	40	0.010	50
1,1,2,2-Tetrachloroethane	30	0.100	30	0.010	50
1,3-Dichlorobenzene	30	0.400	30	0.010	50
1,4-Dichlorobenzene	30	0.400	30	0.010	50
1,2-Dichlorobenzene	30	0.400	30	0.010	50
1,2-Dibromo-3-chloropropane	40	0.010	40	0.010	50
1,2,4-Trichlorobenzene	30	0.200	30	0.010	50
1,2,3-Trichlorobenzene	30	0.200	30	0.010	50
Vinyl Chloride-d3	30	0.010	30	0.010	50
Chloroethane-d5	40	0.010	40	0.010	50
1,1-Dichloroethene-d2	30	0.010	30	0.010	50
2-Butanone-d5	40	0.010	40	0.010	50
Chloroform-d	30	0.010	30	0.010	50
Benzene-d6	30	0.010	30	0.010	50
1,2-Dichloroethane-d4	30	0.010	30	0.010	50
1,2-Dichloropropane-d6	40	0.010	40	0.010	50
Toluene-d8	30	0.010	30	0.010	50
trans-1,3-Dichloropropene-d4	30	0.010	30	0.010	50
2-Hexanone-d5	40	0.010	40	0.010	50
1,1,2,2-Tetrachloroethane-d2	30	0.010	30	0.010	50
1,2-Dichlorobenzene-d4	30	0.010	30	0.010	50

Table 7: Volatiles Raw Data and Forms Reporting Order

Section	Order of Forms and Raw Data Required
Quality Control (QC) Summary	Dueterated Monitoring Compound (DMC) Recovery (Form II VOA-1, VOA-2, VOA-3, VOA-4 or VOA-SIM1, VOA-SIM2)
	Matrix Spike/Matrix Spike Duplicate Recovery (Form III VOA-1, VOA-2). *Not required for SIM analysis.*
	Method Blank Summary (Form IV VOA, VOA - SIM). *Forms arranged in chronological order by data of analysis of method blank and by instrument.*
	GC/MS Instrument Performance Check (Form V VOA). *Forms arranged in chronological order by instrument.*
	Internal Standard Area and RT Summary (Form VIII VOA, VOA-SIM). *Forms arranged in chronological order by instrument.*
Supportive Documentation	Arrange sample data forms and raw data in the following order of increasing EPA sample number, considering both letters and numbers 1. Target Compound Results (Form I VOA-1, VOA-2) followed by Tentatively Identified Compounds (Form I VOA-TIC). 2. Reconstructed Total Ion Chromatogram 3. Quantitation reports of raw data 4. Copies of the compound spectra. 5. Copies of mass spectra for each TIC. 6. EICP of quantitation ion displaying compound peak before and after manual integrations.
Standard Data	Arrange forms and raw data of standards in the following order; calibration standards by instrument in chronological order followed by the opening and closing standards by instrument in chronological order. 1. Target Compound Results (Form VI VOA-1, VOA-2, VOA-3, VOA-SIM) 2. Reconstructed Total Ion Chromatogram 3. Quantitation reports of raw data 4. Copies of the compound spectra. 5. Copies of mass spectra for each TIC. 6. EICP of quantitation ion displaying compound peak before and after manual integrations.
Raw QC Data	Instrument Performance Check (Form V VOA) in chronological order by instrument
	Arrange forms and raw data for blanks by blank type and in chronological order by instrument. 1. Target Compound Results (Form I VOA-1, VOA-2) followed by Tentatively Identified Compounds (Form I VOA-TIC). 2. Reconstructed Total Ion Chromatogram

Section	Order of Forms and Raw Data Required
	3. Quantitation reports of raw data 4. Copies of the compound spectra. 5. Copies of mass spectra for each TIC. 6. EICP of quantitation ion displaying compound peak before and after manual integrations.
	Arrange MS/MSD forms and raw data in the following order of increasing EPA sample number, considering both letters and numbers. *Not required for SIM analysis*. 1. Matrix Spike/Matrix Spike Duplicate Data (Form I VOA-1, VOA-2) 2. Reconstructed Total Ion Chromatogram 3. Quantitation reports of raw data 4. EICP of quantitation ion displaying compound peak before and after manual integrations.
Miscellaneous	Place ETR worksheets, data review narrative, manual integration summary reports signed and dated by primary and secondary reviewers, copies of NCRs, copies of run logs and preservation logs, and screen data on top of the VOA data package to be given to report management.

Appendix A: Standard Preparation Tables

This section lists the recommended formulations for the standard solutions used in this procedure. The formulations are accurate only when the specified concentrations and volumes are used. Any time the volume or concentration of any of the components change, the analyst must adjust the Formulation accordingly. Prepared standard solutions must be stored and maintained at the appropriate conditions and discarded when the expiration date has expired. The preparation of all standard solutions must be documented in a logbook designated for that purpose and all standard solutions must be labeled in accordance with the labeling requirements specified in the laboratory SOP for standard preparation.

Instrument Performance Check Solution (BFB)

Component	Vendor	Catalog #	Concentration (ug/mL)	Volume Added (uL)	Final Concentration (ug/mL)
Tuning Mix	Restek	30003	5000	125	25
P& T Methanol	Omni Solv	NA	NEAT	24875	
			Final Volume	***25000 uL***	

Calibration Mix (TRACE)

Component	Vendor	Catalog #	Concentration (ug/mL)	Volume Added (uL)	Final Concentration (ug/mL)
OLC VOA Mega Mix	Restek	30492	2000	40	20
VOA Ketones	Restek	30006	5000	160	200
Gases	Restek	30042	2000	40	20
DMC Non-Ketone	Cambridge Isotope	ES-528610X	1000	80	20
DMC Ketone	Cambridge Isotope	ES-528710X	5000	160	200
P& T Methanol	Omni Solv	NA	NA	3520	NA
			Final Volume	***4000 uL***	

Calibration Mix (SIM)

Component	Vendor	Catalog #	Concentration (ug/mL)	Volume Added (uL)	Final Concentration (ug/mL)
OLC VOA Mega Mix	Restek	30465	2000	2	1
DMC Non-Ketone	Cambridge Isotope	ES-528610X	1000	4	1
P& T Methanol	Omni Solv	NA	NA	3994	NA
			Final Volume	***4000 uL***	

DMC Mix

Component	Vendor	Catalog #	Concentration (ug/mL)	Volume Added (uL)	Final Concentration (ug/mL)
DMC Non-Ketone	Cambridge Isotope	ES-528610X	1000	40	10
DMC Ketone	Cambridge Isotope	ES-528710X	5000	80	100
P&T Methanol	Omni Solv	NA	NA	1880	NA
			Final Volume	***2000 uL***	

Internal Standard Solution (ISTD)

Component	Vendor	Catalog #	Concentration (ug/mL)	Volume Added (uL)	Final Concentration (ug/mL)
LC VOA ISTD Mix	Restek	30091	2500	16	10
P&T Methanol	Omni Solv	NA	NA	3984	NA
			Final Volume	***4000 uL***	

Matrix Spike Solution (MS)

Component	Vendor	Catalog #	Concentration (ug/mL)	Volume Added (uL)	Final Concentration (ug/mL)
VOA Matrix Spike Mix	Restek	30005	2500	32	20
P&T Methanol	Omni Solv	NA	NA	3968	NA
			Final Volume	***4000 uL***	

Calibration Standard, QC & Sample Preparation Table Summary

SOM Trace

Sample Type	Final Concentration (ppb)	CAL MIX (20 ppm)	ISTD (10 ppm)	DMC (10 ppm)	MS (20 ppm)
CAL Level 1	0.5	1.1 uL	22 uL	NA	NA
CAL Level 2	1.0	2.2 uL	22 uL	NA	NA
CAL Level 3 / CCV	5.0	11 uL	22 uL	NA	NA
CAL Level 4	10	22 uL	22 uL	NA	NA
CAL Level 5	20	44 uL	22 uL	NA	NA
MS/MSD	5.0	NA	22 uL	22 uL	11 uL
Samples & Blank	NA	NA	22 uL	22 uL	NA

Prepare in 44 mL HCl Preserved VOA Vials

SOM SIM

Sample Type	Final Concentration (ppb)	CAL MIX (1 ppm)	ISTD (10 ppm)	DMC (10 ppm)	MS (20 ppm)
CAL Level 1	0.05	2.2 uL	2.2 uL	NA	NA
CAL Level 2	0.1	4.4 uL	2.2 uL	NA	NA
CAL Level 3 / CCV	0.5	22 uL	2.2 uL	NA	NA
CAL Level 4	1.0	44 uL	2.2 uL	NA	NA
CAL Level 5	2.0	88 uL	2.2 uL	NA	NA
Samples & Blank	NA	NA	2.2 uL	2.2 uL	NA

Prepare in 44 mL HCl Preserved VOA Vials

Appendix B: Equations

Relative Response Factor (RRF)

$$RRF = \frac{(A_x)(C_{is})}{(A_{is})(C_x)}$$

Where:
Ax=Area of quantification mass EICP of compound to be measured
A_{is}= Area of quantification mass EICP of associated internal standard
C_{is}=Concentration of internal standard
C_x=Concentration of compound to be measured

Standard Deviation (SD)

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (X_i - \overline{X})^2}{(n-1)}}$$

Where:
X_i=Each value used to calculate the mean
X= The mean of n values
n=Total number of values

Percent Relative Standard Deviation (%RSD)

$$\%RSD = \frac{SD_{RRF}}{\overline{X}} X 100$$

Where:
SD_{RRF}=Standard Deviation of the initial calibration response factors for each compound.
X= Mean value of the initial calibration response factors for each compound.

Mean Relative Response Factor (RRF)

$$\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

Where:
X_i=Each RRF value per compound
X= The mean of n values
n=Total number of values

Percent Difference (%D)

$$\%\,\text{Difference} = \frac{RRF_c - \overline{RRF_i}}{RRF_i} X100$$

Where:
RRF_c = Relative Response Factor from current CCV standard
RRF_i = Mean relative response factor from most recent initial calibration

Sample Concentration

$$C_x = \frac{(A_x)(I_s)(DF)}{(A_{is})(\overline{RRF})(V_o)}$$

Where:
C_x = Concentration of compound (µg/L)
I_{is} = Concentration of associated internal standard (µg/L).
DF = Dilution Factor.
A_{is} = Area of quantification ion for associated internal standard.
A_x = Area of quantification ion for compound.
RRF = Relative Response Factor from the initial calibration standard
V_0 = actual volume purged (mL).

DMC Percent Recovery

$$\%R = \frac{Q_d}{Q_a} X100$$

Where:
Q_d = Concentration or amount determined by analysis.
Q_a = Concentration or amount added to sample/blank.

Matrix Spike/Matrix Spike Duplicate Recovery

$$\text{Matrix Spike Recovery} = \frac{SST - SR}{SA} \times 100$$

Where:
SSR = Spiked Sample Result
SR = Sample Result
SA = Spike Added

Matrix Spike/Matrix Spike Duplicate RPD

$$RPD = \frac{|MSR - MSDR|}{1/2(MSR + MSDR)} x100$$

Where:
MSR = Matrix Spike Recovery
MSDR = Matrix Spike Duplicate Recovery

Appendix C: List of Definitions

BLANK - an analytical sample designed to assess specific sources of laboratory contamination.

BFB-compound chose to establish mass spectral instrument performance for volatile analysis.

EXTRACTION ION CURRNE PROFILE (EICP)-a plot of ion abundance versus time (or scan number) for ion(s) of specified mass(es).

INITIAL CALIBRATION - analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the mass spectrometer or electron capture detector to the target compounds.

INTEGRATION SCAN RANGE-the scan number of the scan at the beginning of the area of integration to the scan number at the end of the area of integration.

INTEGRATION TIME RANGE-the retention time at the beginning of the area of integration to the retention time at the end of the area of integration.

INTERNAL STANDARDS- compound added to every standard, blank, matrix spike, matrix spike duplicate, sample (volatiles) and sample extract (semivolatiles) at a known concentration prior to analysis. Internal standards are used as the basis for quantitation of target compounds.

MATRIX SPIKE - aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

MATRIX SPIKE DUPLICATE - a second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

METHOD BLANK - an analytical control consisting of all reagents, internal standards, and dueterated monitoring compounds that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background, and reagent contamination.

PERCENT DIFFERENCE (%D) - As used in this SOW and elsewhere to compare two values, the percent difference indicates both the direction and the magnitude of the comparison, i.e., the percent difference may be either negative, positive, or zero.

PRIMARY QUANTITATION ION-a contract specified ion used to quantitate a target analyte.

RECONSTRUCTED ION CHROMATOGRAM (RIC)-a mass spectral graphical representation of the separation achieved by a gas chromatograph; a plot of total ion current versus retention time.

RELATIVE PERCENT DIFFERENCE (RPD) - As used in this SOW and elsewhere to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero. In contrast, see percent difference.

RELATIVE RESPONSE FACTOR (RRF)-a measure of the relative mass spectral response of an analyte compared to its internal standard.

RELATIVE RETENTION TIME (RRT) - the ratio of the retention time of a compound to that of a standard (such as an internal standard).

RESPONSE - or Instrumental Response: a measurement of the output of the GC detector (MS, EC, or FID) in which the intensity of the signal is proportionate to the amount (or concentration) detected. Measured by peak area or peak height.

RETENTION TIME (RT) - the time a target analyte is retained on a GC column before elution. The identification of a target analyte is dependent on a target compound's retention time falling within the specified retention time window established for that compound. Retention time is dependent on the nature of the column's stationary phase, column diameter, temperature, flow rate, and other parameters.

DEUTERATED MONITORING COMPOUNDS (DMCs) - added to every blank, sample, matrix spike, matrix spike duplicate, and standard; used to evaluate analytical efficiency by measuring recovery. DMCs are brominated, fluorinated, or isotopically labeled compounds not expected to be detected in environmental media.

Title: Analytical Method for Low/Medium Volatiles
[CLP SOW SOMO1.2]

Approvals (Signature/Date):

William S. Cicero — 12/27/07 Laboratory Director	Name — 12/27/07 Current Department Manager
Kirstin L. McCracken — 12/27/07 Quality Assurance Manager	Bryce E. Stearns — 12/27/07 Technical Director
Bryce E. Stearns — 12/27/07 Interim Health & Safety Coordinator	

This cover page documents management approval for the following changes to this SOP:

- **This SOP has been renamed and was previously identified as SOP No. LM-MV-SOMO1.2 - VOA.**
- **Any reference within this document to Severn Trent Laboratories, Inc. or STL, should be understood to refer to TestAmerica Laboratories, Inc. (formerly known as Severn Trent Laboratories, Inc.)**
- **The effective date of this SOP has been changed to January 1, 2008.**

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STANDARD OPERATING PROCEDURE
TestAmerica BURLINGTON

ANALYTICAL METHOD FOR LOW/MEDIUM VOLATILES
CLP SOW SOM01.2

Applicable Matrix: Water and Soil/Sediment

APPROVAL SIGNATURES

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1.0 SCOPE AND APPLICATION

1.1 This SOP describes the laboratory procedure for the analysis of water, soil and sediment samples for the volatile organic compounds listed in Section 18.0, Table 1. This procedure is specific to the USEPA Contract Laboratory Program (CLP) Statement of Work (SOW) SOM01.2.

1.2 The EPA has identified and published in the SOW the following problems associated with some compounds analyzed by this method:

- Chloromethane, vinyl chloride, bromomethane, and chloroethane can display peak broadening if the compounds are not delivered to the GC column in a tight band.
- Acetone, hexanone, 2-butanone, and 4-methyl-2-pentanone have poor purge efficiencies.
- 1,1,1-Trichloroethane and all the dichloroethanes can dehydrohalogenate during storage or analysis.
- Chloromethane can be lost if the purge flow is to fast.
- Bromoform is one of the compounds most likely to be adversely affected by cold spots and/or active sites in the transfer lines. Response of its quantitation ion (m/z 173) is directly affected by the tuning of the GC/MS to meet the instrument performance criteria for 4-bromofluorobenzene (BFB) at ions m/z 174/176. Increasing the m/z 174/176 ratio may improve bromoform response.

2.0 SUMMARY OF METHOD

2.1 Water Samples

Deuterated monitoring compounds (DMCs) and internal standards are added to each sample and the entire vial is placed in the instrument autosampler. An inert gas is bubbled through 5 mL of sample in a purge and trap chamber maintained at ambient temperature. The purgeable compounds are transferred from the aqueous phase to the vapor phase and swept through a sorbent column where the purgeables are trapped. After purging is complete, the sorbent column is heated and back flushed with the inert gas and the purgeables are desorbed onto a GC column. The GC is temperature programmed to separate the purgeable compounds that are then detected with a mass spectrometer.

2.2 Low-Level Soil/Sediment Sample

Approximately 5 g of sample is analyzed in a pre-weighed 44 mL VOA vial with 5 mL of VOA-free reagent water. DMCs and internal standards are added to each sample and the entire vial is placed in the instrument autosampler at which point an additional 5 mL of VOA-free water is added to the sample vial. The sample vial is heated to 40°C and the

volatiles are purged through a sorbent trap using an inert gas combined with agitation of the sample. After purging is complete, the trap is heated and back flushed with the inert gas and the purgeables are desorbed onto a GC column. The GC is temperature programmed to separate the purgeable compounds that are then detected with a mass spectrometer.

2.3 Medium-Level Soil Sample

A sample weight of 5 g of soil is collected and preserved in methanol. An 880 uL aliquot of the methanol preserved sample is added to VOA-free reagent water in a 44 mL VOA vial. DMCs and internal standards are added to each sample and the entire vial is placed in the instrument autosampler. An inert gas is bubbled through the sample contained in a purge and trap chamber maintained at ambient temperature. The purgeable compounds are transferred from the aqueous phase to the vapor phase and swept through a sorbent column where the purgeables are trapped. After purging is complete, the sorbent column is heated and back flushed with the inert gas and the purgeables are desorbed onto a GC column. The GC is temperature programmed to separate the purgeable compounds that are then detected with a mass spectrometer.

3.0 DEFINITIONS

3.1 See Appendix C for a list of definitions.

4.0 INTERFERENCES

4.1 Method interference may be caused by impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory method and instrument blanks. The use of non-Polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

4.2 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during storage and handling. Therefore samples analyzed by this procedure must be stored separately from other laboratory samples and standards and must be analyzed in a room demonstrated to be free from contaminates.

4.3 Contamination by carryover can occur whenever high level and low level samples are sequentially analyzed. To reduce carryover, the purging device and sampling syringe must be rinsed with reagent water between sample analyses. For samples containing large amounts of water-soluble materials, suspended solids, high-boiling compounds, or high purgeable levels, it may be necessary to wash out the purging device with a detergent solution between analyses, rinse it with distilled water, and then dry it in an oven at 105°C. The trap and other parts of the system are also subjected to contamination; therefore, frequent bake out and purging of the entire system may be required.

4.4 The volatile laboratory and preparation area should be completely free of solvents, except for methanol.

5.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.1 Specific Safety Concerns or Requirements

The toxicity or carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Use reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Safety glasses, gloves and protective clothing must be worn.

The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform, vinyl chloride and 1,4-Dioxane.

5.2 Primary Materials Used

Table 2, Section 18.0 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the Material Safety Data Sheet (MSDS). The table does not include all materials used in the procedure. A complete list of materials used can be found in Section 7.0. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Any questions regarding the safe handling of these materials should be directed to the laboratory's Environmental Health and Safety Coordinator.

6.0 EQUIPMENT AND SUPPLIES

6.1 QEC 44mL Borosilicate glass vials, Teflon-lined septa.

6.2 Syringes: 10 μL-2.5 mL Hamilton Gastight® syringes.

6.3 2 mL and 4 mL Borosilicate glass vials with Mininert® screw-cap on/off valves.

6.4 Autosampler - EST Centurion or Archon.

6.5 Purge and Trap Device – EST Encon, Tekmar LCS 2000 or Velocity XPT.

Trap Specifications - 25 to 30cm x 2.5mm ID minimum, Supelco VOCARB 3000 (K-type trap), or equivalent.

6.6 GC System - Hewlett Packard 5890.

GC Columns - J&W DB624 75m x 0.53mm x 3.0 μm film (jet separator configuration).

6.7 MS System - Mass Spectrometer: Hewlett-Packard 5971.

The MS system must be capable of producing an averaged mass spectrum for the instrument performance check solution (25 ng/uL BFB) that meets the acceptance criteria detailed in Table 3.

6.8 Data System

Data Acquisition - ChemStation Version B.01.00

Data Reporting - Target Version 3.5

7.0 REAGENTS AND STANDARDS

7.1 Reagents

Methanol (CH_3OH), purge & trap quality – OmniSolv high purity solvent.

VOA-Free Reagent Water: Boil water that has been filtered through the laboratory Milli Q Plus ™ filtration system for one hour then purge with helium for a minimum of one hour.

7.2 Standards

Prepare working standard solutions from stock standard solutions purchased from commercial vendors. See Appendix B for the recommended formulation for the preparation of the following standard solutions. Assign an expiration date to the prepared solutions as specified in the following section. Store the stock standards and primary working standard solutions, except the instrument performance check solution, protected from light at a temperature of –10°C to –20°C. Store the instrument performance check solution protected from light at a temperature of 4°C (±2°C). Individual prepared calibration standards may be held for up to 24 hours after time of preparation if they are stored in Teflon sealed screw-cap vials with zero headspace at 4°C (±2°C) and protected from light. Store all standards separately from samples and other chemical materials.

Instrument Performance Check Solution (BFB): The instrument performance check solution consists of 4-Bromofluorobenzene in methanol. Prepare the solution in a volumetric flask using the formulation specified in Appendix B. Assign an expiration date of 6 months from date made unless the expiration date of any parent component is sooner, in which case use the earliest expiration date.

SOM Calibration Mix: The calibration mix contains the target and DMC compounds listed in Table 1, except for 1,4-dioxane and 1,4-dioxane-d_8, in methanol. Prepare the calibration mix in a 4 mL borosilicate glass vial with Mininert® valve and assign an

expiration date of one month from date made unless the expiration date of any parent component is sooner, in which case use the earliest expiration date. Use the calibration mix to prepare the individual calibration standards and the opening and closing CCV standard.

SOM 1,4-Dioxane Calibration Mix: Prepare the 1,4-dioxane calibration mix in a 2 mL borosilicate glass vial with Mininert® valve. Assign an expiration date of one month from date made unless the expiration date of any parent component is sooner, in which case use the earliest expiration date. Use the 1,4-dioxane calibration mix to prepare the individual initial calibration standards and opening and closing CCV.

SOM Internal Standard Spike Mix (ISTD): The ISTD contains 1,4-dichlorobenzene-d_4, chlorobenzene-d_5, and 1,4-difluorobenzene in methanol. Prepare the ISTD in a 4 mL borosilicate glass vial with Mininert® valve. Assign an expiration date of one month from date made unless the expiration date of any parent component is sooner, in which case use the earliest expiration date. Add the ISTD solution all calibration standards, blanks, and samples at a final concentration of 50 ug/L.

DMC Mix: The DMC contains all compounds listed in Table 4 in methanol. Prepare the DMC in a borosilicate 4 mL glass vial with Mininert® valve. Assign an expiration date of one month from date made unless the expiration date of any parent component is sooner, in which case use the earliest expiration date. Add the DMC to all blanks and samples at a concentration of 50 μg/L for each non-ketone DMCs, 100 μg/L for ketone DMCs, and 1000 ug/L1,4-dioxane-d_8.

Matrix Spike Mix (MS): The MS contains compounds listed in Table 5 in methanol. Prepare the MS in a 2 mL borosilicate glass vial with Mininert® valve. Assign an expiration date of one month from date made unless the expiration date of any parent component is sooner, in which case use the earliest expiration date. Add the MS spike to each MS/MSD samples at a concentration of 50 μg/L.

Initial Calibration and Continuing Calibration Verification (CCV) Standards: The initial calibration standards are prepared in 44 mL borosilicate glass vials using the SOM calibration mix and VOA-free reagent water. Prepare five initial calibration standards containing all of the target compounds and DMCs at the following concentrations: all non-Ketone targets and associated DMCs, except 1,4-dioxane at 5.0, 10, 50, 100, and 200 μg/L; all ketones and associated DMCs at 10, 20, 100, 200, and 400 μg/L; and 1,4-dioxane and its associated DMC 1,4-dioxane-d_8 at 100, 200, 1000, 2000, and 4000 μg/L. Note that the m plus p-Xylene isomers total 5.0, 10, 50, 100, and 200 μg/L. Add ISTD to each calibration point at a concentration of 50 μg/L. See Appendix A for initial calibration formulation.

Prepare the opening and closing CCV at the mid-point concentration of the calibration in 44 mL borosilicate glass vials using the SOM calibration mix and VOA-free reagent water. See Appendix A for CCV formulations.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 Sample Collection

The laboratory does not perform sample collection, thus these procedures are not applicable to this SOP. The sample collection procedure performed should be in accordance with the Analytical Method for the Analysis of Volatile Organic Compounds, Exhibit D, USEPA Contract Laboratory Program Statement of Work for Organic Analysis, SOM01.2. The laboratory provides per client request, pre-certified, pre-preserved sample collection containers and Encore sampling devices, which are shipped directly to the sampling site.

8.2 Sample Receipt & Preservation & Storage

Water

Water samples should be received in 44 mL VOA vials that were field preserved to a pH less than 2 at the time of collection. Upon laboratory receipt, store the water samples at a temperature of 4°C ($\pm$2°C) until time of analysis in a refrigerator dedicated to the storage of VOA samples. Store the samples with an aqueous storage blank, which is subsequently analyzed to assess potential contamination that may have occurred during laboratory storage.

Soil/Sediment

Soil and sediment samples may be received from the field in pre-prepared closed system purge and trap vials, pre-weighed glass vials or in field core sampling containers.

Samples that are collected in pre-prepared closed system purge and trap vials may have been field preserved with sodium bisulfate or collected unpreserved in water. Samples that are received unpreserved in water must be analyzed within 24 hours or kept frozen at a temperature of -7°C until time of analysis. Place samples that are to be stored at -7°C on their side prior to being frozen. Store samples that are field preserved with sodium bisulfate at a temperature of 4°C ($\pm$2°C) until time of analysis in a refrigerator dedicated to the storage of VOA samples.

Medium level soil/sediment samples may be received from the field in pre-weighed vials that contain methanol. Store the methanol preserved samples at a temperature of 4°C ($\pm$2°C) until time of analysis in a refrigerator dedicated to the storage of VOA samples.

For samples received in field core sampling containers, the samples must be transferred into pre-prepared closed system purge and trap vials within 24 hours of receipt or the samples must be stored at -7°C. Place samples that are to be stored at -7°C on their side prior to being frozen.

Aqueous storage blanks must be stored with preserved low/medium soils and with water samples at a temperature of 4°C ($\pm$2°C). An inert sand storage blank must be stored with the unpreserved low/medium soil samples at a temperature of -7°C.

Unless otherwise specified by client or regulatory program, all samples are held from the time of receipt until 30 days after delivery of a complete, reconciled data package. After 30 days, any unused portions of the samples may be disposed of in a manner that

complies with all applicable regulations.

8.3 Contract Required Holding Times

Analysis of water must be completed within 10 days of Validated Time of Sample Receipt (VTSR).

9.0 QUALITY CONTROL

9.1 Blanks

A method blank, storage blank and instrument blank(s) are prepared and analyzed to determine the level of contamination that may be associated with sample processing and analysis (method blank), sample storage (storage blank) or carryover from analysis of a previous sample (instrument blank). The frequency requirements for analysis and criteria are summarized as follows:

Method Blank: The method blank is analyzed at least once in every 12 hour time period on each instrument used for analysis. See Section 10.2 for a definition of the 12-hour time period. The method blank must be analyzed after the CCV and before analysis of any samples or storage blanks. If samples are analyzed in the same sequence as initial calibration, the method blank must be analyzed immediately after the calibration.

Storage Blank: The storage blank is analyzed after all samples in the SDG have been analyzed.

Instrument Blank: Instrument blanks are analyzed as needed after any sample for which the target compound exceed the calibration range or when non-target compounds are found at concentrations greater than 200 ug/L or when ions from a compound saturate the detector (excluding peaks in a solvent front).

Blank Acceptance Criteria

1) Each blank must be analyzed on a GC/MS system that has met criteria for the instrument performance check and initial and continuing calibration.
2) 2) The DMC recovery in the blanks must meet the acceptance recovery criteria found in Table 4, Section 18.0. Note the recovery limits for 1,4-dioxane-d_8 are advisory.

3) The percent area response change for each of the internal standards in the blank must be within the inclusive range of 50 to 200 percent of its response in the most recent continuing calibration standard analysis.

4) The retention time shift for each of the internal standards in the blank must be within $\pm$0.50 minutes of its retention time in the most recent continuing calibration standard analysis.

5) The concentration of each target compound in the method blank and storage blank must be less than the CRQL except for methylene chloride, acetone, and 2-butanone which

must be less than 2 times the CRQL. The concentration of each target compound in the instrument blank must be less than the CRQL.

6) Additionally the CLP SOW requires that the concentration of non-target compounds in all blanks must be less than 2.0 ug/L. However the laboratory has found that the DMC stock standard solution commercially available contains non-target compounds, or contaminates, at concentrations exceeding the maximum allowed concentration of 2 ug/L. Until the laboratory is able to obtain a DMC stock standard solution that is free of contaminates, the laboratory identifies the non-target compounds in blanks as unknown TICs and flags with a “X” qualifier in the data package. The laboratory may also use the “X” qualifier to identify siloxanes (column bleed) found in the blank.

   Any method blank that does not meet criteria must be reanalyzed along with all associated samples. Any instrument blank that does not meet criteria requires reanalysis of the samples following the instrument blank that have any target compounds detected above the CRQL. Any storage blank that does not meet criteria must be reanalyzed. If the storage blank contains target compounds above the CRQL, reanalyze to determine if the contamination occurred during storage or if the problem occurred during the analysis. If upon reanalysis, the storage blank meets criteria, then only the results of reanalysis are reported. If after reanalysis, the storage blank still does not meet criteria, the problem is documented in the case narrative along with corrective or preventive actions taken to prevent recurrence.

9.2 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

MS/MSD are performed when requested by the client. MS/MSD are processed and analyzed in the same manner as field samples and at the same concentration as the most concentrated aliquot from which the parent sample analysis is reported. MS/MSD may not be diluted to get either the spiked or non-spiked analytes within calibration range. Additionally, MS/MSD must not be performed on field, trip or rinsate blank samples.

Acceptance Criteria for MS/MSD Analysis

Each MS/MSD must be analyzed on a GC/MS system that has met criteria for the instrument performance check and initial and continuing calibration.

Each MS/MSD must be analyzed within the contract holding time.

The RT shift for each internal standard in the MS/MSD must be within ±0.50 minutes of the retention times for the internal standards found in the most recent opening CCV analysis.

The accuracy and precision of the MS/MSD should be within the limits given in Table 5, Section 18.0. These control limits are advisory and no further action is required unless it is determined that the frequency of failure is indicative of a systematic problem requiring investigation.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Instrument Operation Conditions

Purge Conditions
Configure the purge and trap using the following conditions. Parameters may be optimized as long as the same conditions are used for all standards, samples, and blanks.

Purge Gas: UHP Helium
Purge Flow: ~40 mL/min
Purge Temperature: Ambient (Water)/40°C (Soil)
Purge Time: 11.5 min
Dry Purge Time: 0.5 min
Desorb Preheat Temperature: 250°C
Desorb Temperature: 260°C
Desorb Time 4.0 min
Bake Temperature 270°C
Bake Time 2.5 min
P&T Transfer Line Temperature: 110 °C
P&T Valve Temperature: 110 °C

GC Conditions
The following conditions are recommended and may be optimized as long as the same conditions are used for all standards, samples, and blanks.

Injection Port: 150°C
Jet Separator: 180°C
MS Transfer Line: 250°C

Temperature Program
40°C for 4.4 minutes
12.5°C/min to 165
30°C/min to 220 for 4.47

Mass Spectrometer Conditions
Electron Energy: 70 eV nominal
Mass Range: 35-300 amu
Ionization Mode: Electron Impact (EI)
Scan Time: >1 scan/sec

10.2 GC/MS Tuning & Ion Abundance

The mass calibration of the system is checked at the beginning of each 12-hour period during which samples or standards are analyzed with a BFB tune standard. The injection time of the acceptable BFB starts the 12-hour analysis window. Within this time period, the analysis of all calibration standards, blanks, and samples must occur. All

subsequent standards, samples and QC items associated with a BFB analysis must use the same GC/MS conditions used to acquire the BFB, with the exception of the temperature program. If the closing CCV standard for an analytical sequence meets the acceptance criteria of an opening CCV, then another 12-hour analytical period may begin without the injection of a BFB performance check sample. The new 12-hour analytical period starts at the moment of injection of the passing closing CCV.

To perform the instrument performance check, prepare the 25 ug/mL instrument performance check solution (BFB) and inject 2 uL of BFB standard onto the instrument system to yield an on-column concentration of 50 ug/mL and acquire the data.

The data system acquires the data such that three scans (the peak apex and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required and must be performed using a single scan no more than 20 scans prior to the peak apex. Do not background subtract part of the BFB peak.

Check the results against the ion abundance criteria given in Table 3, Section 18. Criteria must be met prior to further analysis. If criteria are not met, perform necessary corrective actions and repeat the instrument performance check. The BFB must meet all criteria prior to subsequent analysis.

10.3 Initial Calibration

After successful analysis of the instrument performance check standard, calibrate the instrument with a minimum of five concentrations levels. Each calibration level must include all target compounds, DMCs and internal standards. Each calibration is matrix matching, water, clean soil matrix or 880 uL methanol for medium level soils.

Prepare the calibration standards using the formulations specified in Appendix A. Allow the standards to warm to room temperature prior to analysis. Load the samples into the autosampler begin the analytical sequence and acquire the data.

The data system calculates the RRF, the percent relative standard deviation (%RSD), and the mean RRF for each target and system-monitoring compound over the working range of the curve. The primary characteristic ions used for quantification are given in Table 1 along with the internal standard assignments. If interference prevents use of the primary quantification ion, the secondary ion given in Table 1 may be used. Because the m- and p-xylene isomers co-elute, a single RRF for m- and p-xylene is calculated using the area response for that peak and the appropriate concentration. Equations for these calculations can be found in Appendix. B.

The following technical acceptance criteria should be met before further analysis. If it is not, investigate the source of the problem, perform instrument maintenance and recalibrate if necessary.

- The RRF at each calibration level for each target compound or system monitoring compound should be greater than or equal to the compound's minimum acceptable response factor given in Table 6.

- The %RSD for each target compound should be less than or equal to the value given in Table 6.

- Up to 2 target compounds and DMCs may fail to meet the minimum RRF criteria and the maximum %RSD criteria and still be acceptable as long as these compounds have a minimum RRF greater than or equal to 0.010 and a %RSD of less than or equal to 40.0%. The exceptions are 1,4-dioxane and 1,4-dioxane-d8 which must have a minimum RRF of greater than or equal to 0.0050 and a %RSD of less than or equal to 50.0%.

10.4 Continuing Calibration Verification (CCV)

Each day prior to analysis, after the instrument performance check standard analyze an opening CCV. An opening CCV is not required in the same 12 hour window as initial calibration. Analyze another CCV (closing CCV) after all samples and blanks have been analyzed, and before the end of the 12-hour analytical window. In this scenario, the 12 hour time-frame is established as the injection time of the instrument performance check standard (BFB). However, in each case where the closing CCV meets the acceptance criteria for an opening CCV, analysis of another instrument performance check standard is not required. In this scenario, the closing CCV serves as the opening CCV and the analytical window is set by the injection of the closing CCV. If the closing CCV does not meet the technical acceptance criteria for an opening CCV, then analysis of a BFB followed by an opening CCV, is required.

Prepare a calibration standard at the mid level concentration (ICAL Level 3) and analyze the standard using the same instrument conditions as used for the initial calibration.

The data system calculates the relative response factors (RRF) for each target and DMC using the primary characteristic ions found in Table 1 and Table 4. For the internal standards, the primary ion is used unless interference is present. If interference is evident, the secondary ion(s) is used. The data system also calculates the %D between the continuing calibration relative response factor and the most recent initial calibration mean relative response factor for each target and DMC. The equations for the above calculations can be found in Appendix B.

The CCV must meet the following criteria before further analysis. If criteria are not met, investigate the source of the problem, perform instrument maintenance and recalibrate if necessary.

- The RRF for each target compound and DMC in the opening CCV must be greater than or equal to the compound's minimum acceptable response factor given in Table 6. For closing CCVs the RRF for each compound must be at least 0.010 (except for 1,4-dioxane and 1,4 dioxane-d_8, which must be at least 0.0050).

- For the opening CCV the percent difference for each target compound and DMC listed in Table 6 should be less than or equal to the value given. For the closing CCV, the percent difference of the RRF must be an inclusive ±50%.

- In the opening CCV up to 2 compounds may fail the RRF and %RSD criteria listed above, but these compounds must have a minimum RRF greater than or equal to 0.010 and the %D must be less than or equal to ±40%. The exceptions are 1,4-dioxane and 1,4-dioxane-d8 which must have a minimum RRF of greater than or equal to 0.0050 and a %D of less than or equal to 50.0%.

- Excluding ions present in the solvent front (carbon dioxide), no quantification ion may saturate the detector.

- If the opening CCV criteria cannot be met system re-calibration is required.

- If the closing CCV criteria is not met, all samples and blanks acquired within that 12-hour analytical window require reanalysis.

10.5 General System Routine Maintenance and Troubleshooting

Perform the following routine maintenance as needed:

- Clean the injection port and liner
- Change the septa
- Cut 2 to 3 inches off the column
- Fill autosampler rinse vials
- Clean mount and purge vessel
- Check purge flow

Perform the following troubleshooting steps for each specific instrument condition.

<u>BFB Failure</u>
1. Shoot a 2nd BFB.
2. If the 2nd BFB fails evaluate the GC and perform column and or injection port maintenance as needed. Shoot another BFB.
3. If GC maintenance does not work evaluate and adjust the BFB parameters until the BFB passes.

<u>Calibration Linearity Fails Criteria</u>
1. Evaluate the RF summary for the ICAL to determine the reason for the failure.
2. Reprep and reacquire an additional calibration point if one point is different from all others.
3. If the additional calibration point does not fix the linearity perform routine GC maintenance.
4. If GC maintenance does not work to provide passing linearity evaluate standards and reprep if necessary.
5. Retune and begin to acquire another ICAL.
6. Evaluate the failing compound using a different curve fit such as linear regression.

<u>Calibration Fails Minimum Response</u>
1. Evaluate the integrity of the standards and reprep if necessary.

2. Evaluate GC performance and perform routine GC maintenance if necessary.
3. Evaluate MS sensitivity and increase instrumental sensitivity through tuning of the MS.

Calibration Fails RT Drift
1. Look for a leak or a plug in the GC and repair.
2. Recheck all flows to determine if any have changed.

Opening/Closing Standard Fails Linearity
1. Reanalyze a second CCV and reevaluate.
2. If reanalyzing does not work, perform routine GC and injection port maintenance.
3. If maintenance does not fix the failure then evaluate standards and recalibrate.
4. Reanalyze any samples affected by the failure.

Opening/Closing Standard Fails RT Drift
1. Look for a leak or a plug in the GC and repair.
2. Recheck all flows to determine if any have changed.
3. Reanalyze any samples affected by the failure.

Instrument Contamination
1. Check for the source of the contamination by running blank tests.
2. Remove the source of contamination once it is isolated.
3. Reanalyze blanks to prove contamination has disappeared.

Sample RTs Drift/Sensitivity
1. Evaluate the entire window to see if it appears isolated to a particular sample or to the entire window.
2. If it is sample related, evaluate the sample matrix.
3. If it is instrumental, evaluate the GC for a leak or a plug and repair.
4. Reanalyze any affected samples.

11.0 PROCEDURE

11.1 Screen Analysis

Samples should be screened prior to analysis following the procedures given in SOP LM-MV-3810 *VOA Screen Analysis*. The laboratory may choose not to perform screen analysis for samples from which site history is known or available. The results of screen analysis may be used to determine if the concentration of any target compound in a water sample may exceed the calibration range or excessive sample matrix interference may hinder quantification. Despite the screen result, the CLP SOW requires that an original undiluted analysis must be made and reported for all samples. When the laboratory suspects or has evidence of a high concentration sample for target or non-target compounds, for CLP contract work, the laboratory must contact the project administrator (SMO) for further instruction.

11.2 pH determination (Water Samples)

Measure and record the pH for each water sample. If the pH measurement of the sample is > 2, notify appropriate Project Manager. Do not adjust the pH of any sample.

11.3 Sample Preparation

Low Level Water/Soils & Sediment
Allow the samples to warm to ambient temperature. Using a gas tight syringe add a sufficient amount of the internal standard (ISTD) and DMC standards through the septa cap of each vial. Add the appropriate spike volume to each MS/MSD. See the sample preparation table in Appendix A for the volume of standard solution to add to each sample type.

To prepare the method blank and instrument blanks, fill a 44 mL vial with VOA free water and add a sufficient amount of the internal standard (ISTD) and DMC standards through the septa cap of each vial. See the sample preparation in Appendix A for spike solution volumes.

To prepare the storage blank, allow the blank to warm to ambient temperature. Using a gas tight syringe add a sufficient amount of the internal standard (ISTD) and DMC standards through the septa cap of each vial. See sample preparation table in Appendix A for the volume of standard solution to add to each sample type

Medium Level Soil/Sediment
Allow the samples to warm to ambient temperature. Using a 1ml gastight syringe withdraw an 880 µL aliquot of sample and transfer to a 44 mL VOA vial filled with VOA-free reagent water. Using a gas tight syringe add a sufficient amount of the internal standard (ISTD) and DMC standards through the septa cap of each vial. Add the appropriate spike volume to each MS/MSD. See the sample preparation table in Appendix A for the volume of standard solution to add to each sample type.

Sample Analysis

Place samples in autosampler. Create the data acquisition sequence table on the data system, include the necessary sample information and initiate the data collection sequence. Initiate the autosampler sequence. Instrument operations follow the purge and GC/MS conditions outlined in Section 10.1.

11.4 Target Compound Identification

Acquire and process the data. The data system identifies target compounds using their mass spectra and comparing the sample mass spectrum to the mass spectrum of the standard of the suspected compound. The elution of the sample component must be at the same GC relative retention time as the standard component and there must be correspondence of the sample component and standard component mass spectra.

For correspondence, the sample component RRT should compare within ±0.06 RRT of the RRT of the CCV or the mid-point of the initial calibration that was analyzed within the same 12-hour window as the sample. If interference prohibits assignment, assign the

RRT by using extracted ion current profiles for the ions unique to the target compound. For comparison of mass spectra, use the mass spectra obtained for the daily calibration standard for identification purposes provided that the instrument met the acceptance criteria for the BFB.

The requirements for qualitative verification by comparison of mass spectra are as follows:

- All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must to be present in the sample spectrum.

- The relative intensities of these ions must agree within ±20% between the standard and sample spectra.

- Ions greater than 10% in the sample spectrum but not present in the standard spectrum are considered and accounted for by the analyst making the comparison.

The data system determines the concentration of target compounds by the internal standard method from the relative response factor (RRF) from the continuing calibration standard using the equations given in Appendix B.

Evaluate the internal standard response and retention time in all samples by comparing the sample internal standard response and retention times to the internal standard response and retention time of the opening continuing calibration standard (or mid-point of calibration curve when samples are analyzed in the same analytical window as the initial calibration). Evaluate the Extracted Ion Current Profile (EICP) of the internal standards for each sample and QC item.

The following criteria should be met for each sample analysis:

- The sample must be acquired on an instrumentation that has met all of the GC/MS tune, calibration, and blank acceptance criteria as defined in Sections 9 and 10.

- All samples and subsequent required dilutions must be analyzed within the contract holding time.

- The area response of the internal standards of the sample must be within 50% to 200% of the response of the internal standards in the most recent opening CCV.

- The retention time shift for each of the internal standard should be within ±0.50 minutes between the sample and the most recent opening CCV.

- The percent recovery for each DMC must be within the acceptance limits found in Table 4. The recovery limits for 1,4-dioxane-d_8 are advisory. Up to three DMCs (excluding 1,4-dioxane-d_8) may fail to meet the acceptance criteria listed in Table 4.

- Excluding ions in the solvent front (carbon dioxide), no ion may saturate the detector.

- It must be demonstrated that the sample analyses are free of carryover from a previously analyzed contaminated sample whose target compound response exceeds the calibrated range.

Secondary ion quantification may only be performed when there are sample matrix related interferences with the primary ion. Calculate the RRF using the area response from the most intense secondary ion free of interferences. Document the reason in the project narrative.

If any of the system monitoring or internal standard compounds fail to meet RT or recovery acceptance criteria, investigate for error. If instrument or calculation errors are found, correct the problem and re-analyze and/or recalibrate as necessary. If it is suspected that the problem is due to matrix effect, re-analyze the sample. If the results of re-analysis are within control, submit only that analysis. Otherwise provide both sets of data using R1/RE designations for the re-analysis. A failing sample with an associated MS/MSD pair is considered confirmed if failures are consistent in all three analyses.

In those instances were the automated processing system fails to accurately integrate quantification ion EICPs due to matrix interference, co-elution, and/or baseline noise, perform manual integrations. Manually integrate the peak such that it accurately defines the peak without under or over estimation of the absolute area attributable to that component peak. Include EICP printouts that display the compound peak before and after manual integration with raw data. Generate and include the manual integration summary report identifying all samples with manual integrations and signed and dated by the primary person performing manual integrations and the secondary person reviewing all manual integrations. For additional guidance regarding Manual Integration, refer to laboratory SOP LP-LB-0006 *Manual Integration*.

11.5 Non-Target Compound Identification

Perform a library search using the NIST spectral library to tentatively identify up to 30 non-target, non-alkane organic compounds of greatest apparent concentration excluding the system monitoring and internal standards compounds. Assign tentative identification based on mass spectral interpretation.

Do not report the following:

- Substances with responses less than 10 percent of the internal standard.
- Substances that elute earlier than 30 seconds before the first purgeable compound or three minutes after the last purgeable compound.
- Carbon dioxide.
- Semivolatile compounds

TIC peaks that are suspected to be straight chain, branched, or cyclic alkanes must be searched and documentation of the search supplied in the data report. Alkanes are not considered as part of the 30 compound search described earlier. Straight-chain, branched or cyclic alkanes are automatically tabulated and reported as 'total alkanes" on the Form 1 VOA-TIC. When these alkanes are tentatively identified, the concentrations are considered estimated and reported in the project narrative as alkanes by class.

Determine the estimated concentrations for non-target compounds by the internal standard method using the same equations specified for target compounds using an assumed RRF of 1. Qualify the resulting concentrations with a "J" and "N" data flag to indicate the concentration is estimated and that there are qualitative and quantitative uncertainties associated with the result.

The following guidelines should be used for making tentative identification:

- If the library search quality match is 85% or better the peak should be reported using the identification generated by the search routine, unless the mass spectral interpretation specialist feels there is just evidence not to report that identification.

- If the library produces more than one match at or above 85%, report the highest match, or first match if they are the same, unless the mass spectral interpretation specialist feels there is just evidence not to report that identification.

- If the library produces multiple matches at or above 85% (e.g. multiple isomers of a PCB), report the highest match, or first match if they are the same, unless the mass spectral interpretation specialist feels there is just evidence not to report that identification.

- If the mass spectral interpretation specialist has just evidence to support reporting a compound with a tentative identification other than the library selection (with 85% quality match or better) detail the justification in the SDG case narrative.

- If the library search produces no matches at or above 85% quality, the mass spectral interpretation specialist should attempt (where possible) to make a tentative identification of the compound, or its class (e.g. alcohol, chlorinated, etc). Otherwise, the compound should be reported as an "Unknown".

12.0 CALCULATIONS

See Appendix B.

13.0 DATA ASSESSMENT, CRITERIA AND CORRECTIVE ACTION

13.1 Data Review and Corrective Action

Review all samples, standards, and QC samples against the acceptance criteria provided in this SOP. Generate target reports and forms using SOM01-CLP form set and arrange the volatile data following the requirements specified in the Table 7.0.

Arrange SIM data separately at the end of the volatile subsection. If the results do not fall within the criteria, perform corrective action. If corrective action is not taken, or is unsuccessful, document the situation with a nonconformance report (NCR) and qualify the data using an appropriate data qualifier. For additional guidance regarding the laboratory's protocol and required elements for each level of data review (primary, secondary, and tertiary) refer to laboratory SOP LP-QA-003 *Data Review*. Submit VOA data package to Report Management for assimilation into the hardcopy data deliverable.

14.0 METHOD PERFORMANCE

A Method Detection Limit (MDL) must be determined on each instrument used for analysis for each matrix prior to initial use of the method. The MDLs are then verified annually with an MDL Verification Check sample that is subject to the same extraction and cleanup procedures as used for field samples. Some regulatory programs may require that the MDL study be repeated annually, but this is not a requirement of the CLP SOW. The procedure and acceptance criteria for MDL studies and MDL verification are given in laboratory SOP LP-QA-005 *Method Detection Limits.*

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

All waste will be disposed of in accordance with Federal, State, and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.1 Waste Streams Produced by the Method

All waste will be disposed of in accordance with Federal, State, and Local regulations. Where reasonably feasible technological changes have been implemented to minimize the potential for pollution of the environment. Employees must abide the pollution prevention and waste management procedure described in this SOP and the policies for "Waste Management and Pollution Prevention" given in Section 13 of the Corporate Safety Manual.

The following waste streams are produced from this procedure:

1) Acid Preserved Water Samples & Glass Vials
   Satellite Waste Container: 5 Gallon Plastic Bucket labeled "CORROSIVE"

Transfer the waste stream(s) to the appropriate satellite waste container(s) located in your work area. Notify the Environmental Health & Safety (EHS) Coordinator when the satellite container is near full. The EHS Coordinator will make arrangements for authorized personnel to transfer the waste to the waste management room for subsequent disposal. See laboratory SOP LP-LB-001 *Hazardous Waste* for additional information regarding waste management and disposal procedures.

16.0 REVISION HISTORY

16.1 This is the first version of this SOP.

17.0 REFERENCES

17.1 Exhibit D, Analytical Methods for the Analysis of Low/Medium Concentrations of Volatile Organic Compounds, USEPA CLP SOW for Organic Analysis, SOM01.1, May 2005.

17.2 USEPA CLP SOW Clarifications to SOM01.1, November 7, 2005 and September 26, 2006.

17.3 USEPA CLP SOW Modifications Updating SOM01.1 to SOM01.2, October 5, 2006 (Updated 02-12-2007) Amended 04-11-2006.

18.0 TABLES, DIAGRAMS & FLOWCHARTS

18.1 Table 1: Target Compound List, Internal Standard Group Assignments, CRQLs, and Quantification and Qualifier Masses
18.2 Table 2: Primary Materials Used
18.3 Table 3: BFB Criteria
18.4 Table 4: DMC Quantification and Qualifier Masses, Internal Standard Group Assignments, and Recovery Limits
18.5 Table 5: Matrix Spike Recovery, Accuracy, and Precision Limits (Advisory)
18.6 Table 6: Calibration Criteria
18.7 Table 7: Volatiles Raw Data and Forms Reporting Order
18.8 Appendix A: Standard Preparation Tables
18.9 Appendix B: Equations
18.10 Appendix C: Terms and Definitions

Table 1: Target Compound List, Internal Standard Group Assignments, CRQLs, and Quantification and Qualifier Masses

Compound	ISTD Group*	Low Water ug/L	Low Soil ug/Kg	Med Soil ug/Kg	MZ1**	MZ2	MZ3
Dichlorodifluoromethane	1	5	5	250	85	87	
Chloromethane	1	5	5	250	50	52	
Vinyl chloride	1	5	5	250	62	64	
Bromomethane	1	5	5	250	94	96	
Chloroethane	1	5	5	250	64	66	
Trichlorofluoromethane	1	5	5	250	101	103	
1,1-Dichloroethene	1	5	5	250	96	61	63
1,1,2-Trichloro-1,2,2-trifluoroethane	1	5	5	250	101	85	151
Acetone	1	10	10	500	43	58	
Carbon disulfide	1	5	5	250	76	78	
Methyl acetate	1	5	5	250	43	74	
Methylene chloride	1	5	5	250	84	49	86
trans-1,2-Dichloroethene	1	5	5	250	96	61	98
Methyl-t-butyl ether	1	5	5	250	73	57	
1,1-Dichloroethane	1	5	5	250	63	65	83
cis-1,2-Dichloroethene	1	5	5	250	96	61	98
2-Butanone	1	10	10	500	43	72	
Bromochloromethane	1	5	5	250	128	49	130
Chloroform	1	5	5	250	83	85	
1,1,1-Trichloroethane	2	5	5	250	97	99	61
Carbon tetrachloride	2	5	5	250	117	119	
Cyclohexane	2	5	5	250	56	69	84
Benzene	2	5	5	250	78		
1,2-Dichloroethane	1	5	5	250	62	98	
1,4-Dioxane	1	100	100	5000	88	43	58
Trichloroethene	2	5	5	250	95	130	132
Methylcyclohexane	2	5	5	250	83	55	98
1,2-Dichloropropane	2	5	5	250	63	112	65
Bromodichloromethane	2	5	5	250	83	85	127
cis-1,3-Dichloropropene	2	5	5	250	75	77	
4-Methyl-2-pentanone	2	10	10	500	43	58	100
Toluene	2	5	5	250	91	92	
trans-1,3-Dichloropropene	2	5	5	250	75	77	
1,1,2-Trichloroethane	2	5	5	250	97	83	85
Tetrachloroethene	2	5	5	250	164	166	129
2-Hexanone	2	5	5	250	43	58	57
Dibromochloromethane	2	5	5	250	129	127	
1,2-Dibromoethane	2	5	5	250	107	109	188

Compound	ISTD Group*	Low Water ug/L	Low Soil ug/Kg	Med Soil ug/Kg	MZ1**	MZ2	MZ3
Chlorobenzene	2	5	5	250	112	114	77
Ethylbenzene	2	5	5	250	91	106	
m,p-Xylene	2	5	5	250	106	91	
o-Xylene	2	5	5	250	106	91	
Styrene	2	5	5	250	104	78	103
Bromoform	3	5	5	250	173	175	254
Isopropylbenzene	2	5	5	250	105	120	77
1,1,2,2-Tetrachloroethane	2	5	5	250	83	85	131
1,3-Dichlorobenzene	3	5	5	250	146	111	148
1,4-Dichlorobenzene	3	5	5	250	146	111	148
1,2-Dichlorobenzene	3	5	5	250	146	111	148
1,2-Dibromo-3-chloropropane	3	5	5	250	75	155	157
1,2,4-Trichlorobenzene	3	5	5	250	180	182	145
1,2,3-Trichlorobenzene	3	5	5	250	180	182	145

*ISTD 1 – 1,4-Difluorobenzene
ISTD 2 – Chlorobenzene-d_5
ISTD 3 – 1,4-Dichlorobenzene-d_4

**Denotes quantification mass

Table 2: Primary Material Used

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Sodium bisulfate	Irritant	None	Causes mild to severe irritation to the eyes. Prolonged exposure may cause burn if not flushed with water. May cause mild irritation to skin. Prolonged exposure may cause burn if not flushed with water.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Table 3: BFB Criteria

Mass	Ion Abundance Criteria
50	15.0-40.0% of mass 95
75	30.0-80.0% of mass 95
95	base peak, 100% relative abundance
96	5.0-9.0% of mass 95*
173	less than 2.0% of mass 174
174	50.0-120.0% of mass 95
175	5.0-9.0% of mass 174
176	95.0-101% of mass 174
177	5.0-9.0% of mass 176

***-** All ion abundances must be normalized to m/z 95, the nominal bas peak, even though the ion abundance of m/z 174 may be up to 120% that of m/z 95

Table 4: Surrogate: Internal Standard Group Assignment and Recovery and Accuracy Limits

DMC	MZ1	MZ2	MZ3	ISTD Group *	Water		Soil	
					Lower	Upper	Lower	Upper
Vinyl chloride-d3	65	67		1	65	131	68	122
Chloroethane-d5	69	71	51	1	71	131	61	130
1,1-Dichloroethene-d2	63	98	65	1	55	104	45	132
2-Butanone-d5	46	71		1	49	155	20	182
Chloroform-d	84	86	47	1	78	121	72	123
Benzene-d6	84	82		2	77	124	80	121
1,2-Dichloroethane-d4	65	67	51	1	78	129	79	122
1,4-Dioxane-d8**	96	51	66	1	50	150	50	150
1,2-Dichloropropane-d6	67	65	46	2	79	124	74	124
Toluene-d8	98	100	42	2	77	121	78	121
trans-1,3-Dichloropropene-d4	79	81	42	2	73	121	72	130
2-Hexanone-d5	63	46		2	28	135	17	184
1,1,2,2-Tetrachloroethane-d2	84	86		2	73	125	56	161
1,2-Dichlorobenzene-d4	152	150		3	80	131	70	131

*ISTD 1 – 1,4-Difluorobenzene, ISTD 2 – Chlorobenzene-d_5, ISTD 3 – 1,4-Dichlorobenzene-d_4

** Limits for 1,4-Dioxane-d_8 are advisory only

Table 5: Matrix Spike Recovery, Accuracy and Precision Limits (Advisory)

	Water			Soil		
Compound	**Lower**	**Upper**	**RPD**	**Lower**	**Upper**	**RPD**
1,1-Dichloroethene	61	145	0-14	59	172	0-22
Benzene	76	127	0-11	66	142	0-21
Trichloroethene	71	120	0-14	62	137	0-24
Toluene	76	125	0-13	59	139	0-21
Chlorobenzene	75	130	0-13	60	133	0-21

Table 6: Calibration Criteria

Compound	Minimum RRF ICAL & Opening CCV	Maximum %RSD ICAL	Maximum %D Opening CCV	Minimum RRF Closing CCV	Maximum %D Closing CCV
Dichlorodifluoromethane	0.010	40	40	0.010	50
Chloromethane	0.010	40	40	0.010	50
Vinyl chloride	0.100	20	25	0.010	50
Bromomethane	0.100	20	25	0.010	50
Chloroethane	0.010	40	40	0.010	50
Trichlorofluoromethane	0.010	40	40	0.010	50
1,1-Dichloroethene	0.100	20	25	0.010	50
1,1,2-Trichloro-1,2,2-trifluoroethane	0.010	40	40	0.010	50
Acetone	0.010	40	40	0.010	50
Carbon disulfide	0.010	40	40	0.010	50
Methyl acetate	0.010	40	40	0.010	50
Methylene chloride	0.010	40	40	0.010	50
trans-1,2-Dichloroethene	0.010	40	40	0.010	50
Methyl-t-butyl ether	0.010	40	40	0.010	50
1,1-Dichloroethane	0.200	20	25	0.010	50
cis-1,2-Dichloroethene	0.010	40	40	0.010	50
2-Butanone	0.010	40	40	0.010	50
Bromochloromethane	0.050	20	25	0.010	50
Chloroform	0.200	20	25	0.010	50
1,1,1-Trichloroethane	0.100	20	25	0.010	50
Carbon tetrachloride	0.100	20	25	0.010	50
Cyclohexane	0.010	40	40	0.010	50
Benzene	0.400	20	25	0.010	50
1,2-Dichloroethane	0.100	20	25	0.010	50
1,4-Dioxane	0.0050	50	50	0.0050	50
Trichloroethene	0.300	20	25	0.010	50
Methylcyclohexane	0.010	40	40	0.010	50
1,2-Dichloropropane	0.010	40	40	0.010	50
Bromodichloromethane	0.200	20	25	0.010	50

Compound	Minimum RRF ICAL & Opening CCV	Maximum %RSD ICAL	Maximum %D Opening CCV	Minimum RRF Closing CCV	Maximum %D Closing CCV
cis-1,3-Dichloropropene	0.200	20	25	0.010	50
4-Methyl-2-pentanone	0.010	40	40	0.010	50
Toluene	0.400	20	25	0.010	50
trans-1,3-Dichloropropene	0.100	20	25	0.010	50
1,1,2-Trichloroethane	0.100	20	25	0.010	50
Tetrachloroethene	0.100	20	25	0.010	50
2-Hexanone	0.010	40	40	0.010	50
Dibromochloromethane	0.100	20	25	0.010	50
1,2-Dibromoethane	0.010	40	40	0.010	50
Chlorobenzene	0.500	20	25	0.010	50
Ethylbenzene	0.100	20	25	0.010	50
m,p-Xylene	0.300	20	25	0.010	50
o-Xylene	0.300	20	25	0.010	50
Styrene	0.300	20	25	0.010	50
Bromoform	0.050	20	25	0.010	50
Isopropylbenzene	0.010	40	40	0.010	50
1,1,2,2-Tetrachloroethane	0.300	20	25	0.010	50
1,3-Dichlorobenzene	0.600	20	25	0.010	50
1,4-Dichlorobenzene	0.500	20	25	0.010	50
1,2-Dichlorobenzene	0.400	20	25	0.010	50
1,2-Dibromo-3-chloropropane	0.010	40	40	0.010	50
1,2,4-Trichlorobenzene	0.200	20	25	0.010	50
1,2,3-Trichlorobenzene	0.200	20	25	0.010	50
Vinyl Chloride-d3	0.010	20	25	0.010	50
Chloroethane-d5	0.010	40	40	0.010	50
1,1-Dichloroethene-d2	0.010	20	25	0.010	50
2-Butanone-d5	0.010	40	40	0.010	50
Chloroform-d	0.010	20	25	0.010	50
Benzene-d6	0.010	20	25	0.010	50
1,2-Dichloroethane-d4	0.010	20	25	0.010	50
1,4-Dioxane-d8	0.0050	50	50	0.0050	50
1,2-Dichloropropane-d6	0.010	40	40	0.010	50
Toluene-d8	0.010	20	25	0.010	50
trans-1,3-Dichloropropene-d4	0.010	20	25	0.010	50
2-Hexanone-d5	0.010	40	40	0.010	50
1,1,2,2-Tetrachloroethane-d2	0.010	20	25	0.010	50
1,2-Dichlorobenzene-d4	0.010	20	25	0.010	50

Table 7: Volatiles Raw Data and Forms Reporting Order

Section	Order of Forms and Raw Data Required
Quality Control (QC) Summary	Dueterated Monitoring Compound (DMC) Recovery (Form II VOA-1, VOA-2, VOA-3, VOA-4 or VOA-SIM1, VOA-SIM2).
	Matrix Spike/Matrix Spike Duplicate Recovery (Form III VOA-1, VOA-2). *Not required for SIM analysis.*
	Method Blank Summary (Form IV VOA, VOA - SIM). *Forms arranged in chronological order by data of analysis of method blank and by instrument.*
	GC/MS Instrument Performance Check (Form V VOA). *Forms arranged in chronological order by instrument.*
	Internal Standard Area and RT Summary (Form VIII VOA, VOA-SIM). *Forms arranged in chronological order by instrument.*
Supportive Documentation	Arrange sample data forms and raw data in the following order of increasing EPA sample number, considering both letters and numbers. 1. Target Compound Results (Form I VOA-1, VOA-2) followed by Tentatively Identified Compounds (Form I VOA-TIC). 2. Reconstructed Total Ion Chromatogram 3. Quantitation reports of raw data 4. Copies of the compound spectra. 5. Copies of mass spectra for each TIC. 6. EICP of quantitation ion displaying compound peak before and after manual integrations.
Standard Data	Arrange forms and raw data of standards in the following order; calibration standards by instrument in chronological order followed by the opening and closing standards by instrument in chronological order. 1. Target Compound Results (Form VI VOA-1, VOA-2, VOA-3, VOA-SIM) 2. Reconstructed Total Ion Chromatogram 3. Quantitation reports of raw data 4. Copies of the compound spectra. 5. Copies of mass spectra for each TIC. 6. EICP of quantitation ion displaying compound peak before and after manual integrations.
Raw QC Data	Instrument Performance Check (Form V VOA) in chronological order by instrument.
	Arrange forms and raw data for blanks by blank type and in chronological order by instrument. 1. Target Compound Results (Form I VOA-1, VOA-2) followed by Tentatively Identified Compounds (Form I VOA-TIC). 2. Reconstructed Total Ion Chromatogram 3. Quantitation reports of raw data

Section	Order of Forms and Raw Data Required
	4. Copies of the compound spectra. 5. Copies of mass spectra for each TIC. 6. EICP of quantitation ion displaying compound peak before and after manual integrations.
	Arrange MS/MSD forms and raw data in the following order of increasing EPA sample number, considering both letters and numbers. *Not required for SIM analysis*. 1. Matrix Spike/Matrix Spike Duplicate Data (Form I VOA-1, VOA-2) 2. Reconstructed Total Ion Chromatogram 3. Quantitation reports of raw data 4. EICP of quantitation ion displaying compound peak before and after manual integrations.
Miscellaneous	Place ETR worksheets, data review narrative, manual integration summary reports signed and dated by primary and secondary reviewers, copies of NCRs, copies of run logs and preservation logs, and screen data on top of the VOA data package to be given to report management.

Appendix A: Standard Preparation Tables

This appendix provides formulations for the standard solutions used in this procedure and are accurate only when the specified concentrations and volumes are used. Any time the volume or concentration or of any of the components change, the analyst must adjust the preparation accordingly. In general, stock standard solutions of a known purity and/or concentration are purchased from commercial vendors and diluted in an appropriate solvent to the desired concentration. The prepared standard solutions are stored and maintained at the appropriate conditions and are discarded when the expiration date has expired. Expiration dates shall be assigned to the prepared standard solution as specified in Section 7.2 of this SOP. The preparation of all standard solutions must be documented in a logbook designated for that purpose and all standard solutions must be labeled according to the laboratory SOP for standard preparation.

Instrument Performance Check Solution (BFB)

Component	Vendor	Catalog #	Concentration (ug/mL)	Volume Added (uL)	Final Concentration (ug/mL)
Tuning Mix	Restek	30003	5000	125	25
P& T Methanol	Omni Solv	NA	NEAT	24875	
			Final Volume	***25000 uL***	

Calibration Mix

Component	Vendor	Catalog #	Concentration (ug/mL)	Volume Added (uL)	Final Concentration (ug/mL)
OLC VOA Mega Mix	Restek	30492	2000	200	100
VOA Ketones	Restek	30006	5000	160	200
Gases	Restek	30042	2000	200	100
DMC Non-Ketone	Cambridge Isotope	ES-528610X	1000	400	100
DMC Ketone	Cambridge Isotope	ES-528710X	5000	160	200
P& T Methanol	Omni Solv	NA	NA	2880	NA
			Final Volume	***4000 uL***	

1,4-Dioxane Calibration Mix

Component	Vendor	Catalog #	Concentration (ug/mL)	Volume Added (uL)	Final Concentration (ug/mL)
1,4-Dioxane	Restek	30287	4000	1000	2000
1,4-Dioxane-d8	Cambridge Isotope	ES-528810X	12500	320	2000
P&T Methanol	Omni Solv	NA	NA	680	NA
			Final Volume	***2000 uL***	

DMC Mix

Component	Vendor	Catalog #	Concentration (ug/mL)	Volume Added (uL)	Final Concentration (ug/mL)
DMC Non-Ketone	Cambridge Isotope	ES-528610X	1000	400	100
DMC Ketone	Cambridge Isotope	ES-528710X	5000	160	200
DMC 1,4 Dioxane-d8	Cambridge Isotope	ES-528810X	12500	640	2000
P&T Methanol	Omni Solv	NA	NA	2640	NA
			Final Volume	***4000 uL***	

Internal Standard Solution (ISTD)

Component	Vendor	Catalog #	Concentration (ug/mL)	Volume Added (uL)	Final Concentration (ug/mL)
LC VOA ISTD Mix	Restek	30091	2500	160	100
P&T Methanol	Omni Solv	NA	NA	3840	NA
			Final Volume	***4000 uL***	

Matrix Spike Solution (MS)

Component	Vendor	Catalog #	Concentration (ug/mL)	Volume Added (uL)	Final Concentration (ug/mL)
VOA Matrix Spike Mix	Restek	30005	2500	80	100
P&T Methanol	Omni Solv	NA	NA	1920	NA
			Final Volume	***2000 uL***	

Calibration Standard, QC & Sample Preparation Table Summary

SOM Low-Water and Medium-Level Soils in 44 mL

Sample Type	Final Concentration (ppb)	CAL MIX (100 ppm)	1,4-Dioxane Cal Mix (2000 ppm)	ISTD (100 ppm)	DMC (100 ppm)	MS (100 ppm)
CAL Level 1	5	2.2 uL	2.2 uL	22 uL	NA	NA
CAL Level 2	10	4.4 uL	4.4 uL	22 uL	NA	NA
CAL Level 3 / CCV	50	22 uL	22 uL	22 uL	NA	NA
CAL Level 4	100	44 uL	44 uL	22 uL	NA	NA
CAL Level 5	200	88 uL	88 uL	22 uL	NA	NA
MS/MSD	50	NA		22 uL	22 uL	22 uL
Samples & Blank	NA	NA		22 uL	22 uL	NA

Prepare HCl preserved VOA vials

SOM Low- Soil in 5 mL

Sample Type	Final Concentration (ppb)	CAL MIX (100 ppm)	1,4-Dioxane Cal Mix (2000 ppm)	ISTD (100 ppm)	DMC (100 ppm)	MS (100 ppm)
CAL Level 1	5	Footnote$_1$	Footnote$_1$	Footnote$_1$	NA	NA
CAL Level 2	10	0.5 uL	0.5 uL	0.5 uL	NA	NA
CAL Level 3 / CCV	50	2.5 uL	2.5 uL	2.5 uL	NA	NA
CAL Level 4	100	5 uL	5 uL	5 uL	NA	NA
CAL Level 5	200	10 uL	10 uL	10 uL	NA	NA
MS/MSD	50	NA		2.5 uL	2.5 uL	2.5 uL
Samples & Blank	NA	NA		2.5 uL	2.5 uL	NA

1: Prepare calibration level 1 in 44 mL and transfer 5 mL to a new vial for analysis.

Appendix B: Equations

Relative Response Factor (RRF) Calculation

$$RRF = \frac{(A_x)(C_{is})}{(A_{is})(C_x)}$$

Where:
Ax=Area of quantification mass EICP of compound to be measured
A_{is}= Area of quantification mass EICP of associated internal standard
C_{is}=Concentration of internal standard
C_x=Concentration of compound to be measured

Standard Deviation (SD) Calculation

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (X_i - \overline{X})^2}{(n-1)}}$$

Where:
X_i=Each value used to calculate the mean
X= The mean of n values
n=Total number of values

Percent Relative Standard Deviation (%RSD) Calculation

$$\%RSD = \frac{SD_{RRF}}{\overline{X}} X100$$

Where:
SD_{RRF}=Standard Deviation of the initial calibration response factors for each compound.
X= Mean value of the initial calibration response factors for each compound.

Mean Relative Response Factor (RRF) Calculation

$$\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

Where:
X_i=Each RRF value per compound
X= The mean of n values
n=Total number of values

Percent Difference (%D) Calculation

$$\%\text{Difference} = \frac{RRF_c - \overline{RRF_i}}{RRF_i} X100$$

Where:
RRF_c=Relative Response Factor from current CCV standard
RRF_i=Mean relative response factor from most recent initial calibration

Water Sample Concentration

$$C_x = \frac{(A_x)(I_s)(DF)}{(A_{is})(\overline{RRF})(V_o)}$$

Where:
C_x = Concentration of compound (µg/L)
I_{is} = Concentration of associated internal standard (µg/L).
DF = Dilution Factor.
A_{is} = Area of quantification ion for associated internal standard.
A_x = Area of quantification ion for compound.
RRF = Relative Response Factor from the initial calibration standard
V_0 = actual volume purged (mL).

Low-Level Soil Concentration

$$C_x = \frac{(A_x)(I_s)(DF)}{(A_{is})(\overline{RRF})(W_s)(D)}$$

Where:
C_x = Concentration of compound (µg/Kg dry weight).
A_x = Area of quantitation ion for compound.
I_{is} = Concentration of associated internal standard (µg/L).
A_{is} = Area of quantification ion for associated internal standard.
RRF = Relative Response Factor from the initial calibration standard.
W_s= Weight of sample added to purge vessel (g).
DF = Dilution Factor.

$$D = \frac{100 - \%\text{Moisture}}{100}$$

Medium Level Soil Concentration

$$C_x = \frac{(A_x)(I_s)(AV_t)(1000)(DF)}{(A_{is})(\overline{RRF})(V_a)(W_s)(D)}$$

Where:
C_x = Concentration of compound (µg/Kg dry weight).
A_x = Area of quantification ion for compound.
I_{is} = Concentration of associated internal standard (µg/L).
AV_t=Adjusted extract volume

$AV_t=V_t+(W_s-(W_s \times D))$

(V_t=Initial volume of methanol extract before correction, typically 5.0 or 10.0 mL)

A_{is} = Area of quantification ion for associated internal standard.
RRF = Relative Response Factor from the initial calibration standard.
V_a=sample extract aliquot volume (uL)
W_s= Weight of sample added to purge vessel (g).
DF = Dilution Factor.

$$D = \frac{100 - \%\text{Moisture}}{100}$$

DMC Percent Recovery Calculation

$$\%R = \frac{Q_d}{Q_a} X100$$

Where:
Q_d = Concentration or amount determined by analysis.
Q_a = Concentration or amount added to sample/blank.

Matrix Spike/Matrix Spike Duplicate Recovery

$$\text{MatrixSpikeRecovery} = \frac{SSR - SR}{SA} x100$$

Where,
SSR = Spiked Sample Result
SR = Sample Result
SA = Spike Added

Matrix Spike/Matrix Spike Duplicate RPD

$$RPD = \frac{|MSR - MSDR|}{1/2(MSR + MSDR)} x100$$

Where,
MSR = Matrix Spike Recovery
MSDR = Matrix Spike Duplicate Recovery

Appendix C: List of Definitions

BAR GRAPH SPECTRUM: a plot of the mass-to-charge ratio (m/e) versus relative intensity of the ion current.

BLANK - an analytical sample designed to assess specific sources of laboratory contamination.

BFB-compound chose to establish mass spectral instrument performance for volatile analysis.

EXTRACTION ION CURRNE PROFILE (EICP)-a plot of ion abundance versus time (or scan number) for ion(s) of specified mass(es).

INITIAL CALIBRATION - analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the mass spectrometer or electron capture detector to the target compounds.

INTEGRATION SCAN RANGE-the scan number of the scan at the beginning of the area of integration to the scan number at the end of the area of integration.

INTEGRATION TIME RANGE-the retention time at the beginning of the area of integration to the retention time at the end of the area of integration.

INTERNAL STANDARDS- compound added to every standard, blank, matrix spike, matrix spike duplicate, sample (volatiles) and sample extract (semivolatiles) at a known concentration prior to analysis. Internal standards are used as the basis for quantitation of target compounds.

MATRIX SPIKE - aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

MATRIX SPIKE DUPLICATE - a second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

METHOD BLANK - an analytical control consisting of all reagents, internal standards, and deuterated monitoring compounds, that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background, and reagent contamination.

PERCENT DIFFERENCE (%D) - as used in this SOW and elsewhere to compare two values, the percent difference indicates both the direction and the magnitude of the comparison, i.e., the percent difference may be either negative, positive, or zero.

PRIMARY QUANTITATION ION-a contract specified ion used to quantitate a target analyte.

RECONSTRUCTED ION CHROMATOGRAM (RIC)-a mass spectral graphical representation of the separation achieved by a gas chromatograph; a plot of total ion current versus retention time.

RELATIVE PERCENT DIFFERENCE (RPD) - as used in this SOW and elsewhere to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero. In contrast, see percent difference.

RELATIVE RESPONSE FACTOR (RRF)-a measure of the relative mass spectral response of an analyte compared to its internal standard.

RELATIVE RETENTION TIME (RRT) - the ratio of the retention time of a compound to that of a standard (such as an internal standard).

RESPONSE - or Instrumental Response: a measurement of the output of the GC detector (MS, EC, or FID) in which the intensity of the signal is proportionate to the amount (or concentration) detected. Measured by peak area or peak height.

RETENTION TIME (RT) - the time a target analyte is retained on a GC column before elution. The identification of a target analyte is dependent on a target compound's retention time falling within the specified retention time window established for that compound. Retention time is dependent on the nature of the column's stationary phase, column diameter, temperature, flow rate, and other parameters.

DEUTERATED MONITORING COMPOUND (DMCs) - added to every blank, sample, matrix spike, matrix spike duplicate, and standard; used to evaluate analytical efficiency by measuring recovery. DMCs are brominated, fluorinated, or isotopically labeled compounds not expected to be detected in environmental media.

Title: SVOCs by GC/MS and GC/MS SIM (CLP SOM01.2)

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1.0 Scope and Application

This SOP describes the laboratory procedure used to analyze samples from hazardous waste sites for the determination of semivolatile organic compounds (SVOCs) by Gas Chromatography with Mass Spectrometer (GC/MS) and GC/MS using Selected Ion Monitoring (SIM).

This SOP is applicable to the instrument procedure. Procedures for extraction and extract cleanup are described in separate SOPs.

1.1 Analytes, Matrices, and Reporting Limits

This procedure may be used for a variety of matrices including: water, soil, and sediment.

The list of target compounds that can be determined from this SOP along with the Contract Required Quantitation Limit (CRQL) are provided in Table 1. This SOP has been modified from the EPA SOW to provide for full scan analysis of 1,4 Dioxane.

The EPA has documented the following problems associated with the following compounds analyzed by this procedure:

- Dichlorobenzidine and 4-chloroaniline can be subject to oxidative losses during solvent concentration.
- Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reactions in acetone solution, and photochemical decomposition.
- N-nitrosodiphenylamine decomposes in the gas chromatograph inlet forming diphenylamine and, consequently, may be detected as diphenylamine.

2.0 Summary of Method

Soil extracts are screened to determine if the sample should be analyzed by the low-level or the medium level method and/or if samples should be analyzed by dilution. If medium level analysis is required, the extraction laboratory is notified and the samples are re-extracted by the medium level extraction procedure.

Extracts are prepped for analysis with the addition of internal standards then 2 uL of extract is injected onto a GC system which uses a temperature program to separate the target compounds which are then detected by a mass spectrometer (MS). Target analytes are identified by comparison of their mass spectra with the electron impact (or electron impact-like) spectra of standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard. Non-target analytes are identified by comparing their mass spectra to mass spectra contained in a mass spectral library and quantiated by comparing the mass spectra response from the reconstructed ion chromatogram to the mass spectra from the nearest internal standards.

If SIM is requested, full-scan analysis is performed first and if PAHs and pentachlorophenoal are detected in the full scan analysis, then SIM is not performed.

This SOP is based on the following reference methods:

- Exhibits B & D, Analytical Methods for the Analysis of Semivolatiles, USEPA CLP SOW for Organic Analysis, SOM01.1, May 2005.

- USEPA CLP SOW Clarifications to SOM01.1, November 7, 2005 and September 26, 2006.
- USEPA CLP SOW Modifications Updating SOM01.1 to SOM01.2, October 5, 2006 (Updated 02-12-2007) Amended 04-11-2006.
- Section 8.3.4 General Analytical Requirements NJDEP USEPA Contract, Laboratory Program Analysis.

3.0 Definitions

A list of terms and definitions are provided in Appendix A.

4.0 Interferences

Contaminants in solvents, reagents, glassware, and other sample processing hardware may cause method interferences such as discrete artifacts and/or elevated baselines. All of these materials routinely must be demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks.

When using the SIM technique, carryover contamination from the injection port is especially problematic due to increased sensitivity, and routine injection port, guard column and chromatographic column maintenance should be performed to ensure that the analytical system is free of any potential sources of contamination. The late eluting PAHs are particularly susceptible to carryover contamination.

Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source. The extent of the interference will vary by matrix and is minimized using the various cleanup procedures described in this SOP.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

The gas chromatograph contains zones that have elevated temperatures. The analyst must be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.2 Primary Materials Used

Table 2 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as

identified in the MSDS. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

6.0 Equipment and Supplies

Catalog numbers listed in this SOP are subject to change at the discretion of the vendor. Analysts are cautioned to be sure equipment used meets the specification of this SOP.

6.1 Miscellaneous

- Autosampler Vials, National Scientific or equivalent.

- Volumetric Syringes, Class "A" (10µl, 25µl, 50µl, 100µl, 250µl and 500µl), Hamilton or equivalent.

6.2 Analytical System

- Gas Chromatograph: Hewlett-Packard 5890 Series II equipped with CTC, HP7673 injector, Hp7683B injector or equivalent autosampler, injection port for split/splitless analysis, and all the required accessories, including syringes, septa, injection port liners, and column.

- Mass Spectrometer: Hewlett-Packard 5971 MSD, 5972 MSD, 5973 MSD, 5975 MSD capable of operating in full scan and SIM mode.

- Primary Column: Restek Rxi-5ms 30m x 0.25mm x .25 um, or equivalent

- Data System: Hewlett-Packard ChemStation. Data Processing - Hewlett-Packard 9000-series computers, HP 9000 K200 (Chemsvr5)/ HP-UX 10.20HP Chemsystem Unix based computer. ThruPut Target 3.5 Data Processing Software.

7.0 Reagents and Standards

7.1 Reagents

- Acetone: Pesticide Residue Analysis Grade, JT Baker or equivalent.
- Methanol: Pesticide Residue Analysis Grade, JT Baker or equivalent.
- Methylene Chloride: Pesticide Residue Analysis Grade, JT Baker or equivalent.
- Iso-octane: Pesticide Residue Analysis Grade, JT Baker or equivalent.
- 2-Propanol: Pesticide Residue Analysis Grade, JT Baker or equivalent.
- Toluene: Pesticide Residue Analysis Grade, JT Baker or equivalent.

7.2 Standards

Purchase stock standard solutions from commercial vendors and from these prepare calibration and working standards by diluting a known volume of stock standard in an appropriate solvent to the final volume needed to achieve the desired concentration. The recommended formulation for each standard used in this procedure is provided in Appendix B along with the recommended source materials, expiration dates and storage conditions.

Store standard solutions 4°C (± 2°C) in Teflon-lined screw cap amber bottles and unless specified, prepare fresh standards every twelve months. Protect all standards from light and store samples, sample extracts and standards separately.

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection so these procedures are not included in this SOP.

Extracts must be analyzed within 40 days from date sample extraction was initiated.

USEPA CLP contract samples are kept for 60 days from validation and extracts are retained for a minimum of 365 days after provision of the project report and then disposed of in accordance with applicable regulations. For all other projects, unless otherwise specified by the client, samples and extracts are retained for a minimum of 30 days after provision of the project report and then disposed of in accordance with applicable regulations.

9.0 Quality Control

9.1 Sample QC

The laboratory prepares the following quality control samples with each batch of samples.

QC Item	Frequency	Acceptance Criteria
Method Blank (MB)	1 in 20 or fewer samples	See Table 10
Matrix Spike(s) MS/MSD	Client Request	See Table 10
Sample Duplicate (SD)	Client Request	See Table 10

9.2 Instrument QC

The following instrument QC is performed:

QC Item	Frequency	Acceptance Criteria
Initial Calibration (ICAL)	Initially; when CCV fails	See Section 10
Continuing Calibration Verification (CCV)	Beginning and end of each analytical sequence	See Section 10
Tune Standard	Opens each 12-Hour window	See Section 10

10.0 Procedure

10.1 Instrument Operating Conditions

The following conditions are recommended. Other conditions may be used provided that all technical criteria are met. Once the operating conditions are established from the instrument performance check standard (DFTPP) the same conditions must be used for instrument calibration, and the same conditions used for instrument calibration must be used for all standards, samples, MS/MSD and blanks associated to the calibration.

Gas Chromatograph (GC):

Initial Column Conditions:	35ºC for 2 minutes.
Column Temperature:	35ºC to 320ºC at 14º/min.
Final Temperature:	320ºC for 5.6 min, or until Benzo(g,h,i)perylene has eluted
Injector Temperature:	225ºC
Transfer Line Temperature:	300ºC
Injector:	Grob-like, splitless
Sample volume:	2µL
Carrier Gas:	Helium

Mass Spectrometer (MS):

Electron Energy:	70 volts
Mass Range:	35-500 amu
Scantime:	Not to exceed 1 second per scan

SIM Operating Conditions:

Column Temperature:	45ºC to 320ºC at 12º/min.
Final Temperature:	320ºC until Benzo(g,h,i)perylene has eluted
Injector Temperature:	225ºC
Transfer Line Temperature:	300ºC
Injector:	Grob-like, splitless
Sample volume:	2µL
Carrier Gas:	Helium

10.2 GC/MS Instrument Performance Check (Tune/DFTPP)

Analyze the instrument performance check solution (DFTPP) at the beginning of each 12 hour time period to start the analytical window. The 12 hour click begins at the time of injection of the DFTPP analysis. For SIM mode, analysis of the DFTPP is optional. For SIM, the time-frame of the analytical window is established by the injection time of the first calibration standard or the first CCV when calibration is not performed.

Prepare the DFTPP using the formulation given in Appendix A. Transfer some of the standard to an autosampler vial. Analyze the DFTPP using the procedure that begins in section 10.7. Inject 2 uL of the 25 ng/uL solution to provide an on-column concentration of 50 ng/uL.

The data processing system is set to acquire the mass spectrum as follows: average three spectral points (the apex scan, the scan prior to the apex, and the scan immediately following the apex), and to perform background subtraction using a single scan acquired no more than 20 scans prior to the elution of the DFTPP.

Review the results against the abundance criteria provided in Table 3. If criteria are not met, perform instrument maintenance as necessary and re-tune the instrument system. Do not proceed with analysis until criteria are met.

10.3 Initial Calibration (ICAL)

After successful analysis of the DFTPP standard calibrate the instrument with a minimum of five concentrations for each target analyte. Repeat initial calibration when corrective actions that

affect the calibration criteria has occurred (e.g. ion source cleaning, repair, column replacement) or when continuing calibration acceptance criteria are not met.

Prepare the intermediate and working calibration standards using the formulations given in Appendix A. If using already prepared solutions, let them warm to room temperature before use. Transfer an amount of the working calibration standard to an autosampler vial and analyze the calibration standards using the procedure that begins in section 10.7. Inject 2 uL of each calibration standard onto the instrument.

NOTE: The working calibration standard formulation includes the addition of DMC and internal standards. A 2 uL injection provides for an on-column internal standard concentration of 20 ng/uL.

The data processing system calculates the relative response factors (RRF) for each target and DMC. For internal standards the primary ion is used unless interference is present in which case the secondary ion(s) is used. See Table 4 for internal standard associations. The data system also calculates the mean relative response factor for all compounds and the % relative standard deviation (%RSD) of the RRF values for the initial calibration. Equations for the calculations can be found in Appendix C.

Review the results against the following criteria. If criteria are not met, troubleshoot the problem, perform instrument maintenance as necessary or take other corrective actions as needed and reanalyze the calibration standards.

- The RRF at each calibration concentration for each target compound and DMC should be greater than or equal to the compound's minimum acceptable RRF listed in Table 7.

- The %RSD of the RRFs over the initial calibration range for each target compound and DMC that has a required %RSD should be less than or equal to the %RSD listed in Table 7. For full scan analysis, up to four target compounds may fail to meet criteria listed in Table 7. However, these four compounds must meet a minimum RRF criterion of 0.010 and have a %RSD less than or equal to 40 percent. For SIM analysis, up to two compounds may fail to meet criteria listed in Table 7. However, these 2 compounds must meet a minimum RRF criterion of 0.010 and have a %RSD less than or equal to 40 percent.

- Excluding those ions in the solvent front, no quantification ion may saturate the detector.

If criteria are met and if time remains in the 12-hour time period samples may be analyzed without continuing calibration verification (CCV). If time does not remain, begin a new analytical sequence by analysis of a DFTPP followed by a CCV.

10.4 Calibration Verification (CCV)

Analyze a CCV (opening CCV) immediately after the DFTPP standard, except in 12 hour window that includes ICAL, in which case, an opening CCV is not required. Analyze a closing CCV using the same standard as the opening CCV before the end of the 12-hour analytical window.

NOTE: The CLP SOW allows a closing CCV to be used as an opening CCV it the acceptance criteria for the opening CCV are met. In this scenario, a DFTPP is not required and the next 12-hour window begins at the injection time of the closing CCV.

Prepare the CCV standard at the mid level concentration of the ICAL using the formulation specified in Appendix B. Transfer a portion of prepared standard to an autosampler vial for each CCV. Analyze the CCV in the analytical sequence as specified in Section 10.7. Inject 2 uL of the standard onto the instrument.

NOTE: The working calibration standard formulation includes the addition of DMC and internal standards. A 2 uL injection provides for an on-column internal standard concentration of 20 ng/uL.

The data system calculates the relative response factors (RRF) for each target and DMC using the primary characteristic ions found in Table 5 and Table 6. For internal standards the primary ion is used unless interference is present in which case the secondary ion(s) is used. The data system also calculates the %D between the continuing calibration relative response factor and the most recent initial calibration mean relative response factor for each target and DMC. The equations for the above calculations can be found in Appendix C.

Review the results against the following criteria. If criteria are not met, troubleshoot the problem, perform instrument maintenance as necessary or take other corrective actions as needed. If the opening CCV criteria are not met, recalibrate. If the closing CCV are not met, reanalyze all samples QC and field samples in the analytical window.

Opening CCV:

- The RRF for each target compound and DMC should be greater than or equal to the compound's minimum acceptable RRF listed in Table 7. Up to four target compounds and DMCs, excluding those with minimum RRF requirements of 0.010 may fail to meet criteria but these compounds must still meet the maxium %D requirements of ± 40%.

- The RRF percent difference for each target compound and DMC must be within the inclusive range listed in Table 7.

- Excluding ions in the solvent front, no quantification ion may saturate the detector.

- SIM: Up to two target compounds and DMCs excluding those with minimum RRF requirements of 0.010 may fail to meet criteria but these compounds must still meet the minimum RRF requiements of 0.010. Up to two target compounds and DMCs, excluding those with maximum %D requirements of ± 40% may fail criteria but those compounds must still meet the maximum %D requirements of ± 40%.

Closing CCV:

- The RRF for each target compound and DMC must be greater than or equal to 0.010.

- The RRF percent difference for each target compound must be in the inclusive range of ±50.

- Excluding ions in the solvent front, no quantification ion may saturate the detector.

- SIM: All criteria must be met.

10.5 Troubleshooting

- Benzidine is subject to oxidative loss during extraction and chromatographs poorly, injection port and/or column maintenance may be required.

- Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet, injection port and/or column maintenance may be required.

- N-nitrosodiphenylamine decomposes in the inlet and cannot be separated from diphenylamine. Compound is reported as N-nitrosodiphenylamine.

- 1,2-Diphenylhydrazine decomposes to Azobenzene in the analytical portion of the procedure and as such is reported as Azobenzene.

- Acid compounds are subject erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material, injection port and/or column maintenance may be required.

- Loss of sensitivity for higher boiling compounds and internal standards may be indicative of a leak at the inlet. Replace septa and/or re-tighten lower inlet connection.

- Carryover contamination may indicate empty rinse vials.

10.6 Sample Preparation

10.6.1 Screen Analysis

Waters and Soil extracts may be screened at the discretion of the laboratory to determine if dilution is needed and/or samples that are over calibration range require dilution and soils are always screened to determine with level extraction method is required.

10.6.2 Sample Dilutions

Use the results of the original or screen analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range. The dilution factor chosen should keep the concentration of the largest peak for a target compound in the upper half of the calibration range of the instrument. Do not submit data for more than two analyses, i.e., the original sample extract and one dilution, or if the samples were screened, from the most concentrated dilution analyzed and one further dilution. The maximum dilution factor permitted for low level soils is 30. If a low level soil requires a dilution factor greater than 30 in order to bring target compounds within calibration range, then the medium level method shall be used.

10.6.3 Internal Standard Addition

Add a sufficient amount of internal standard to each extract to result in an on-column concentration of 20 ng/uL for full-scan analysis or 0.2 ng/uL for SIM. If samples require dilution, add the internal standard solution after dilution.

10.7 Analysis

10.7.1 Analytical Sequence

Load the extracts and standards into the autosampler and enter the sample ID's into the data acquisition program in the same order that the extracts and standards were placed in the autosampler.

Example Analytical Sequence:

Full Scan ICAL Sequence

Injection #	Calibration Standard	EPA Sample Number
1	DFTPP Tune	DFTPP##
2	ICAL #1	SSTD080
3	ICAL #2	SSTD040
4	ICAL #3	SSTD020
5	ICAL #4	SSTD010
6	ICAL #5	SSTD005
7	SBLK ##	Method Blank ##
8 - ?	Samples	
	CCVC	SSTD020

SIM ICAL Sequence

Injection #	Calibration Standard	EPA Sample Number
1	ICAL #1	SSTD001
2	ICAL #2	SSTD0.8
3	ICAL #3	SSTD0.4
4	ICAL #4	SSTD0.2
5	ICAL #5	SSTD0.1
6	SBLK##	Method Blank ##
7 -?	Samples	Samples
	CCVC	SSTD800

11.0 Calculations / Data Reduction

11.1 Qualitative Identification

Target Compounds

The data system identfies target compounds by comparing the sample mass spectrum to the reference standard of the suspected compound. The compound is present if the elution of the sample analyte is within the relative retention time window established from the continuing calibration verification standard and if the sample analyte and calibration standard component mass spectra correspond. The RRT of the sample component should compare within ±0.06 RRT units of the RRT standard component. If samples were analyzed immediately following the initial calibration, the analyte retention times are compared to the mid point calibration standard. For target analytes the spectra generated from the working calibration standard is used as the primary spectral reference.

The requirements are as follows:

- All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.

- The relative intensities of these ions should agree within plus or minus 20% between the standard and sample spectra.

- Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be verified and reported to favor false positives. If the concentration is less than the CRQL but the spectrum meets identification criteria, manually apply a "J" flag.

- If a compound cannot be verified by all of the above criteria, but in the technical judgment of the mass spectra interpretation of the analyst, the identification is considered correct, report the compound.

Non-Target Compounds (Full-Scan Only)

Perform a library search for non-target compounds using the NIST spectral library and report up to 30 non-alkane Tentatively Identified Compounds (TICS) of greatest apparent concentration, excluding the internal standard compounds, DMCs and target compounds. Do not report carbon dioxide and compounds with responses less than 10% of the internal standard in which they are quantified as part of the 30 TIC count.

Report peaks that are tentatively identified as straight-chain, branched, or cyclic alkanes, and are alone or part of alkane series as "Total Alkanes". Sum the concentration of each alkane and report "Total Alkanes" as a single result. Do not include alkanes in the count of TICs described earlier.

Search for, count and report peaks that are suspected to be aldol-condensation reaction products as part of the 30 most intense non-target compounds. Qualify these products with an "A" flag on the deliverable form.

Use the following guidelines for making tentative identification:

- Compounds with a library search match of 85% or higher should be considered "probable match" and reported unless there is sound technical basis not to do so. If the search produces more than one compound with greater than 85% match, report the TIC with the higher percent match. If the search produces a series of obvious isomer compound with matches greater than 8%, reporte the compound with the highest library match. Any analyst decision not report a TIC that meets these criteria must be documented with a nonconformance memo (NCM) and the reason for the analyst rejection of the match included in the project narrative.

- If no valid tentative identification can be made, the compound is reported as "unknown". Additional characterization can be made according to groups or classes. (e.g. "unknown aromatic compound", "unknown chlorinated compound", etc).

Do not report the following:

- Compounds with responses less than 10 percent of the internal standard.

- Compounds that elute earlier than 30 seconds before the first compound or three minutes after the last target compound listed in Table 1.
- Volatile compounds.

11.2 Quantitative Identification

Target compounds are quantified by the internal standard method. The internal standard used is the one assigned to that analyte for quantification as specified in Table 4. The EICP area of the primary characteristic ions of analytes listed in Tables 5 and Table 6 are used for quantification.

Use the relative response factor (RRF) from the continuing calibration analysis to calculate the concentration in the sample using the equations given in Appendix C. For samples analyzed in the same 12-hour window as the initial calibration standards use the RRF value from the 40ng standard. Use secondary ion quantification only when there is sample interference from the primary ion. If secondary ion quantification is performed, note the reason in the project narrative.

An estimated concentration for non-target compounds is generated using the internal standard method by using the nearest internal standard free of interferences. The equations for calculation of concentration are given in Appendix B. Total area counts from the total ion chromatograms are used for both the internal standard and the compound to be measured. Assume a relative response factor of 1 and qualify the resulting concentration with a “J” and an “N” data qualifier to indicate qualitative and quantitative uncertainty.

11.3 Calculations

See Appendix C.

11.4 Data Review

11.4.1 Primary Review

Confirm qualitative and quantitative identification criteria using the criteria provided in Sections 11.1 and 11.2. If necessary, perform manual integration in accordance with laboratory SOP BR-QA-006 Manual Integration.

Upload the data files into the LIMS batch. Evaluate the results against the performance criteria given in Section 10 and Table 3 and perform corrective action as necessary. If corrective action is not taken or is not successful, initiate a NCM for every occurrence for which results are reported outside established criteria.

Evaluate the results of samples analyzed immediately after high concentration samples for signs of carry-over. Reanalyze the sample if carry over is suspected.

Dilute and reanalyze samples whose results exceed the calibration range. The diluted analysis should result in a determination within the upper half of the calibration curve.

Complete the worksheet information and set results to primary, secondary or rejected as appropriate. Add sample suffix and manually apply data qualifiers as needed. Verify QC and sample associations. Set batch to first level review.

11.4.2 Secondary Review

Verify quantitative and qualitative identification in the initial calibration standards and spot check such for ~15% of the remaining data in the batch.

If manual integrations were performed:

- Review eachintegration to verify that the integration meets the requirements for manual integration as specified in laboratory SOP BR-QA-006. If an error is suspected or found consult with the analyst that performed the integration analyst and request correction or notify the Department Manager, Technical Director or QA Manager. Do not "fix" the integration. Reintegration by a secondary data reviewer must not be performed except in limited circumstances as approved by the department supervisor or other laboratory management. If those instances where the secondary reviewer performs the integration, this person is now considered the primary analyst and each integration performed by the secondary reviewer must be subsequently reviewed by a peer analyst or the department supervisor to verify the integration is consistent and compliant with the requirements specified in laboratory SOP BR-QA-006.

- Check to ensure an appropriate technical reason code is provided for each manual integration. Acceptable technical reason codes are provided in laboratory SOP BR-QA-005.

- Print the Manual Integration Summary Report. Document your review of manual integrations on the summary report and obtain any review signatures of integrations performed during secondary review as required.

Review project documents such as the Project Plan (PP), Project Memo or any other document/process used to communicate project requirements to ensure those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Verify that the acceptance criteria for the calibration and QC items listed in Table 1 were met. If the results do not fall within the established limits verify the recommended corrective actions were performed. If not, initiate corrective actions and/or verify an NCM was created to document the criteria exception. Verify analytical results are qualified accordingly. Set samples to 2nd level review.

Run the LIMS QC Checker, investigate and correct any problems found. Run and review the deliverable. Fix any problems found then set the method chain to lab complete.

11.5 Data Reporting

The report format, application of data qualifiers and creation of the data deliverable is performed by the LIMS using the formatter set by the project manager during log-in. The LIMS formatter for CLP SOM has been programmed to comply with the reporting and deliverable specifications in the CLP SOW.

Records of electronic and hardcopy data are maintained as described in laboratory SOP BR-QA-014.

12.0 Method Performance

12.1 Method Detection Limit (MDL)

Establish an MDL for each taget compound on each instrument used for analysis using the procedures described in laboratory SOP BR-QA-005. MDLs for CLP SOW are matrix and level specific and must be verified annually.

12.2 Demonstration of Capabilities (DOC)

Perform a method demonstration of capability at initial set-up and when time there is a significant change in instrumentation or procedure.

Each analyst that performs the analytical procedure must complete an initial demonstration of capability (IDOC) prior to independent analysis of client samples. Each analyst must demonstrate on-going proficiency (ODOC) annually thereafter. DOC procedures are further described in the laboratory's quality system manual (QAM) and in the laboratory SOP BR-QA-011.

12.3 Training Requirements

Any employee that performs any portion of the procedure described in this SOP must have documentation in their employee training file that they have read this version of this SOP.

Instrument analysts, prior to independent analysis of client samples, must also have documentation of demonstration of initial proficiency (IDOC) and annual on-going proficiency (ODOC) in their employee training files.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to BR-EH-001 *Hazardous Waste*. The following waste streams are produced when this method is carried out.

- Vials containing sample extracts: Satellite container: 15 gallon bucket connected to a fume hood.
- Solvent Waste: Satellite container: 1 L glass bottle located in fume hood.

15.0 References / Cross-References

- Exhibits B & D, Semivolatiles USEPA CLP SOW for Organic Analysis, SOM01.1, May 2005.
- USEPA CLP SOW Clarifications to SOM01.1, November 7, 2005 and September 26, 2006.
- USEPA CLP SOW Modifications Updating SOM01.1 to SOM01.2, October 5, 2006 (Updated

02-12-2007) Amended 04-11-2006.

- Laboratory SOP BR-QA-005 *Determination of LOD, LOQ & RL.*
- Laboratory SOP BR-QA-003 *Document Control.*
- Laboratory SOP BR-QA-011 *Procedures for Employee Training & Demonstration of Proficiency.*
- Laboratory SOP BR-QA-014 *Laboratory Records.*
- Laboratory SOP BR-QA-019 *Data Review*.
- Laboratory SOP BR-QA-006 *Manual Integrations Requirements*.
- Laboratory SOP BR-EH-001 *Hazardous Waste*
- Laboratory Quality Assurance Manual (QAM)
- Corporate Environmental Health and Safety Manual (CW-E-M-001)

16.0 Method Modifications

Modification Number	Method Reference	Modification
1	NA	1,4-Dioxane added as a target analyte

17.0 Attachments

- Table 1: Target Compound List and Reporting Limits
- Table 2: Primary Materials Used
- Table 3: DFTPP Key Ions and Abundance Criteria
- Table 4: Internal Standards with Corresponding Target Compounds and Surrogates
- Table 5: Characteristic Ions for Internal Standards
- Table 6: Characteristic Ions for Target Compounds and Surrogates.
- Table 7: RRF Criteria
- Table 8: Matrix Spike Recovery and RPD limits.
- Table 9: Deuterated Monitoring Compound Recovery Limits.
- Table 10: QC Summary and Recommended Corrective Action (Insert)
- Appendix B: Standard Formulations
- Appendix C: Equations

18.0 Revision History

BR-MS-001, Revision 1:

- Updated Title Page and Approval Signatures
- All Sections: Changed language to active tense and added reference to new LIMS (TALS)
- All Sections: Wherever necessary, Table 1, Appendices, etc. added information for the analysis of non-SOW compound 1,4 Dioxane.

Table 1: Target Compound List and CRQL

Compound	Contract Required Quantitation Limit				
	Water by SIM (ug/L)	Water (ug/L)	Soil by SIM ug/Kg	Low Soil (ug/Kg)	Medium Soil (ug/Kg)
*1,4-Dioxane		2.0		67	
Benzaldehyde		5.0		170	5000
Phenol		5.0		170	5000
Bis(2-chloroethyl) ether		5.0		170	5000
2-Chlorophenol		5.0		170	5000
2-Methylphenol		5.0		170	5000
2,2'-Oxybis(1-chloropropane)		5.0		170	5000
Acetophenone		5.0		170	5000
4-Methylphenol		5.0		170	5000
N-Nitroso-di-n-propylamine		5.0		170	5000
Hexachloroethane		5.0		170	5000
Nitrobenzene		5.0		170	5000
Isophorone		5.0		170	5000
2-Nitrophenol		5.0		170	5000
2,4-Dimethylphenol		5.0		170	5000
Bis(2-chloroethoxy) methane		5.0		170	5000
2,4-Dichlorophenol		5.0		170	5000
Napthalene	0.10	5.0	3.3	170	5000
4-Chloroaniline		5.0		170	5000
Hexachlorobutadiene		5.0		170	5000
Caprolactum		5.0		170	5000
4-Chloro-3-methylphenol		5.0		170	5000
2-Methylnaphthalene	0.10	5.0	3.3	170	5000
Hexachlorocyclopentadiene		5.0		170	5000
2,4,6-Trichlorophenol		5.0		170	5000
2,4,5-Trichlorophenol		5.0		170	5000
1,1'Biphenyl		5.0		170	5000
2-Chloronaphthalene		5.0		170	5000
2-Nitroaniline		10.0		330	10000
Dimethylphthalate		5.0		170	5000
2,6-Dinitrotoluene		5.0		170	5000
Acenaphthylene	0.10	5.0	3.3	170	5000
3-Nitroaniline		10.0		330	10000
Acenaphthene	0.10	5.0	3.3	170	5000
2,4-Dinitrophenol		10.0		330	10000
4-Nitrophenol		10.0		330	10000
Dibenzofuran		5.0		170	5000
2,4-Dinitrotoluene		5.0		170	5000
Diethylphthalate		5.0		170	5000
Fluorene	0.10	5.0	3.3	170	5000
4-Chlorophenyl-phenyl ether		5.0		170	5000

Table 1: Continued

Compound	Quantitation Limits				
	Water by SIM (ug/L)	Low Water (ug/L)	Soil by SIM (ug/Kg)	Low Soil (ug/Kg	Medium Soil (ug/Kg)
4-Nitroaniline		10.0		330	10000
4,6-Dinitro-2-methylphenol		10.0		330	10000
N-Nitrosodiphenylamine		5.0		170	5000
1,2,4,5-Tetrachlorobenzene		5.0		170	5000
4-Bromophenyl-phenyl ether		5.0		170	5000
Hexachlorobenzene		5.0		170	5000
Atrazine		5.0		170	5000
Pentachlorophenol	0.20	10.0	6.7	330	10000
Phenanthrene	0.10	5.0	3.3	170	5000
Anthracene	0.10	5.0	3.3	170	5000
Carbazole		5.0		170	5000
Di-n-butylphthalate		5.0		170	5000
Fluoranthene	0.10	5.0	3.3	170	5000
Pyrene	0.10	5.0	3.3	170	5000
Butylbenzyl phthalate		5.0		170	5000
3,3-Dichlorobenzidine		5.0		170	5000
Benzo(a)anthracene	0.10	5.0	3.3	170	5000
Chrysene	0.10	5.0	3.3	170	5000
Bis(2-ethylhexyl) phthalate		5.0		170	5000
Di-n-octyl-phthalate		5.0		170	5000
Benzo(b)fluoranthene	0.10	5.0	3.3	170	5000
Benzo(k)fluroanthene	0.10	5.0	3.3	170	5000
Benzo(a)pyrene	0.10	5.0	3.3	170	5000
Indeno(1,2,3-cd)pyrene	0.10	5.0	3.3	170	5000
Dibenzo(a,h)anthracene	0.10	5.0	3.3	170	5000
Benzo(g,h,i)perylene	0.10	5.0	3.3	170	5000
2,3,4,6-Tetrachlorophenol		5.0		170	5000

Reporting Limits represent those that can be achieved in a blank matrix. Individual reporting limits will vary based upon sample matrix, target analyte concentration, co-extracted interferences, and dry weight of samples.

* Non CLP compound.

Table 2: Primary Materials Used

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Table 3: DFTPP Key Ions and Abundance Criteria

Mass	Ion Abundance Criteria
51	10.0-80% of mass 198
68	Less than 2.0% of mass 69
69	Present
70	Less than 2.0% of mass 69
127	10.0-80.0% of mass 198
197	Less than 2.0% of mass 198
198	Base peak, 100% relative abundance
199	5.0-9.0% of mass 198
275	10.0-60.0% of mass 198
365	Greater than 1.0% of mass 198
441	Present, but less than mass 443
442	50.0-100.0% of mass 198
443	15.0-24.0 percent of mass 442

NOTE: All ion abundance MUST be normalized to m/z 198, the nominal base peak, even though the ion abundance of m/z 442 may be up to 100 percent that of m/z 198.

Table 4: Internal Standards with Corresponding Target Compounds and Surrogates

1,4-Dichlorobenze-d4	Naphthalene-d8	Acenaphthene-d10
1,4-Dioxane	Nitrobenzene	Hexachlorocyclopentadiene
Benzaldehyde	Isophorone	2,4,6-Trichlorophenol
Phenol	2-Nitrophenol	2,4,5-Trichlorophenol
Bis(2-chloroethyl)ether	2,4-Dimethylphenol	2,3,4,6-Tetrachlorophenol
2-Chlorophenol	Bis(2-chloroethoxy)methane	1,1'Biphenyl
2-Methylphenol	2,4-Dichlorophenol	2-Chloronaphthalene
2,2'-Oxybis(1-chloropropane)	4-Chloroaniline	2-Nitroaniline
Acetophenone	Hexachlorobutadiene	Dimethylphthalate
4-Methylphenol	Caprolactam	Acenaphthylene
N-Nitroso-di-n-propylamine	4-Chloro-3-methylphenol	3-Nitroaniline
Hexachloroethane	2-Methylnaphthalene	Acenaphthene
Phenol-d5 (DMC)	Naphthalene	2,4-Dinitrophenol
Bis(2-chloroethyl)ether-d8 (DMC)	Nitrobenzene-d5 (DMC)	4-Nitrophenol
2-Chlorophenol-d4 (DMC)	2-Nitrophenol-d4 (DMC)	Dibenzofuran
4-Methylphenol-d8 (DMC)	2,4-Dichlorophenol-d3 (DMC)	2,4-Dinitrotoluene
1,4-Dioxane-d_4 (DMC)	4-Chloroaniline-d4 (DMC	2,6-Dinitrotoluene
	2-Methylnapthalene-d10 (SIM DMC)	1,2,4,5-Tetrachlorobenzene
		Diethylphthalate
		4-Chlorophenyl-phenyl ether
		Fluorene
		4-Nitroaniline
		Acenaphthylene-d8 (DMC)
		4-Nitrophenol-d4 (DMC)
		Dimethylphthalate-d6 (DMC)
		Fluorene-d10 (DMC)

Phenanthrene-d10	Chrysene-d12	Perylene-d12
4,6-Dinitro-2-methylphenol	Pyrene	Di-n-octyl phthalate
N-Nitrosodiphenylamine	Butylbenzylphthalate	Benzo(b)fluoranthene
4-Bromophenyl-phenylether	3,3'Dichlorobenzidine	Benzo(k)fluroanthene
Hexachlorobenzene	Benzo(a)anthracene	Benzo(a)pyrene
Atrazine	Bis(2-ethylhexyl)phthalate	Indeno(1,2,3-cd) Pyrene
Pentachlorophenol	Chrysene	Dibenzo(a,h) anthracene
Phenanthrene	Pyrene-d10 (DMC)	Benzo(g,h,i)perylene
Anthracene		Benzo(a)pyrene-d12 (DMC)
Carbazole		
Di-n-butylphthalate		
Fluroanthene		
4,6-Dinitro-2-methylphenol –d2 (DMC)		
Fluoranthene-d10 (SIM DMC)		
Anthracene-d10 (DMC)		

Table 5: Characteristic Ions for Internal Standards

Internal Standards	Primary Quantitation Ion	Secondary Ion(s)
1,4-Dichlorobenzene-d4	152	115
Naphthalene-d8	136	68
Acenaphthene-d10	164	162, 160
Phenanthrene-d10	188	94, 80
Chrysene-d12	240	120, 236
Perylene-d12	264	260, 265

Table 6: Characteristic Ions for Target Compounds and Surrogates

Parameter	Primary Quantitation Ion	Secondary Ion(s)
1,4-Dioxane	88	58,43
Benzaldehyde	77	105, 106
Phenol	94	65, 66
Bis(2-chloroehyl)ether	93	63, 95
2-Chlorophenol	128	64, 130
2-Methylphenol	108	107
2,2'-Oxybis(1-chloropropane)	45	77, 79
Acetophenone	105	77, 51
4-Methylphenol	108	107
N-nitroso-di-n-propylamine	70	42, 101, 130
Hexachloroethane	117	201, 199
Nitrobenzene	77	123, 65
Isophorone	82	95, 138
2-Nitrophenol	139	65, 109
2,4-Dimethylphenol	107	121, 122
Bis(2-chloroethoxy)methane	93	95, 123
2,4-Dichlorophenol	162	164, 98
Naphthalene	128	129, 127
4-Chloroaniline	127	129,65
Hexachlorobutadiene	225	223, 227
Caprolactam	113	55, 56
4-Chloro-3-methylphenol	107	144, 142
2-Methylnaphthalene	142	141, 115
Hexachlorocyclopentadiene	237	235, 272
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 200
1,1'Biphenyl	154	153, 76
2-Chloronaphthalene	162	164, 127
2-Nitroaniline	65	92, 138
Dimethylphthalate	163	194, 164
Acenaphthylene	152	151, 153
2,6-Dinitrotoluene	165	89, 121
3-Nitroaniline	138	108, 92
Acenaphthene	153	152, 154
2,4-Dinitrophenol	184	63, 154
4-Nitrophenol	109	139, 65
Dibenzofuran	168	139, 169
2,4-Dinitrotoluene	165	63, 182

Table 6: Continued

Diethylphthalate	149	177, 150
1,2,4,5-Tetrachlorobenzene	216	214, 179, 108, 143, 218
4-Chlorophenyl-phenylether	204	206, 141
Fluorene	166	165, 167
4-Nitroaniline	138	92, 108
4,6-Dinitro-2-methylphenol	198	182, 77
N-Nitrosodiphenylamine	169	168, 167
4-Bromophenyl-phenylether	248	250, 141
Hexachlorobenzene	284	142, 249
Atrazine	200	173, 215
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176
Anthracene	178	179, 176
Carbazole	167	166, 139
Di-n-butylphthalate	149	150, 104
Fluoranthene	202	101, 100
Pyrene	202	101, 100
Butylbenzylphthalate	149	91, 206
3,3'Dichlorobenzidine	252	254, 126
Benzo(a)anthracene	228	229, 226
Bis(2-ethylhexyl)phthalate	149	167, 279
Chrysene	228	226, 229
Di-n-Octyl phthalate	149	None
Benzo(b)fluoranthene	252	253, 125
Benzo(k)fluoranthene	252	253, 125
Benzo(a)pyrene	252	253, 125
Indeno(1,2,3-cd)pyrene	276	138, 277
Dibenzo(a,h)anthracene	278	139, 279
Benzo(g,h,i)perylene	276	138, 277
2,3,4,6-Tetrachlorophenol	232	131, 230, 166, 234, 168
Deuterated Monitoring Compounds		
1,4-Dioxane-d8	96	95,64,46
Phenol-d5	71	42, 99
Bis(2-chloroethyl)ether-d8	67	99, 69
2-Chlorophenol-d4	132	134, 68, 66
4 Methylphenol-d8	113	115, 54
Nitrobenzene-d5	128	82, 54
2-Nitrophenol-d4	143	69, 41, 42
2,4-Dichlorophenol-d3	165	167, 101
4-Chloroaniline-d4	131	133, 69
Dimethylphthalate-d6	166	78
Acenaphthylene-d8	160	80, 158
4-Nitrophenol-d4	143	113, 41, 42
Fluorene-d10	176	174, 87, 86
4,6-Dinitro-2-methylphenol-d2	200	170, 52
Anthracene-d10	188	94, 80
Pyrene-d10	212	106, 104
Benzo(a)pyrene-d12	264	132, 118

Table 7: RRF Criteria

Parameter	Minimum RRF	Maximum %RSD	Maximum %Diff
1,4-Dioxane	0.010	50.0	±50.0
Benzaldehyde	0.010	40.0	±40.0
Phenol	0.800	20.0	±25.0
Bis(2-chloroehyl)ether	0.700	20.0	±25.0
2-Chlorophenol	0.800	20.0	±25.0
2-Methylphenol	0.700	20.0	±25.0
2,2'-Oxybis(1-chloropropane)	0.010	40.0	±40.0
Acetophenone	0.010	40.0	±40.0
4-Methylphenol	0.600	20.0	±25.0
N-nitroso-di-n-propylamine	0.500	20.0	±25.0
Hexachloroethane	0.300	20.0	±25.0
Nitrobenzene	0.200	20.0	±25.0
Isophorone	0.400	20.0	±25.0
2-Nitrophenol	0.100	20.0	±25.0
2,4-Dimethylphenol	0.200	20.0	±25.0
Bis(2-chloroethoxy)methane	0.300	20.0	±25.0
2,4-Dichlorophenol	0.200	20.0	±25.0
Naphthalene	0.700	20.0	±25.0
4-Chloroaniline	0.010	40.0	±40.0
Hexachlorobutadiene	0.010	40.0	±40.0
Caprolactam	0.010	40.0	±40.0
4-Chloro-3-methylphenol	0.200	20.0	±25.0
2-Methylnaphthalene	0.400	20.0	±25.0
Hexachlorocyclopentadiene	0.010	40.0	±40.0
2,4,6-Trichlorophenol	0.200	20.0	±25.0
2,4,5-Trichlorophenol	0.200	20.0	±25.0
1,1'Biphenyl	0.010	40.0	±40.0
2-Chloronaphthalene	0.800	20.0	±25.0
2-Nitroaniline	0.010	40.0	±40.0
Dimethylphthalate	0.010	40.0	±40.0
2,6-Dinitrotoluene	0.200	20.0	±25.0
Acenaphthylene	0.900	20.0	±25.0
3-Nitroaniline	0.010	40.0	±40.0
Acenaphthene	0.900	20.0	±25.0
2,4-Dinitrophenol	0.010	40.0	±40.0
4-Nitrophenol	0.010	40.0	±40.0
Dibenzofuran	0.800	20.0	±25.0
2,4-Dinitrotoluene	0.200	20.0	±25.0
Diethylphthalate	0.010	40.0	±40.0
1,2,4,5-Tetrachlorobenzene	0.010	40.0	±40.0
4-Chlorophenyl-phenylether	0.400	20.0	±25.0
Fluorene	0.900	20.0	±25.0
4-Nitroaniline	0.010	40.0	±40.0
4,6-Dinitro-2-methylphenol	0.010	40.0	±40.0
4-Bromophenyl-phenylether	0.100	20.0	±25.0
N-Nitrosodiphenylamine	0.010	40.0	±40.0
Hexachlorobenzene	0.100	20.0	±25.0
Atrazine	0.010	40.0	±40.0
Pentachlorophenol	0.050	20.0	±25.0
Phenanthrene	0.700	20.0	±25.0

Anthracene	0.700	20.0	±25.0

Table 7: Continued

Carbazole	0.010	40.0	±40.0
Di-n-butylphthalate	0.010	40.0	±40.0
Fluoranthene	0.600	20.0	±25.0
Pyrene	0.600	20.0	±25.0
Butylbenzylphthalate	0.010	40.0	±40.0
3,3'-Dichlorobenzidine	0.010	40.0	±40.0
Benzo(a)anthracene	0.800	20.0	±25.0
Chrysene	0.700	20.0	±25.0
Bis(2-ethylhexyl) phthalate	0.010	40.0	±40.0
Di-n-octylphthalate	0.010	40.0	±40.0
Benzo(b)fluoranthene	0.700	20.0	±25.0
Benzo(k)fluoranthene	0.700	20.0	±25.0
Benzo(a)pyrene	0.700	20.0	±25.0
Indeno(1,2,3-cd)pyrene	0.500	20.0	±25.0
Dibenzo(a,h)anthracene	0.400	20.0	±25.0
Benzo(g,h,i)perylene	0.500	20.0	±25.0
2,3,4,6-Tetrachlorophenol	0.100	20.0	±25.0
Deuterated Monitoring Compounds			
1,4-Dioxane-d8	0.010	40.0	±40.0
Phenol-d5	0.010	20.0	±25.0
Bis(2-chloroethyl)ether-d8	0.010	20.0	±25.0
2-Chlorophenol-d4	0.010	20.0	±25.0
4 Methylphenol-d8	0.010	20.0	±25.0
Nitrobenzene-d5	0.010	20.0	±25.0
2-Nitrophenol-d4	0.010	20.0	±25.0
2,4-Dichlorophenol-d3	0.010	20.0	±25.0
4-Chloroaniline-d4	0.010	40.0	±40.0
Dimethylphthalate-d6	0.010	40.0	±40.0
Acenaphthylene-d8	0.010	20.0	±25.0
4-Nitrophenol-d4	0.010	40.0	±40.0
Fluorene-d10	0.010	20.0	±25.0
4,6-Dinitro-2-methylphenol-d2	0.010	40.0	±40.0
Anthracene-d10	0.010	20.0	±25.0
Pyrene-d10	0.010	20.0	±25.0
Benzo(a)pyrene-d12	0.010	20.0	±25.0

Table 8: Matrix Spike Recovery and Relative Percent Difference Limits

Compound	Water		Soil	
	%R	%RPD	%R	%RPD
Phenol	12-110	42	26-90	35
2-Chlorophenol	27-123	40	25-102	50
N-Nitroso-di-n-propylamine	41-116	38	41-126	38
4-Chloro-3-Methylphenol	23-97	42	26-103	33
Acenaphthene	46-118	31	31-137	19
4-Nitrophenol	10-180	50	11-114	50
2,4-Dinitrotoluene	24-96	38	28-89	47
Pentachlorophenol	9-103	50	17-109	47
Pyrene	26-127	31	35-142	36

Table 9: Deuterated Monitoring Compound Recovery Limits

Compound	Water	Soil
	%R	%R
1,4-Dioxane-d8	40-150	40-150
Phenol-d5	39-106	17-103
Bis(2-chloroethyl) ether-d8	40-105	12-98
2-Chlorophenol-d4	41-106	13-101
4 Methylphenol-d8	25-111	8-100
Nitrobenzene-d5	43-108	16-103
2-Nitrophenol-d4	40-108	16-104
2,4-Dichlorophenol-d3	37-105	23-104
4-Chloroaniline-d4	1-145	1-145
Dimethylphthalate-d6	47-114	43-111
Acenaphthylene-d8	41-107	20-97
4-Nitrophenol-d4	33-116	16-166
Fluorene-d10	42-111	40-108
4,6-Dinitro-2-methylphenol-d2	22-104	1-121
Anthracene-d10	44-110	22-98
Pyrene-d10	52-119	51-120
2-Methylnaphthalene-d10 (SIM)	50-150	50-150
Fluoranthene-d10 (SIM)	50-150	50-150
Benzo(a)pyrene-d12	32-121	43-111

Table 10: QC Summary and Recommended Corrective Action (SOM)

QC Item	Minimum Frequency	Acceptance Criteria	Recommended Corrective Action
DFTPP	Before initial and continuing calibration, every 12 hours	See Table 3	Re-analyze, retune mass spectrometer
ICAL	Before sample analysis, when CCVs indicate calibration is no longer valid; after major instrument maintenance	See Table 5 for RRF criteria Linear Regression: $r \geq 0.99$ Quadratic: $r^2 \geq 0.99$	Correct problem and repeat calibration.
ICV	After each initial calibration	%Recovery ± 25%	Correct problem and verify second source standard. If that fails, repeat initial calibration.
Opening CCV	Beginning of each 12-hour window, as established by a compliant DFTPP.	See Table 7	Re-prepare standard and re-analyze once, if still outside criteria perform corrective action, sequence can be re-started if two successive CCVs at different concentrations pass, otherwise repeat ICAL and all associated samples since last successful CCV, unless CCV is high and samples are non-detects.
MB	One per extraction batch of 20 or fewer samples	All Targets < RL	Examine project DQO's and take appropriate corrective action, which may include re-analysis of MB, re-extraction of batch, and/or non-conformance report (NCR). Corrective action must be documented on NCR. If there are no detects in samples, or if all detects are > 10 X MB level, re-prep and reanalysis may not be required.
LCS	One per extraction batch of 20 or fewer samples	See Table 8	Examine project DQO's and take appropriate corrective action, which may include re-analysis of LCS, re-extraction of batch, and/or non-conformance report (NCR). Corrective action must be documented on NCR. Flag all reported values outside of control limits.
MS/MSD	One per extraction batch of 20 or less samples.	See Table 8	Evaluate data and determine if a matrix effect or analytical error is indicated. If analytical error, re-analyze and/or re-extract. Flag all reported values outside of control limits.
DMC Standard	All field and QC samples	See Table 9	Evaluate data and determine if a matrix effect or analytical error is indicated. If analytical error, re-analyze or re-extract. If matrix effect, review project DQOs to determine if a matrix effect must be confirmed by re-analysis. Flag all reported values outside of control limits.
Internal Standard	All field and QC samples	Area between 50-200% of area of daily calibration internal standard area	Same as above.

Appendix A: Terms & Definitions

Batch: environmental samples, which are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria.

Calibration Curve: the graphical relationship between the known values or a series of calibration standards and their instrument response.

Concentration Level (low or medium): characterization of soil samples or sample fractions as low concentration or medium concentration is made on the basis of the laboratory's preliminary screen, not on the basis of information entered on the Traffic Report (C-O-C) by the sampler.

Continuing Calibration Verification (CCV): a single or multi-parameter calibration standard used to verify the stability of the method over time. Usually from the same source as the calibration curve.

Decafluorotriphenylphosphine (DFTPP): compound chosen to establish mass spectral instrument performance for semivolatile analysis.

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Deuterated Monitoring Compound(DMC): for semivolatiles, added to every blank, sample, matrix spike, matrix spike duplicate, and standard; used to evaluate analytical efficiency by measuring recovery. DMCs are isotopically labeled compounds not expected to be detected in environmental media.

Extractable: a compound that can be partitioned into an organic solvent from the sample matrix and is amenable to gas chromatography. Extractables include semivolatile (BNA) and pesticide/Aroclor compounds.

GEL Permeation Chromatography (GPC): a size-exclusion chromatographic technique that is used as a cleanup procedure for removing large organic molecules, particularly naturally occurring macro-molecules such as lipids, polymers, viruses, etc.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

Initial Calibration Verification (ICV): solution prepared from a separate source from that which is used to prepare the calibration curve.

Intermediate Standard: a solution made from one or more stock standards at a concentration between the stock and working standard. Intermediate standards may be certified stock standard solutions purchased from a vendor and are also known as secondary standards.

Internal Standards: compounds added to every standard, blank, matrix spike, matrix spike duplicate, sample at a known concentration, prior to analysis. Internal standards are used as the basis for quantitation of the target compounds.

Isotopic Dilution: a process whereby the determination of the concentration of target analytes is based upon the recovery of spiked analogues.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Matrix: the predominant material of which the sample to be analyzed is composed. For the purpose of this SOW, a sample matrix is either water, soil/sediment, or tissue. Matrix is not synonymous with phase (liquid or solid).

Matrix Duplicate (MD): duplicate aliquot of a sample processed and analyzed independently; under the same laboratory conditions; also referred to as Sample Duplicate.

Matrix Effect: in general, the effect of a particular matrix (water or soil/sediment) on the constituents with which it contacts. This is particularly pronounced for clay particles, which may absorb chemicals and catalyze reactions. Matrix effects may prevent extraction of target analytes, and may affect surrogate recoveries. In addition, non-target analytes may be extracted from the matrix causing interferences.

Matrix Spike (MS): a field sample to which a known amount of specific target analytes are added.

Matrix Spike Duplicate (MSD): a field sample to which a known amount of specific target analytes are added as a duplicate of Matrix Spike.

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which relative uncertainty is ±100%. The MDL represents a range where qualitative detection occurs. Quantitative results are not produced in this range.

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Relative Response Factor (RRF): a measure of the relative mass spectral response of an analyte compared to its internal standard. Relative Response Factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples. See Section 12.0 Calculations.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample. The RL must be minimally at or above the MDL.

Selective Ion Monitoring (SIM): a mass spectrometer acquisition mode in which the instrumentation is configured to selectively scan and acquire only those ions necessary for identification and quantitation of the target compounds. The limited mass range enables greater dwell times per mass than can be accomplished with full scan mode thereby enabling greater instrument sensitivity.

Stock Standard: a solution made with one or more neat standards usually with a high concentration. Also known as a primary standard. Stock standards may be certified solutions purchased from a vendor.

Appendix B: Standard Preparation Tables

The standard formulations contained in this Appendix are recommended and are subject to change. If the concentration of the stock standard is different than those noted in this table, adjust the standard preparation formulation accordingly. Unless otherwise specified, prepare the standard solutions in methylene chloride using Class A volumetric glassware and Hamilton syringes. Unless otherwise specified for a standard solution, assign an expiration date of 6 months from date of preparation unless the parent standard expires sooner in which case use the earliest expiration date. See laboratory SOP BR-QA-002 *Standard Preparation* for further guidance.

The components and initial concentrations of the components that comprise the stock standard solutions purchased from commercial vendors are recorded in the in the reagent module of the laboratory's LIMS along with the final concentration of the prepared standard.

SOM01.2 Decafluorotriphenylphosphine (DFTPP) Solution

Stock Standard	Vendor (Catalog No.)	Stock Standard Concentration (ug/mL)	Volume Added (uL)	Final Volume (mL)	Final Concentration (ug/mL)
SV GC/MS Tuning Standard	Ultra Scientific (GCM-150)	1000	400	16.0	25

SOM01.2 Internal Standard Solution

Stock Standard	Vendor (Catalog No.)	Stock Standard Concentration (ug/mL)	Volume Added (uL)	Final Volume (mL)	Final Conc. (ug/mL)
SV Internal Standard Mix	Restek (31006)	4000	1000	8.0	500

SOM01.2 Calibration Stock Solution

Stock Standard	Vendor (Catalog No.)	Stock Standard Concentration (ug/mL)	Volume Added (mL)	Final Volume (uL)	Final Concentration (ug/mL)
8270 MegaMix	Restek (31850)	1000	1240	7440	167
Custom Rev. AP9 Adds w/ Benzoic Acid	Restek (564928)	1000	1240		

SOM01.2 Added/Surrogate Solution

Stock Standard	Vendor (Catalog No.)	Stock Standard Concentration (ug/mL)	Volume Added (mL)	Final Volume (uL)	Final Concentration (ug/mL)
DMC Acids	Absolute (94448)	2000	1100	2200	1000
DMC Base/Neutrals	Absolute (94449)	2000	1100		

SOM01.2/OLM04 Added Solution

Stock Standard	Vendor (Catalog No.)	Stock Standard Concentration (ug/mL)	Volume Added (uL)	Final Volume (mL)	Final Concentration (ug/mL)
CLP SOW OLM 04 Semi-volatiles Mix	Supelco/Sigma-Aldrich (47514-U)	2000	1250	2.5	1000

SOM01.2 Benzidines Added Solution

Stock Standard	Vendor (Catalog No.)	Stock Standard Concentration (ug/mL)	Volume Added (uL)	Final Volume (mL)	Final Concentration (ug/mL)
8270 Benzidines Mixture	Restek (31852)	2000	1000	2.0	1000

SOM01.2 Dioxane Added Solution 1000 ug/mL

Stock Standard	Vendor (Catalog No.)	Stock Standard Concentration (ug/mL)	Volume Added (mL)	Final Volume (uL)	Final Concentration (ug/mL)
1,4-Dioxane	Restek (30287)	2000	1100	2200	1000
1,4-Dioxane-d8	Restek (30614)	2000	1100		

SOM01.2 Dioxane Added Solution 100 ug/mL

Stock Standard	Vendor (Catalog No.)	Stock Standard Concentration (ug/mL)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/mL)
SOM01.2 1,4-Dioxane Solution	TABTV	1000	200	2.0	100

SOM01.2 ICV Solution

Stock Standard	Vendor (Catalog No.)	Stock Standard Concentration (ug/mL)	Volume Added (uL)	Final Volume (mL)	Final Concentration (ug/mL)
BNA Mix	NSI Solutions (C-701)	1000	400	4.0	100
Benzoic Acid	NSI Solutions (541)	5000	80		
Benzo(e)pyrene	Absolute (71016)	1000	400		
Perylene	Absolute (70471)	1000	400		

SOM01.2 Benzidines Added ICV Solution

Stock Standard	Vendor (Catalog No.)	Stock Standard Concentration (ug/mL)	Volume Added (uL)	Final Volume (uL)	Final Concentration (ug/mL)
Benzidines Mix	NSI Solutions (C-402)	2000	1250	2500	1000

SOM01.2/OLMO4 Added ICV Solution

Stock Standard	Vendor (Catalog No.)	Stock Standard Concentration (ug/mL)	Volume Added (uL)	Final Volume (mL)	Final Concentration (ug/mL)
CLP BNA Additionals Mix	NSI Solutions (C-601)	2000	1000	2.0	1000

SOM01.2 Routine Working Calibration Standard Preparation

Sample Type	Final Conc. (ng/uL)	Dioxane Final Conc (ng/uL)	Calibration Stock 167 ppm (uL)	SOM 01.2 Added 1000 ppm (uL)	OLM04 Added 1000 ppm (uL)	Benzidines Added 1000 ppm (uL)	Dioxane Added 1000 ppm (uL)	Dioxane Added 100 ppm (uL)	ISTD 500 ppm (uL)	$MeCl_2$ (uL)	Final Vol. (uL)
CAL Level 1	5.0	2.0	3.0	0.5	0.5	0.5	0	2.0	4.0	93.5	104
CAL Level 2	10	4.0	6.0	1.0	1.0	1.0	0	4.0	4.0	87	104
CAL Level 3	20	20	12	2.0	2.0	2.0	2.0	0	4.0	80	104
CAL Level 4	40	40	24	4.0	4.0	4.0	4.0	0	4.0	60	104
CAL Level 5	80	80	48	8.0	8.0	8.0	8.0	0	4.0	20	104

SOM01.2 Routine Working ICV Standard Preparation

Sample Type	Final Conc. (ng/uL)	SOM01.2 ICV Solution (uL)	Benzidines ICV (uL)	OLM04 ICV (uL)	ISTD (uL)	MeCl2 (uL)	Final Volume (uL)
ICV	50	50	5	5	4.0	40	104

SIM SOM01.2 Calibration Solution

Stock Standard	Vendor (Catalog No.)	Stock Standard Concentration (ug/mL)	Volume Added (uL)	Final Volume (mL)	Final Concentration (ug/mL)
SV Calibration Mix #5	Restek (31011)	2000	4.0	4.0	2.0
2-Methylnaphthalene	Restek (31285)	1000	8.0		
Hexachlorobenzene	Restek (32231)	1000	8.0		
Pentachlorophenol Solution	Ultra Scientific (GCS-120)	1000	8.0		
2-Methylnaphthalene-d10	Absolute (72614)	1000	8.0		
Fluoranthene-d10	Absolute (71198)	1000	8.0		

SIM SOM1.2 Internal Standard Solution

Stock Standard	Vendor (Catalog No.)	Stock Standard Concentration (ug/mL)	Volume Added (uL)	Final Volume (mL)	Final Concentration (ug/mL)
SOM01.2 Internal Standard Solution	TABTV	500	60	3.0	10

SIM SOM01.2 ICV Solution

Stock Standard	Vendor (Catalog No.)	Stock Standard Concentration (ug/mL)	Volume Added (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Custom SIMPAH ICV Mixture	Ultra Scientific (CUS-11197)	100	100	5.0	2.0
PAH Mixture	Ultra Scientific (PM-611-1)	100	100		

SIM SOM01.2 Working Calibration Standard Preparation

Sample Type	Final Concentration (ng/uL)	Calibration Solution (uL)	ISTD (uL)	MeCl2 (uL)	Final Volume (uL)
CAL Level 1	0.1	5.0	4.0	95	104
CAL Level 2	0.2	10	4.0	90	104
CAL Level 3	0.4	20	4.0	80	104
CAL Level 4	0.8	40	4.0	60	104
CAL Level 5	1.0	50	4.0	50	104

SIM SOM Working ICV Standard Preparation

Sample Type	Final Concentration (ng/uL)	ICV Solution (uL)	ISTD (uL)	MeCl2 (uL)	Final Volume (uL)
ICV	0.4	20	4.0	80	104

APPENDIX C: EQUATIONS

These equations were taken from reference method SOM01.0 and from SW-846 8000B, Test Methods for Evaluation of Solid Waste Revision 2, December 1996. USEPA.

Resolution

$$\%\text{Resolution} = \frac{(H - V)}{H} \otimes 100$$

Where:

V = Height of the valley between the two peaks measured from the drawn baseline to the floor of the valley between the two peaks.

H = Height of the shorter of the adjacent peaks.

Absolute Retention Times

$$\overline{RT} = \frac{\sum_{i=1}^{n} RT_i}{n}$$

Where:

$\overline{RT}$ = Mean Absolute Retention Time of analyte

RT_i = Absolute Retention Time of analyte

n = Number of measurements

Percent Breakdown

$$\%\,\text{Breakdown of DDT} = \frac{\text{amount found (ng) (DDE + DDD)}}{\text{amount (ng) of DDT injected}} \otimes 100$$

$$\%\,\text{Breakdown of Endrin} = \frac{\text{amount found (ng) (endrin aldehyde + endrin ketone)}}{\text{amount (ng) of endrin injected}} \otimes 100$$

$$\text{Combined \% Breakdown} = \%\,\text{Breakdown DDT} + \%\,\text{Breakdown Endrin}$$

Calibration Factor (CF_i)

$$CF = \frac{\text{Peak Area (or Height) of the Compound in the Standard}}{\text{Mass Injected (ng)}}$$

Mean Calibration Factor ($\overline{CF}$)

$$\overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

Where:
CF_i = Calibration Factor
n = Number of Calibration Standards

Standard Deviation of the Calibration Factor (SD)

$$SD = \sqrt{\frac{\sum_{i=1}^{n} \left(CF_i - \overline{CF}\right)_2}{n-1}}$$

Where:
CF_i = Calibration Factor
$\overline{CFi}$ = Mean Calibration Factor
n = Number of calibration levels

Percent Relative Standard Deviation (RSD) of the Mean Calibration Factor

$$\%RSD = \frac{SD}{\overline{CF}} \otimes 100$$

Where:
SD = Standard Deviation of Calibration Factors
$\overline{CF}$ = Mean Calibration Factor

Percent Difference (%D)
Percent Difference (%D): Used for Calibration Verification Standards

$$\%D = \frac{CF_v - \overline{CF}}{\overline{CF}} \otimes 100$$

Where:
CF_v = Calibration Factor from the Continuing Calibration Verification (CCV)

Percent Difference (%D): Used for PEM standards

$$\%D = \frac{C_{calc} - C_{nom}}{C_{nom}} \otimes 100$$

Where:
C_{calc} = Calculated concentration
C_{nom} = Nominal concentration

Percent Difference (%D): Used for Form X

$$\%D = \frac{Conc_H - Conc_L}{Conc_L} \otimes 100$$

Where:
$Conc_H$ = Higher of the two concentrations
$Conc_L$ = Lower of the two concentrations

Percent Recovery (%R)

$$\%R = \frac{C_s}{C_n} \otimes 100$$

Where:
C_s Concentration of the Spiked Field or QC Sample
C_n Nominal Concentration of Spike Added

Percent Recovery (%R) for MS/MSD

$$\%R = \frac{C_s - C_u}{C_n} \otimes 100$$

Where:
C_s = Concentration of the Spiked Sample
C_u = Concentration of the Unspiked Sample
C_n = Nominal Concentration of Spike Added

Relative Percent Difference (RPD)

$$RPD = \frac{|MSR - MSDR|}{1/2(MSR + MSDR)} \otimes 100$$

Where:
MSR = Matrix Spike Recovery
MSDR = Matrix Spike Duplicate Recovery

Sample Concentration

Water

$$Concentration_{sample}(ug/L) = \left(\frac{A_x}{\overline{CF}}\right)\left(\frac{DF}{V_i}\right)\left(\frac{V_t}{V_o}\right)\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_1\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_2 K\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_n$$

Where:
A_x = Peak area or peak height of the compound to be measured
$\overline{CF}$ = Mean Calibration Factor determined from the initial calibration for the compound to be measured, in height/ng

DF = Dilution Factor
V_i = Volume of extract injected in uL
V_t = Volume of extract produced by the preparation process (extraction and concentration), and before cleanup, in uL
V_o = Volume of the original water sample extracted in mL. Note: for instrument and sulfur blanks assume a volume of 1000mL
CV_{out} = Volume of extract produced by a cleanup process (cleanup and concentration), in uL
CV_{in} = Volume of extract subjected to a cleanup process, in uL
E = The efficiency of the cleanup process expressed as a fraction of material that passes through or is not mechanically lost during the cleanup step (e.g. 50% efficiency must be expressed as 0.50)

Soil/Sediment

$$\text{Concentration}_{\text{sample}}\,(\text{ug/kg}) = \left(\frac{A_x}{\overline{CF}}\right)\left(\frac{DF}{V_i}\right)\left(\frac{V_t}{W_t \otimes D}\right)\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_1\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_2 K\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_n$$

Where:
A_x = Peak area or peak height of the compound to be measured
$\overline{CF}$ = Mean Calibration Factor determined from the initial calibration for the compound to be measured, in height/ng
DF = Dilution Factor
V_i = Volume of extract injected in uL
V_t = Volume of extract produced by the preparation process (extraction and concentration), and before cleanup, in uL
W_t = Weight of the original soil sample extracted in g.
CV_{out} = Volume of extract produced by a cleanup process (cleanup and concentration), in uL
CV_{in} = Volume of extract subjected to a cleanup process, in uL
E = The efficiency of the cleanup process expressed as a fraction of material that passes through or is not mechanically lost during the cleanup step (e.g. 50% efficiency must be expressed as 0.50)

$$D = \frac{100 - \%\text{Moisture}}{100}$$

Water Adjusted CRQL

$$\text{Adjusted CRQL} = (\text{Contract CRQL})\left(\frac{V_x}{V_o}\right)\left(\frac{V_t}{V_y}\right)(DF)\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_1\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_2 K\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_n$$

Where:
Contract CRQL = The CRQL value reported in Exhibit C – Pesticide (ug/L)
V_x = Contract sample volume (1000 mL)
V_o = Volume of the original water sample extracted in mL. Note: for instrument and sulfur blanks assume a volume of 1000mL
V_t = Volume of concentrated extract, in uL
V_y = Contract concentrated extract volume (10,000 uL)
DF = Dilution Factor

CV_{out} = Volume of extract produced by a cleanup process (cleanup and concentration), in uL
CV_{in} = Volume of extract subjected to a cleanup process, in uL
E = The efficiency of the cleanup process expressed as a fraction of material that passes through or is not mechanically lost during the cleanup step (e.g. 50% efficiency must be expressed as 0.50)

Soil/Sediment Adjusted CRQL

$$\text{Adjusted CRQL} = (\text{Contract CRQL})\left(\frac{V_x}{V_s \otimes D}\right)\left(\frac{V_t}{V_y}\right)(DF)\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_1\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_2 K\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_n$$

Where:
Contract CRQL = The CRQL value reported in Exhibit C – Pesticide (ug/Kg)
W_x = Contract sample weight (30 g)
W_s = Weight of sample extracted in grams (g)
$D = \frac{100 - \%\text{Moisture}}{100}$
V_t = Volume of concentrated extract, in uL
V_y = Contract concentrated extract volume (10,000 uL)
DF = Dilution Factor
CV_{out} = Volume of extract produced by a cleanup process (cleanup and concentration), in uL
CV_{in} = Volume of extract subjected to a cleanup process, in uL
E = The efficiency of the cleanup process expressed as a fraction of material that passes through or is not mechanically lost during the cleanup step (e.g. 50% efficiency must be expressed as 0.50)

Title: Determination of Trace Metals by ICP- OES (CLP SOW ISM01.3)

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1.0 Scope and Application

This SOP describes the laboratory procedure for the use of inductively coupled atomic plasma-optical emission spectroscopy (ICP-OES) to determine the concentration of total recoverable and dissolved elements in samples taken from hazardous waste sites.

1.1 Analytes, Matrix(s), and Reporting Limits

This procedure may be used for a variety of matrices including: waters, soils/sediments, wipes, and air filters.

The elements that may be determined by this procedure and the associated CRQL (Contract Required Quantitation Limit is provided in Table 1.

2.0 Summary of Method

Samples are treated with acids and heat to solubilize the metals present. The digestates are analyzed for trace metals by optical emission spectroscopy (OES) in which the samples are nebulized and the aerosol produced is transported to a plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed and the intensities of the lines are monitored by a photosensitive device that generates signal(s) processed by a computer. Background correction is performed to compensate for variable background contribution to the spectra. Each metal is quantified at specific wavelengths of light emitted as the electrons relax to lower energy states. The sample is analyzed by multiple integrations (3) and the average integration is converted to a concentration from a calibration curve.

This procedure is based on the following reference method:

This procedure is based on CLP SOW ISM01.2, Exhibit D (ICP-AES).

3.0 Definitions

A list of terms and definitions are provided in Appendix B.

4.0 Health and Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

4.1 Specific Safety Concerns or Requirements

Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added. Protective clothing such as a lab coat, safety glasses and latex gloves must be worn while performing this procedure.

The ICP plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma.

4.2 Primary Materials Used

Table 2 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the MSDS. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

4.3 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

4.4 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to BR-EH-001 *Hazardous Waste*. The following waste streams are produced when this method is carried out.

- Acidic Waste – Satellite Container: 5 Gallon Polyethylene Container

5.0 <u>Personnel Qualifications</u>

5.1 SMO Notification

Each individual who performs this method must submit a resume to the SMO prior to beginning work.

5.2 Education and Experience

Staff that perform the procedures in this SOP must have the combination of experience and education needed for their position as defined in the job description created by and maintained by the human resources (HR) staff. The laboratory makes every effort to hire analytical staff that holds a college degree in an applied science with some chemistry in the curriculum. Exceptions are made based on the individual's experience and ability to learn. Selection of qualified candidates for employment with the organization begins with documentation of minimum education, training, and experience prerequisites needed to perform the prescribed task.

Refer to the job descriptions posted on the company's internet for the minimum education and training requirements for each position. If the reader of this SOP is not a TestAmerica employee; a copy of the job description may be requested from a company representative.

5.3 Training Requirements

Any employee that performs any portion of the procedure described in this SOP must have documentation in their employee training file that they have read this version of this SOP.

The ISM SOW does not require demonstration of a capability (DOC) for technical staff. However, some state regulatory programs do. Therefore, an initial DOC and annual DOC is required for any technical staff that perform this procedure. Refer to laboratory SOP BR-QA-011 for these procedures.

6.0 Interferences

Overlap of a spectral line from another element, unresolved overlap of molecular band spectra, background contribution from continuous or recombination phenomena, and/or background contribution from stray light from the high concentration elements are examples of spectral interference that may cause target concentrations to be artificially high. These effects are compensated by using computer correction of the raw data by monitoring and measurement of the interfering element and/or background correction adjacent to the analyte line.

Change in viscosity and surface tension can cause significant inaccuracies especially in samples that contain high dissolved solids and/or acid concentrations. The use of a peristaltic pump, internal standardization or sample dilution will minimize these interferences.

Chemical interferences such as molecular compound formation, ionization effects and solute vaporization effects are highly dependent on matrix type and specific analyte elements. These interferences are not typical with ICP-OES analysis but if observed, can be minimized by matrix matching, buffering the sample and careful selection of instrument operating conditions.

6.1 Interelement Corrections

Determine interelement correction factors (IECs) before any field samples are analyzed under the CLP contract and annually thereafter. Prepare the instrument for analysis as described in the operator's manual and this SOP. Deactivate the current IEC factors.

Analyze a single element standard for each element at a sufficient to generate a interference. Do not exceed the LDR. For each element solution analyzed, record which of the other elements (if any) have a absolute value above the CRQL. The presence of the other elements indicates that the element in solution indicates the need for a IEC. For example, if the result of analysis of the single element solution for aluminum yields an absolute value for lead that is above the CRQL, aluminum will interfere with lead and a correction factor needs to be applied.

To calculate the correction factor, divide the concentration of the element noted above the CRQL by the concentration of the element causing interference. For instance, using the earlier example, in the solution analyzed for aluminum, lead was above the CRQL indicating aluminum may interfere with lead, therefore divide the concentration of lead by the concentration of aluminum. Enter the correction factor in the instrument software system and TALS equipment limit group.

7.0 Apparatus and Materials

Catalog numbers listed in this SOP are subject to change at the discretion of the vendor. Analysts are cautioned to be sure equipment used meets the specification of this SOP.

7.1 Miscellaneous

- Block Digester: Capable of maintaining temperature of 95±3°C.
- Adjustable Volumetric Pipettes: Calibrated daily.
- Class A Volumetric Glassware.
- Top-Loading Balance with 300g capacity and ±1mg sensitivity.
- Filter apparatus.
- Ribbed Watch glasses.
- Whatman No. 41 Filter Paper or equivalent.
- Polyethylene Digestion Vessels with Volumetric Indicators.

7.2 Analytical System

- Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES); Thermo iCAP 6500 equipped with a Cetac AS-520 autosampler or equivalent.
- TALS data processing system.

7.3 Glassware cleaning

All glassware must be washed as prescribed in SOP BR-ME-002. Monitor preparation blanks for contamination. If the preparation blank is routinely greater than 2 times the calculated MDL contamination should be suspected and investigated. Preparation blank results that exceed CRQL are unacceptable and shall be corrected.

7.4 Reagents and Standards

7.4.1 Reagents

- Reagent Water - ASTM Type II Water (ASTM D1193-77) or equivalent.
- Hydrochloric Acid, Concentrated (specific gravity 1.19); reagent grade; JT Baker or equivalent
- Nitric Acid, Concentrated (specific gravity 1.41) Hydrochloric Acid; reagent grade; JT Baker or equivalent.
- Hydrogen Peroxide (30%); Hydrochloric Acid; reagent grade; JT Baker or equivalent.

Hydrochloric Acid (1:1): Fill a carboy half full with reagent water then slowly add an equal volume of concentrated hydrochloric acid to the carboy. Swirl to mix.

Nitric Acid, (1:1): Fill a carboy half full with reagent water and slowly add an equal volume of concentrated nitric acid. Swirl to mix.

Assign an expiration date of 6 months from date solution is made and store prepared solutions in a fume hood at ambient temperature.

7.4.2 Standards

Purchase all standards as stock solutions of known purity greater than 99.9% from reputable vendors. No standards are to be prepared by the laboratory from neat materials. Preferable vendors are Spex Certiprep, SCP Science, and/or Inorganic Ventures. Other vendors may be utilized as needed provided they meet the accuracy and purity standards required. Review the certificate of analysis provided by the vendor for impurities that may affect the accuracy of the working solution. Reject any purchased stock solution whose purity or contaminant levels could affect the accuracy of working solutions. Prepare intermediate and working standard solutions by diluting volumes of stock standards with acidified reagent water in volumetric flasks to obtain the appropriate concentration. Assign expiration dates according to expiration date of the parent standard. Prepare standard solutions as needed or on the expiration date, whichever occurs first. Document and assay prepared standards as outlined in SOP BR-QA-002. The components and recommended concentrations for calibration, working and secondary dilution standards are given in Appendix A.

The ICV, ICSA, and ICSAB solutions are prepared from stock solutions provided by EPA.

8.0 Handling and Preservation

The laboratory does not perform sample collection so these procedures are not included in this SOP. Listed below are the laboratory recommended minimum sample size, preservation and holding time requirements:

Matrix	Container	Minimum Sample Size	Preservation	Holding Time	Reference
Water	Glass or Polyethylene	100 mL	pH < 2 with Nitric Acid , Cool to 4± 2ºC	180 Days VTSR	ISM SOW
Soil	Glass or Polyethylene	25 g	Cool to 4± 2ºC	180 Days VTSR	ISM SOW
Wipe	Glass or Polyethylene	N/A	N/A	180 Days VTSR	ISM SOW
Air Filter	Glass or Polyethylene	N/A	N/A	180 Days VTSR	ISM SOW

Holding time is calculated from verified time of sample receipt (VTSR). If dissolved metals are to be determined, immediately after sample collection and prior to chemical preservation, the field sample should filter the sample per the instruction in the SOW.

Unless otherwise specified by client or regulatory program, after analysis, samples and extracts are retained for a minimum of 60 days after provision of the project report and then disposed of in accordance with applicable regulations. Sample digestates are stored for 180 days after delivery of the complete, reconciled data package.

9.0 Instrument Calibration

Calibrate the instrument daily. First allow the instrument to become stable following the manufacturer's instrument operating parameters. Profile the instrument by aspirating the ICV solution and acquiring 3 replicate integrations for all analytes present in the solution. Record the intensity reading of the Ytrium lines daily in the instrument maintenance logbook. Visually inspect the spectra of each analyte. If the integration of the peak does not correspond to the actual maximum of the profile, perform an auto peak adjustment. If the intensity is low perform a torch alignment routine, by aspirating a 2ppm Zn solution and following the software instruction.

9.1 Support Equipment Calibration

Check the calibration of the top-loading balance used to measure sample weights on the day of use prior to use. Record the calibration check in the logbook designated for this purpose.

Check the accuracy of mechanical pipettes used to measure quantitative volumes using the procedure and at the frequency specified in laboratory SOP BR-QA-008.

10.0 Sample Preparation

10.1.1 SMO Notification Requirements

If insufficient sample amount (less than 90% of required amount) notify the laboratory project manager (PM) and wait for further instruction. The PM must contact SMO and notify them of the situation and obtain instruction from SMO on how to proceed. Document the situation along with any instructions provided with a nonconformance memo (NCM) in the laboratory LIMS system (TALS).

If multiphase samples are received notify the PM. The PM must contact SMO and obtain instruction(s) on how to proceed. Document the situation along with any instructions provided with a nonconformance memo (NCM) in the laboratory LIMS system (TALS).

If % solids determination are ≤ 50% notify the PM.

If % solids determination is ≤30% for any sample notify the PM. The PM must contact SMO and notify them of the situation and obtain instruction from SMO on how to proceed. Use the sample mass dictated in Table 5.

Document the situation(s) along with any instructions provided with a nonconformance memo (NCM) in the laboratory LIMS system (TALS).

10.1.2 Water/Aqueous (Method 200.7, Revision 4.4, 1994)

If insufficient volume is available return to section 10.1.2.

NOTE: The following instructions are for use of a 100 mL sample volume. The CLP SOW allows for use of a reduced sample volume of 50 mL. If 50 mL of sample volume is used, reduce the final volumes and reagent volumes accordingly.

Check the pH of each sample using a transfer pipette and test strips designated for this task. If the pH is not ≤2 adjust with 70% Nitric acid dropwise. Once the pH correctly adjusted the sample must be held for 24hrs prior to digestion. Record the Analyst initial date, time, and lot number of Nitric acid used in a separate batch and create an NCM. Check the pH again prior to digestion and repeat as necessary. Document the situation in a NCM.

Shake the sample to mix then transfer 100 mL of sample to a labeled digestion vessel. Transfer two additional portions of the sample selected as the sample duplicate (D) and the matrix spike (S) to a labeled digestion vessel. Add 1 mL of matrix spike solution to the matrix spike.

Use 100 mL of reagent water for the method blank (PB) and the laboratory control sample (LCS). Add 1 mL of the ISM01.2 ICP-OES LCS solution to the LCS.

Add 2 mL of 1:1 HNO_3 and 1 mL of 1:1 HCl to each digestion vessel. Cover the digestion vessel(s) with a watch glass and place them in the heated block digesters located in the fume hood. Maintain the temperature so that evaporation occurs at 95°C (+/-3°C). Heat until the sample volume is reduced to about 20 mL. Do not boil.

Cover the digestion vessel loosely with a cap and continue to reflux the sample for 30 minutes. Monitor the digestion to ensure that the sample does not boil and that the digestion vessel does not go dry. After 30 minutes, let the vessels cool then adjust the volume to 100 mL with reagent water. Let the digestates sit to settle any undissolved material.

Complete the preparation batch in TALS then forward the digestates to the instrument lab.

10.1.3 Soil/Sediment / Wipe (Method 3050B, Revision 2, December 1996)

Record all weight measurements to the nearest 0.01g.

Note: The following instructions are for soils/sediments. If wipe is the matrix for digestion, substitute 1 wipe for the sample mass and follow the same instructions. Use the wipes provided for MB and LCS. If blank wipes were not provided substitute 1g of Teflon chips.

Mix the sample thoroughly to achieve homogeneity according to laboratory SOP BR-QA-020 *Sample Homogenization and Subsampling.* Review the % solids results. If solids are <50% return to section 10.1.2 before proceeding. If necessary use alternate mass from table 5. Otherwise Transfer 1.00 to 1.50 g of sample into a tared and labeled digestion vessel. Weigh two additional portions of the sample selected as the sample duplicate (D) and matrix spike (S) into tared labeled digestion vessel(s). Add 2 mL of matrix spike solution to the matrix spike.

Use 1.00 – 1.50 g of reagent water for the method blank (PB). For the LCS, use 1 mL of the ISM01.2 ICP-OES LCS solution.

Add 10 mL of 1:1 HNO_3 to each digestion vessel. Cover the digestion vessel(s) with a watch glass and place them in the heated block digesters located in the fume hood. Maintain the temperature so that evaporation occurs at 95°C (+/-3°C). Heat the sample for 10 - 15 minutes without boiling.

Let the samples cool then add 5 mL of concentrated nitric acid. Replace the cover and reflux for 30 minutes. If brown fumes are created, oxidation is taking place. Repeat the addition of nitric acid in 5 mL amounts until no brown fumes are given off. Evaporate the solution to ~ 5 mL at

95°C (+/-3°C) for 2 hours. Do not allow the digestion vessel to go dry and ensure the vessels are covered at all times.

Let the samples cool then add 2 mL of reagent water and 3 mL of 30% hydrogen peroxide. Replace the watch glass and return the vessel to the block digester. Heat until the effervescence subsides. Cool the vessels then continue to add 30% hydrogen peroxide in 1 mL aliquots with warming until the effervescence is minimal or until sample appearance remains unchanged but do not add more than 10 mL of 30% hydrogen peroxide. Cover the digestate with the watch glass and continue heating at 95°C (+/-3°C) for 2 hours without boiling. Monitor the process to ensure that digestion vessels do not go dry.

Let the samples cool then add 10 mL of concentrated HCl to each vessel. Replace the watch glass and return the vessel to the block digester. Reflux at 95°C (+/-3°C) for 15 minutes.

Let the digestates cool, adjust to 100 mL with reagent water and let the sample site to settle any undissolved material. This digestates may be centrifuged if necessary.

Complete the preparation batch in TALS then forward the digestates to the instrument lab.

10.1.4 Filter Digestion (Method 7300)

Remove the filter from the cassette and transfer to a 50 mL beaker.

For the blank use the filter provided by the client. If a blank filter was not provided, use 1mL of reagent water.

For the LCS use the blank filter provided by the client. If a blank filter was not provided, use 1mL of reagent water. Add 0.1 mL of the ISM01.2 ICP-OES LCS solution to the LCS.

Add 3 mL of concentrated nitric acid and 1 mL of 30% of hydrogen peroxide and cover with a watch glass. Heat the sample to 95°C (±3°C) on a hotplate and reflux until the volume has been reduced to approximately 0.5 mL. Monitor the temperature of the hotblock with a 50mL flask equipped with a thermometer and filled with approximately 20mL of reagent water.

Rinse the watch glass and the sides of the beaker with 3 mL of 5% (v/v) nitric acid and heat until the sample volume has been reduced to approximately 0.5 mL.

Add 1 mL of concentrated hydrochloric acid and heat for 10 minutes at 95°C (±3°C). Allow the sample to cool.

Adjust the final volume to 10.0 mL (±0.1 mL) with reagent water. The sample may be filtered to remove solid particles. The sample is now ready for analysis

10.2 Analysis

10.2.1 Sample Screening & Dilutions

If high concentrations are suspected, screen the samples by ICP-OES at a 500 fold dilution. Analyze all samples undiluted unless screen results indicate high concentrations of analytes or interferents. High concentrations are those which may result in damage to the detector or excessive salt deposits and clogging of the nebulizer. Dilute analyte concentrations that exceed

the upper calibration range such that concentrations are within the upper 75% of the calibration range. Dilute interference concentrations to within the established LDR. Create an NCM in the LIMS system for any dilution resulting in a sample concentration below the upper 75% of the calibration range.

10.2.2 Analytical Sequence

Allow the instrument to equilibrate for at least 30 minutes prior to analysis. Check the sample flow through the pump tubing to ensure that flow to the nebulizer and drain flow is smooth. If the flow is erratic, check the tubing placement on the pump rollers and replace, as necessary. Perform Instrument Calibrations and Stability report as outlined in section 9.0 prior to analysis of samples.

Place one of the peristaltic pump sippers into the working internal standard solution.

Transfer approximately 50 mL of each working calibration standard, ICV, CCV, ICSA and ICSAB into an autosampler tube.

Transfer approximately 10 mL of each digestate into an autosampler tube.

Prepare the serial dilution by transferring 2 mL of the parent sample to an autosampler tube then add 8 mL of the 5% hydrochloric acid/2% nitric acid solution to the tube.

Prepare a post digestion spike by transferring 9.9 mL of the remaining volume of parent sample to an autosampler tube then add 0.1 mL of the post-spike solution to the tube.

Note: A post digestion spike and serial dilution analyses are routinely performed on the same sample used as the matrix spike. For initial analysis the concentration of the post digestion spike standard is equivalent to 2X the CRQL for all elements. If the matrix spike recovery for any element is outside control limits, the unspiked sample result for that element does not exceed four times the concentration of spike added and if the indigenous level in the unspiked sample for that element is higher than 2X the CRQL, then the post-digestion spike is repeated with a spike concentration equivalent to 2X the indigenous level in the unspiked sample for those elements.

On the PC connected to the instrument, select the autosampler template ISM01.3 and enter the sample Ids in the order of analysis. The template is designed to monitor all lines in table 1, and includes necessary quality control standards at the specified frequencies. Additional lines may be added as necessary. Identify the need for additional lines during annual IEC studies or through review of the sample full scan data. Place the samples, serial dilution, post-digestion spike, calibration blanks, mixed calibration standards, and performance check standards in the position on the autosampler rack that corresponds to their assigned position in the autosampler template. Use the method template designed for analysis.

An example analytical sequence that includes initial calibration (ICAL) is provided below.

Injection Number	Lab Description
1	Calibration Blank
2	Calibration Standard #1
3	Calibration Standard #2
4	Calibration Standard #3

5	Calibration Standard #4
6	Calibration Standard #5
7	ICV
8	ICB
9	ICSA
10	ICSAB
11	CCV
12	CCB
13-22	10 Samples*
23	CCV
24	CCB
25-34	10 Samples*
35	CCV
36	CCB

**The number of samples between each CCB/CCV (10) includes preparation blanks, laboratory control samples, matrix spikes, sample duplicates, serial dilutions and the post digestion spike. A rinse blank is performed between each acquisition to flush the system and remove traces of the previous sample.*

Place the autosampler rack in the autosampler tray and initiate the software macro to begin analysis.

10.2.3 Initial Calibration (ICAL) and Verification (ICV/ICB)

Prepare calibration standards using the formulations provided in Appendix A. Calibrate the instrument before each analytical sequence using a blank and five calibration standards, with the lowest standard at a concentration at or below the CRQL for each element.

Immediately after calibration, check the accuracy of the calibration with the second source ICV standard provided by the EPA.

Immediately after the ICV, analyze an initial calibration blank (ICB).

10.2.4 Interference Check Samples (ICSA and ICSAB)

Immediately after the ICB, analyze the ICS solutions provided by the EPA following the procedure that begins in section 10.3. The solutions must be run sequentially (ICSA precedes ICSAB) and the initial run of the ICS solutions must be undiluted after which dilution of the ICS for the highest concentration elements may be necessary to meet the calibrated range values of the instrument.

10.2.5 Continuing Calibration Blanks and Verification (CCV/CCB)

Immediately after the ICS solutions analyze a continuing calibration verification standard (CCV) followed by a continuing calibration blank (CCB). See the appendix for the formulations.

Repeat analysis of a CCV/CCB pair every 10 samples or every 2 hours, whichever is more frequent, and at the end of the analytical sequence. The same acceptance criterion applies. If

criteria are not met, stop analysis, fix the problem and reanalyze all samples since the last compliant CCV/CCB pair.

10.2.6 Internal Standards

Internal standard solution and sample solution are pumped together and mixed at a tee connection prior to introduction into the nebulizer.

11.0 Data Calculations

Unless otherwise specified, calculations are performed using data analysis software.

Percent Difference (Calibration)

$$\%D = \frac{Found - ExpectedValue}{ExpectedValue} * 100\%$$

Found= Concentration as determined based upon calibration equation..
Expected Value= Concentration as spiked

Relative Standard Deviation

$$\%RSD = \frac{100\sqrt{\frac{(r_1 - r_m)^2 + (r_2 - r_m)^2 + (r_1 - r_m)^2}{n-1}}}{r_m}$$

Where:
r_1 = replicate result one
r_2 = replicate result two
r_3 = replicate result three
r_m = Mean of replicates
n= number of replicate measurements

Percent Recovery (%R) LCS and CCVs

$$\%R = \frac{SR}{SA} * 100\%$$

Where:
SR = Sample Result
SA = Concentration of Spike Added

Percent Recovery (%R) MS

$$MSRecovery(\%) = \frac{SSR - SR}{SA} * 100\%$$

Where:
SSR = Matrix Spike Result
SR = Sample Result
SA = Concentration of Spike Added

Relative Percent Difference (%RPD)

$$\%RPD = \frac{|D_1 - D_2|}{\frac{D_1 + D_2}{2}} * 100$$

Where:
D1 = Sample result
D2 = Duplicate Result

Water Sample Concentration

$$C_{(ug/L)} = \frac{\mu g}{L_{dig}} * \frac{V_{dig}}{V_{samp}} * DF$$

Where:
$\mu g/L_{dig}$ = Instrument result
V_{dig} = Final digestate volume
V_{samp} = Sample volume
DF=Dilution Factor

Solid Sample Concentration

$$C_{(mg/Kg\ drywt.)} = \frac{\mu g}{L_{dig}} * \frac{V_{dig}}{g_{samp}} * \frac{100}{\%\ solids} * DF$$

Where:

$\mu g/L_{dig}$ = Instrument result
V_{dig} =Final digestate volume
g_{samp} = Sample weight in grams
% Solids = Percent solids to nearest 0.1%
DF=Dilution Factor

12.0 Quality Control

12.1 Sample QC

The laboratory prepares the following quality control samples with each batch of samples.

QC Item	Frequency	Acceptance Criteria
Method Blank (MB)	1 per digestion batch	See Table 3
Laboratory Control Sample (LCS)	1 per digestion batch	See Table 3
Matrix Spike (MS)	1 per digestion batch or SDG which ever is more frequent	See Table 3
Sample Duplicate (SD)	1 per digestion batch or SDG which ever is more frequent	See Table 3

Serial Dilution	1 per digestion batch or SDG per matrix	See Table 3
Post Digestion Spike	1 per digestion batch or SDG if the matrix spike fails	See Table 3

12.2 Instrument QC

The following instrument QC is performed:

QC Item	Frequency	Acceptance Criteria
Initial Calibration (ICAL)	Prior to each analytical run	See Section 10
Initial Calibration Verification (ICV)	Once, after each ICAL	See Section 10
Interference Check Sample (ICS)	Beginning of each analytical batch but not before an ICV/ICB	See Section 10
Continuing Calibration Verification (CCV)	Daily, every 10 samples or not to exceed every 2 hours, end of sequence	See Section 10
Initial and Continuing Calibration Blanks (ICB/CCB)	Immediately after ICV and each CCV	See Section 10
Rinse Blank	Between every sample and/or standard	none

12.2.1 Initial Calibration (ICAL)

The correlation coefficient r^2 must be greater than or equal to 0.995.

Check the calibration equation to establish the representativeness of the data that were used to produce the calibration equation. This check involves the comparison of the calculated concentration of each of the standards against the expected concentration of the associated standard. If the Percent Differences for each of the non-blank standards do not fall within ±30%, remake the standards and perform a new calibration.

Check the absolute value of the y-intercept from the linear of the calibration equation to ensure it is below the CRQL. If it is not below the CRQL, the calibration fails, Remake the calibration standards and repeat the calibration.

12.2.2 Initial Calibration Verification (ICV)

The recovery of elements in the ICV should be within 90-110%. The three integrations of the ICV measurement must have an %RSD of ≤5%. If criteria are not met, stop analysis, fix the problem and reanalyze. If the second attempt fails, perform further corrective action, recalibrate and reanalyze.

12.2.3 Initial Calibration Blank (ICB)

The absolute value of the ICB must be less than the CRQL. If it is not, stop analysis, fix the problem and reanalyze. If the second attempt fails, perform further corrective action, recalibrate and reanalyze.

12.2.4 Interference Check Samples (ICSA and ICSAB)

Immediately after the ICB, analyze the ICS solutions provided by the EPA following the procedure that begins in section 10.3. The solutions must be run sequentially (ICSA precedes ICSAB) and the initial run of the ICS solutions must be undiluted after which dilution of the ICS for the highest concentration elements may be necessary to meet the calibrated range values of the instrument.

The results of ICSA and the ICSAB (for the analytes in the ICSAB) must be within ±20% of the true value or ±2 times the CRQL whichever is greater. If the true value is not provided for the ICSA, assume the true value is zero and use the limit of ±2 times the CRQL.

For example; if the CRQL for Copper is 2 ug/L and the true value of copper in the ICSA solution is 8 ug/L, thus the control window is 8± 4 ug/L (2X CRQL) because 2X CRQL is greater than 20% of the true value (1.6 ug/L).

If the results of the ICS solutions are not within criteria, stop analysis, fix the problem and reanalyze. If the second attempt fails, perform further corrective action, recalibrate and reanalyze.

12.2.5 Continuing Calibration Blanks and Verification (CCV/CCB)

Immediately after the ICS solutions analyze a continuing calibration verification standard (CCV) followed by a continuing calibration blank (CCB) following the procedure that begins in Section 10.3. The concentration of the CCV should be at or near the mid point of the calibration curve and must be different than the concentration of the ICV. See the appendix for the formulation.

The absolute value of the CCB must be less than the CRQL and the CCV percent recovery must be within 90-110%. The three integrations of the CCV measurement must have RSD of ≤5%. If these criteria are not met, stop analysis, fix the problem and reanalyze. If the second attempt fails, perform further corrective action, recalibrate and reanalyze.

Repeat analysis of a CCV/CCB pair every 10 samples or every 2 hours

12.2.6 Internal Standards

Internal standards are used to correct for instrument drift and physical interference. A list of internal standards used for this procedure is given in Table 3. .

The internal standard solution is mixed in with sample flow by the peristaltic pump system on the instrument. Internal standard solution and sample solution are pumped together and mixed at a tee connection prior to introduction into the nebulizer.

12.3 Analytical Sequence

If high concentrations are suspected, screen samples at a 500 fold dilution prior to analysis.
Transfer ~ 25 mL of each prepared standard to individual, labeled autosampler tubes. Use 25 mL of the 5% hydrochloric acid/2% nitric acid solution into individual, labeled autosampler tubes for the calibration blank.

Transfer ~ 10 mL of digestate to individual, labeled autosampler tubes.

Prepare the serial dilution by transferring 2 mL of the parent sample to an autosampler tube then add 8 mL of the 5% hydrochloric acid/2% nitric acid solution to the tube.

Prepare a post digestion spike by transferring 9.9 mL of the remaining volume of parent sample to an autosampler tube then add 0.1 mL of the post-spike solution to the tube.

Note: A post digestion spike and serial dilution analyses are routinely performed on the same sample used as the matrix spike. For initial analysis the concentration of the post digestion spike standard is equivalent to 2X the CRQL for all elements. If the matrix spike recovery for any element is outside control limits, the unspiked sample result for that element does not exceed four times the concentration of spike added and if the indigenous level in the unspiked sample for that element is higher than 2X the CRQL, then the post-digestion spike is repeated with a spike concentration equivalent to 2X the indigenous level in the unspiked sample for those elements.

On the PC connected to the instrument, select the autosampler template and enter the sample Ids in the order of analysis. Place the samples, serial dilution, post-digestion spike, calibration blanks, mixed calibration standards, and performance check standards in the position on the autosampler rack that corresponds to their assigned position in the autosampler template.

An example analytical sequence that includes initial calibration (ICAL) is provided below.

Injection Number	Lab Description
1	Calibration Blank (S0)
2	Calibration Standard (S)
3	Calibration Standard (S)
4	Calibration Standard (S)
5	Calibration Standard (S)
6	Calibration Standard (S)
7	ICV
8	ICB
9	ICSA
10	ICSAB
11	CCV
12	CCB
13-22	samples*
23	CCV
24	CCB
25-32	samples*
33	CCV
34	CCB

**The number of samples between each CCB/CCV (10) includes method blanks, laboratory control samples, matrix spikes, sample duplicates, serial dilutions and the post digestion spike.*

Place the autosampler rack in the autosampler tray and initiate the software macro to begin the sequence.

13.0 Data Reduction

13.1 Quantitative Identification

The instrument is configured sample to analyze multiple integrations (3) and use the average integration to calculate concentration in ppb units from the calibration curve.

14.0 Data Review

14.1 Primary Review

Evaluate the results of the instrument performance check samples and field and QC samples against the established acceptance criteria. If criteria are not met, perform corrective action. If any data is reported outside criteria, initiate a nonconformance memo (NCM).

The instrument method is configured to rinse between each sample and/or standard. Rinse times are based upon the time required for instrument response to return to baseline following a standard at the LDR. However, it is impossible to predict the memory characteristics of every sample. Therefore carefully monitor samples analyzed immediately after high concentration samples for signs of carry-over. Reanalyze the sample if carry over is suspected.

Dilute and reanalyze samples whose results exceed the concentration of the established linear range.

Upload the data into TALS. Enter the batch information in the TALS batch. Set results to primary or acceptable as appropriate, check QC linkages then set the TALS batch to first level review. Complete the data review checklist designed for this task.

14.2 Secondary Data Review

Review project documents such as the Project Plan (PP), Project Memo or any other document/process used to communicate project requirements to ensure those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Verify that the acceptance criteria for the calibration and QC items listed in Table 3 were met. If the results do not fall within the established limits verify the recommended corrective actions were performed. If not, initiate corrective actions and/or verify an NCM was created to document the criteria exception. Verify analytical results are qualified accordingly and the TALS batch information is complete. Set samples to 2nd level review.

Run the LIMS QC Checker, investigate and correct any problems found. Run and review the deliverable. Fix any problems found then set the method chain to lab complete. Complete the data review checklist designated for this task.

14.3 Data Reporting

The report format, application of data qualifiers and creation of the data deliverable is performed by the LIMS using the formatter set by the project manager during log-in. The LIMS formatter for CLP SOW is designed to match the reporting specifications given in the CLP SOW.

Records of electronic and hardcopy data are maintained as described in laboratory SOP BR-QA-014.

Complete the deliverable checklist designated for this task.

15.0 Corrective Action Procedures

Corrective action procedures for QC failures are provided in Section 12 and Table 4.

16.0 Data Management and Records Management

All data generated in the performance of this method is managed in accordance with SOP BR-CLPSOW-QAP and BR-QA-014.
Any ancillary data, such as instructional correspondence shall be scanned attached to the appropriate batch in the LIMS system.

17.0 Method Performance

17.1 Method Detection Limit Study (MDL)

Determine a method detection limit (MDL) on each instrument used for analysis for each matrix and non-prepared analyses prior to initial use of the method and annually thereafter.

Refer to laboratory SOP BR-QA-005 for the laboratory's procedure for method detection limit studies.

18.0 References / Cross-References

- Exhibit D, Analytical Methods, USEPA CLP SOW for Inorganics Superfund Methods, ISM01.2, January 2010.
- Laboratory SOP BR-QA -019 *Data Review*
- Laboratory SOP BR-QA-011 *Procedures for Employee Training & Demonstration of Proficiency.*
- Laboratory SOP BR-QA-014 *Laboratory Records*
- Laboratory SOP BR-QA-002 *Standard Preparation*
- Laboratory SOP BR-QA-005 *Determination of LOD, LOQ & RL*.
- Laboratory SOP BR-QA-020 *Sample Homogenization and Subsampling*
- Laboratory SOP BR-EH-001 *Hazardous Waste*
- Laboratory Quality Assurance Manual (QAM)
- Corporate Environmental Health and Safety Manual (CW-E-M-001)

19.0 Method Modifications

N/A

20.0 Attachments

- Table 1: Target Analyte List (TCL), CRQLs and Analyte Wavelengths Used by Instrument
- Table 2: Primary Materials Used
- Table 3: QC Summary & Recommended Corrective Action
- Appendix A: Standard Preparation Tables
- Appendix B: Terms and Definitions
- Appendix C: Equations

21.0 Revisions

BR-ME-019, Revision 1:

- Title Page: Updated approval signatures.
- All Sections: The format of the SOP was updated to match the SOP format specification of the SOW.
- Section 5.0: Personnel Qualification requirements updated.
- Section 6.1: Interference correction procedure updated
- Section 7.5: Source material qualification updated.
- Section 9.3: Support Equipment Calibration information added
- Section 10.0: SMO notification procedures added
- Section 10.1.1: pH check procedure added
- Section 10.2: Screening instructions added.
- Section 12 and Table 4: QC criteria and corrective actions updated to method.
- Table 1: Interferences added to table.
- Appendix A: Recommended standards updated to match lab practice and ISM01.3 changes.

BR-ME-019, Revision 0:

This is the first release of this SOP.

Target Analyte List (TAL), CRQLs and Analyte Wavelengths Used by Instrument

Analyte	CAS No.	CRQL				
		Water (ug/L)	Soil (mg/kg)	Wipes (ug)	Filters (ug)	Analyte Wave-length (nm)
Aluminum	7429-90-5	200	20	20	2	396.152
Antimony	7440-36-0	60	6	6	0.6	206.833
Arsenic	7440-38-2	10	1	1	0.1	189.042
Barium	7440-39-3	200	20	20	2	233.527
Beryllium	7440-41-7	5	0.5	0.5	0.05	313.042
Cadmium	7440-43-9	5	0.5	0.5	0.05	228.802
Calcium	7440-70-2	5000	500	500	50	318.128
Chromium	7440-47-3	10	1	1	0.10	205.552
Cobalt	7440-48-4	50	5	5	0.5	228.616
Copper	7440-50-8	25	2.5	2.5	0.25	324.754
Iron	7439-89-6	100	10	10	1	271.441
Lead	7439-92-1	10	1	1	0.1	220.353
Magnesium	7439-95-4	5000	500	500	50	279.079
Manganese	7439-96-5	15	1.5	1.5	0.15	257.61
Nickel	7440-02-0	40	4	4	0.4	231.604
Potassium	7440-09-7	5000	500	500	50	766.49
Selenium	7782-49-2	35	3.5	3.5	0.35	196.09
Silver	7440-22-4	10	1	1	0.10	328.068
Sodium	7440-23-5	5000	500	500	50	589.592
Thallium	7440-28-0	25	2.5	2.5	0.25	190.856
Vanadium	7440-62-2	50	5	5	0.5	292.402
Zinc	7440-66-6	60	6	6	0.60	213.856

Table 2: Primary Materials Used

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Table 3: QC Summary and Recommended Corrective Action

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (ICAL)	Prior to each analytical run.	Correlation Coefficient >0.995 ±30% Difference for each non zero point Absolute value of Y intercept <CRQL	Correct problem and repeat ICAL.
Initial Calibration Verification (ICV)	Once, after each ICAL.	%R 90-110 RSD from Replicate integrations < 5%	Stop analysis, correct problem and reanalyze. If second attempt fails, perform further corrective action and initiate a new analytical run.
Initial Calibration Blank (ICB)	Once, after each ICV.	Absolute value of all analytes < CRQL	. If second attempt fails, perform further corrective action and initiate a new analytical run.
Continuing Calibration Verification (CCV)	At the beginning and end of each analytical run and every 10 samples or not to exceed every 2 hours.	%R 90-110 RSD from Replicate integrations < 5%	Stop analysis, correct problem and reanalyze CCV. If that fails, initiate a new analytical run and reanalyze all samples since last successful CCV.
Calibration Blank (CCB)	After every CCV during the analytical run and every 10 samples or not to exceed every 2 hours.	Absolute value of all analytes < CRQL	Stop analysis, correct problem and reanalyze CCB. If that fails, initiate a new analytical run and reanalyze all samples since last successful CCB.
Interference Check Sample (ICS)	At the beginning of each analytical run but not before the ICV/ICB pair.	See Section 10.2.3	Stop analysis, correct problem and initiate a new analytical run.
Method Blank (PB)	One per digestion batch or SDG, whichever is more frequent	Absolute Value of MB< CRQL or MB<10X sample concentration L	Redigest and reanalyze PB, LCS and all associated samples if samples <10X concentration of blank contamination.
Laboratory Control Sample (LCS)	One per digestion batch or SDG, whichever is more frequent.	%Recovery 70-130	Redigest and reanalyze PB, LCS and all associated samples if samples <10X concentration of blank contamination.
Matrix Spike (MS)	Matrix matched one per digestion batch of twenty samples or less	%R 75-125 when parent concentration is < 4 times spike added	Perform a post digestion spike at 2 times the parent concentration or 2 times the CRQL is parent concentration is below CRQL. Sample data is flagged with an “N” on deliverable forms.
Sample Duplicate (SD)	Matrix matched one per digestion batch of twenty samples or less	<20% RPD for samples ≥5X CRQL	Samples are flagged with a “*” on deliverable forms.
Serial Dilution (L	Matrix matched one per digestion batch of twenty samples or less	<10% Difference if result in parent sample is greater than 50X MDL.	Samples are flagged with an “E” on deliverable forms.
Post Digestion Spike (PDS)	One per Matrix Spike Failure	%R 75-125	Samples are flagged with “V”

Appendix A: Standard Preparation Tables

The standard formulations contained in this Appendix are recommended and are subject to change. If the concentration of the stock standard is different than those noted in this table, adjust the standard preparation formulation accordingly. Unless otherwise specified, prepare the standard solutions with a 5% HCl / 2% HNO3 solution using Class A volumetric glassware and Hamilton syringes. Unless otherwise specified for a standard solution, assign an expiration date of 14 days from date of preparation unless the parent standard expires sooner in which case use the earliest expiration date. See laboratory SOP BR-QA-002 *Standard Preparation* for further guidance.

Mixed Element Calibration Standards

Calibration Standard 8

Single Element Stock Standard	Volume Used (mL)	Final Volume (mL)	Final Concentration (ug/L)
10000 ppm Aluminum	30.0	1000	300000
1000 ppm Antimony	2.5	1000	2500
1000 ppm Arsenic	2	1000	2000
1000 ppm Barium	12.5	1000	12500
1000 ppm Beryllium	6.25	1000	6250
1000 ppm Cadmium	2	1000	2000
10000 ppm Calcium	30	1000	300000
1000 ppm Chromium	4	1000	4000
1000 ppm Cobalt	5	1000	5000
1000 ppm Copper	12.5	1000	12500
10000 ppm Iron	30	1000	300000
1000 ppm Lead	12.5	1000	12500
10000 ppm Magnesium	30.0	1000	300000
1000 ppm Manganese	12.5	1000	12500
1000 ppm Nickel	12.5	1000	12500
10000 ppm Potassium	10.0	1000	100000
1000 ppm Selenium	2	1000	2000
1000 ppm Silver	1	1000	1000
10000 ppm Sodium	10.0	1000	100000
1000 ppm Thallium	2	1000	2000
1000 ppm Vanadium	12.5	1000	12500
1000 ppm Zinc	12.5	1000	12500

Calibration Standard Intermediate #1

Single Element Stock Standard	Volume Used (mL)	Final Volume (mL)	Final Concentration (ug/L)
10000 ppm Aluminum	0.64	2000	3200
1000 ppm Antimony	1.92	2000	960
1000 ppm Arsenic	0.32	2000	160
1000 ppm Barium	6.40	2000	3200
1000 ppm Beryllium	0.16	2000	80
1000 ppm Cadmium	0.16	2000	80
10000 ppm Calcium	8.0	2000	40000
1000 ppm Chromium	0.32	2000	160
1000 ppm Cobalt	1.60	2000	800
1000 ppm Copper	0.80	2000	400
10000 ppm Iron	0.32	2000	1600
1000 ppm Lead	0.32	2000	160
10000 ppm Magnesium	8.0	2000	40000
1000 ppm Manganese	0.48	2000	240
1000 ppm Nickel	1.28	2000	640
10000 ppm Potassium	8.0	2000	40000
1000 ppm Selenium	0.56	2000	280
1000 ppm Silver	0.32	2000	160
10000 ppm Sodium	8.0	2000	40000
1000 ppm Thallium	0.80	2000	400
1000 ppm Vanadium	1.60	2000	800
1000 ppm Zinc	1.92	2000	960

Calibration Standard 7 (S7)

Source Material	Components	Final Concentration (ug/L)	Volume Used (mL)	Final Volume (mL)	Final Concentration (ug/L)
Calibration STD 8	Aluminum	300000	50	100	150000
	Antimony	2500			12500
	Arsenic	2000			1000
	Barium	12500			6250
	Beryllium	6250			3125
	Cadmium	2000			1000
	Calcium	300000			150000
	Chromium	4000			2000
	Cobalt	5000			2500
	Copper	12500			6250
	Iron	300000			150000
	Lead	12500			6250
	Magnesium	300000			150000
	Manganese	12500			6250
	Nickel	12500			6250
	Potassium	100000			50000
	Selenium	2000			1000
	Silver	1000			500
	Sodium	100000			50000
	Thallium	2000			1000
	Vanadium	12500			6250
	Zinc	12500			6250

Calibration Standard 6 (S6)

Source Material	Components	Final Concentration (ug/L)	Volume Used (mL)	Final Volume (mL)	Final Concentration (ug/L)
Calibration STD	Aluminum	300000	20	100	60000

8	Antimony	2500			500
	Arsenic	2000			400
	Barium	12500			2500
	Beryllium	6250			1250
	Cadmium	2000			400
	Calcium	300000			60000
	Chromium	4000			800
	Cobalt	5000			1000
	Copper	12500			2500
	Iron	300000			60000
	Lead	12500			2500
	Magnesium	300000			60000
	Manganese	12500			2500
	Nickel	12500			2500
	Potassium	100000			20000
	Selenium	2000			400
	Silver	1000			200
	Sodium	100000			20000
	Thallium	2000			400
	Vanadium	12500			2500
	Zinc	12500			2500

Calibration Standard 5 (S5)

Source Material	Components	Final Concentration (ug/L)	Volume Used (mL)	Final Volume (mL)	Final Concentration (ug/L)
Calibration STD 8	Aluminum	300000	8	100	24000
	Antimony	2500			200
	Arsenic	2000			160
	Barium	12500			1000
	Beryllium	6250			500
	Cadmium	2000			160
	Calcium	300000			24000
	Chromium	4000			320
	Cobalt	5000			400
	Copper	12500			1000
	Iron	300000			24000
	Lead	12500			1000
	Magnesium	300000			24000
	Manganese	12500			1000
	Nickel	12500			1000

	Potassium	100000			8000
	Selenium	2000			160
	Silver	1000			80
	Sodium	100000			8000
	Thallium	2000			160
	Vanadium	12500			1000
	Zinc	12500			1000

Calibration Standard 4 (S4)

Source Material	Components	Final Concentration (ug/L)	**Volume Used (mL)**	**Final Volume (mL)**	**Final Concentration (ug/L)**
Calibration STD 8	Aluminum	300000	3.2	100	9600
	Antimony	2500			80
	Arsenic	2000			64
	Barium	12500			400
	Beryllium	6250			200
	Cadmium	2000			64
	Calcium	300000			9600
	Chromium	4000			128
	Cobalt	5000			160
	Copper	12500			400
	Iron	300000			9600
	Lead	12500			400
	Magnesium	300000			9600
	Manganese	12500			400
	Nickel	12500			400

	Potassium	100000			3200
	Selenium	2000			64
	Silver	1000			64
	Sodium	100000			3200
	Thallium	2000			64
	Vanadium	12500			400
	Zinc	12500			400

Calibration Standard #3 (S3)

Source Material	Components	Final Concentration (ug/L)	**Volume Used (mL)**	**Final Volume (mL)**	**Final Concentration (ug/L)**
Calibration Intermediate #1	Aluminum	300000	1.28	100	3840
	Antimony	2500			32
	Arsenic	2000			25.6
	Barium	12500			160
	Beryllium	6250			80
	Cadmium	2000			25.6
	Calcium	300000			3840
	Chromium	4000			51.2
	Cobalt	5000			64
	Copper	12500			160
	Iron	300000			3840
	Lead	12500			160
	Magnesium	300000			3840

	Manganese	12500			160
	Nickel	12500			160
	Potassium*	100000			1280*
	Selenium	2000			25.6
	Silver	1000			25.6
	Sodium*	100000			1280*
	Thallium	2000			25.6
	Vanadium	12500			160
	Zinc	12500			160

***These elements are not calibrated from this standard.**

Calibration Standard #2 (S2)

Source Material	Components	Final Concentration (ug/L)	Volume Used (mL)	Final Volume (mL)	Final Concentration (ug/L)
Calibration Intermediate #1	Aluminum	3200	12.5	100	400
	Antimony	960			120
	Arsenic	160			20
	Barium	3200			400
	Beryllium	80			10
	Cadmium	80			10
	Calcium	40000			10000
	Chromium	160			20
	Cobalt	800			100
	Copper	400			50
	Iron	1600			200
	Lead	160			20
	Magnesium	40000			5000
	Manganese	240			30
	Nickel	640			80
	Potassium	40000			5000
	Selenium	280			35
	Silver	160			20

	Sodium	40000			5000
	Thallium	400			50
	Vanadium	800			100
	Zinc	960			120

Calibration Standard 1 (S1)

Source Material	Components	Final Concentration (ug/L)	Volume Used (mL)	Final Volume (mL)	Final Concentration (ug/L)
Calibration Intermediate #1	Aluminum	3200	6.25	100	200
	Antimony	960			60
	Arsenic	160			10
	Barium	3200			200
	Beryllium	80			5
	Cadmium	80			5
	Calcium	40000			2500
	Chromium	160			10
	Cobalt	800			50
	Copper	400			25
	Iron	1600			100
	Lead	160			10
	Magnesium	40000			2500
	Manganese	240			15
	Nickel	640			40
	Potassium	40000			2500
	Selenium	280			17.5
	Silver	160			10
	Sodium	40000			2500
	Thallium	400			25
	Vanadium	800			50
	Zinc	960			60

Interference Check (ICS) Solutions

ICSA Standard Solution
MEISMOESICSAw

Multi-Element Stock Standard	Volume Used (mL)	Final Volume (mL)	Final Concentration (ug/L)
EPA Interference Check Sample ICP-AES ICSA	10	100	See below
Aluminum			244100
Calcium			234900
Chromium			43
Iron			95600
Magnesium			247500
Manganese			19
Lead			10

ICSAB Standard Solution
MEISMOESICSABw

Multi-Element Stock Standard	Volume Used (mL)	Final Volume (mL)	Final Concentration (ug/L)
EPA Interference Check Sample ICP-AES ICSA	10	100	See above
EPA Interference Check Sample ICP-AES ICSAB	10		See below
Aluminum			241100
Antimony			589
Arsenic			101
Barium			495
Beryllium			475
Cadmium			940
Calcium			231100
Chromium			511
Cobalt			461
Copper			548
Iron			94800
Lead			61
Magnesium			251100
Manganese			502
Nickel			984
Selenium			53
Silver			206
Thallium			103
Vanadium			494
Zinc			1028

Initial Calibration Verification (ICV)
MEISMOESICVw

Multi-Element Stock Standard	Volume Used (mL)	Final Volume (mL)	Final Concentration (ug/L)
EPA Initial Calibration Verification Solution ICV1	10	100	See below
Aluminum			2521
Antimony			994
Arsenic			999
Barium			497
Beryllium			495
Cadmium			496
Calcium			10026
Chromium			490
Cobalt			499
Copper			492
Iron			5082
Lead			1002
Magnesium			6074
Manganese			499
Nickel			503
Potassium			10021
Selenium			1029
Silver			501
Sodium			10097
Thallium			1028
Vanadium			501
Zinc			1025

Matrix Spike Solution
MEISMOESSPKi

Single Element Stock Standard	Volume Used (mL)	Final Volume (mL)	Final Concentration (ug/L)
10000 ppm Al	2	100	200000
1000 ppm Sb	1	100	10000
1000 ppm As	0.4	100	4000
1000 ppm Ba	20	100	200000
1000 ppm Be	0.5	100	5000
1000 ppm Cd	0.5	100	5000
1000 ppm Cr	2	100	20000
1000 ppm Co	5	100	50000
1000 ppm Cu	2.5	100	25000
10000 ppm Fe	1	100	100000
1000 ppm Pb	0.2	100	2000
1000 ppm Mn	5	100	50000
1000 ppm Ni	5	100	50000
1000 ppm Se	1.0	100	10000
1000 ppm Tl	0.5	100	5000
1000 ppm V	5	100	50000
1000 ppm Zn	5	100	50000
1000 ppm B	5	100	50000
1000 ppm Mo	5	100	50000
1000 ppm Ag	0.5	100	5000

Aqueous LCS Solution
MEISMOESLCS

Single Element Stock Standard	Volume Used (mL)	Final Volume (mL)	Final Concentration (ug/L)
10000 ppm Aluminum	0.4	100	40000

1000 ppm Antimony	1.2	100	12000
1000 ppm Arsenic	0.2	100	2000
1000 ppm Barium	4	100	40000
1000 ppm Beryllium	0.1	100	1000
1000 ppm Cadmium	0.1	100	1000
10000 ppm Calcium	10	100	1000000
1000 ppm Chromium	0.2	100	2000
1000 ppm Cobalt	1	100	10000
1000 ppm Copper	0.5	100	5000
10000 ppm Iron	0.2	100	2000
1000 ppm Lead	0.2	100	2000
10000 ppm Magnesium	10	100	1000000
1000 ppm Manganese	0.3	100	3000
1000 ppm Nickel	0.8	100	8000
10000 ppm Potassium	10	100	1000000
1000 ppm Selenium	0.7	100	7000
1000 ppm Silver	0.2	100	2000
10000 ppm Sodium	10	100	1000000
1000 ppm Thallium	0.5	100	5000
1000 ppm Vanadium	1	100	10000
1000 ppm Zinc	1.2	100	12000

Appendix B: List of Definitions

Analyte: The element or ion an analysis seeks to determine; the element of interest.

Analytical Sequence: The actual instrumental analysis of the samples from the time of instrument calibration through the analysis of the final CCV or CCB.

Background Correction: A technique to compensate for variable background contribution to the instrument signal in the determination of trace elements.

Batch: A group of samples prepared at the same time in the same location using the same method.

Blank: An analytical sample designed to assess specific sources of contamination.

Calibration: The establishment of an analytical curve based on the absorbance, emission intensity, or other measured characteristic of known standards.

Calibration Blank: A blank solution containing all of the reagents and in the same concentration as those used in the analytical sample preparation.

Calibration Standards: A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve).

Continuing Calibration Verification (CCV): A single parameter or multiparameter standard solution prepared by the analyst and used to verify the stability of the instrument calibration with time, and the instrument performance during the analysis of samples.

Contract Required Quantitation Limit (CRQL): Minimum level of quantitation acceptable under the contract Statement of Work (SOW).

Contract Required Quantitation Limit (CRQL) Check Standard (CRI): A single parameter or multi-parameter standard solution prepared at the CRQL and used to verify the instrument calibration at low levels.

Control Limits: A range within which specified measurement results must fall to be compliant. Control limits may be mandatory, requiring corrective action if exceeded, or advisory, requiring that noncompliant data be flagged.

Dissolved Metals: Analyte elements in a water/aqueous sample which will pass through a 0.45 micrometer (µm) filter.

Dry Weight: The weight of a sample based on percent solids. The weight after drying in an oven.

Duplicate: A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

Holding Time: The elapsed time expressed in days from the date of receipt of the sample by the Contractor until the date of its analysis.

Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) – A technique for the simultaneous or sequential multi-element determination of elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Characteristic atomic line emission spectra are produced by excitation of the sample in a radio frequency inductively coupled plasma.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations; used to define the quantitative response, linearity, and dynamic range of the instrument to target analytes.

I**nitial Calibration Verification (ICV):** Solution(s) prepared from stock
standard solutions, metals or salts obtained from a source separate from that utilized to prepare the calibration standards. The ICV is used to verify the concentration of the calibration standards and the adequacy of the instrument calibration.

Interference Check Sample: A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors.

Interferents: Substances which affect the analysis for the element of interest.

Laboratory Control Sample (LCS): A control sample of known composition.

Linear Range, Linear Dynamic Range: The concentration range over which the instrument response remains linear.

Matrix: The predominant material of which the sample to be analyzed is composed.

Matrix Effect: In general, the effect of particular matrix constituents.

Matrix Spike: Aliquot of a sample (water/aqueous or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

Method Detection Limit (MDL): The concentration of a target parameter that, when a sample is processed through the complete method, produces a signal with 99 percent probability that it is different from the blank. For 7 replicates of the sample, the mean value must be 3.14s above the blank, where “s” is the standard deviation of the 7 replicates.

Percent Difference (%D): The difference between the two values divided by one of the values.

Percent Solids (%S): The proportion of solid in a soil sample determined by drying an aliquot of the sample.

Preparation Blank: An analytical control that contains reagent water and reagents, which is carried through the entire preparation and analytical procedure.

Relative Percent Difference (Rpd): The relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero.

Sample: A portion of material to be analyzed that is contained in single or multiple containers and identified by a unique sample number.

Sensitivity: The slope of the analytical curve (i.e., functional relationship between instrument response and concentration).

Serial Dilution: The dilution of a sample by a factor of five. When corrected by the dilution factor, the diluted sample must agree with the original undiluted sample within specified limits. Serial dilution may reflect the influence of interferents.

Stock Solution: A standard solution which can be diluted to derive other standards.

Target Analyte List (TAL): A list of Inorganic Analytes (metals and cyanide) as designated in Exhibit C.

Validated Time Of Sample Receipt (VTSR): The date on which a sample is received at the Contractor's facility, as recorded on the shipper's delivery receipt and Sample Traffic Report/Chain of Custody Record.

Appendix C: Equations

Unless otherwise specified, calculations are performed using data analysis software.

Percent Recovery (%R) LCS and CCVs

$$\%R = \frac{SR}{SA} * 100\%$$

Where:
SR = Sample Result
SA = Concentration of Spike Added

Percent Recovery (%R) MS

$$MSRecovery(\%) = \frac{SSR - SR}{SA} * 100\%$$

Where:
SSR = Matrix Spike Result
SR = Sample Result
SA = Concentration of Spike Added

Relative Percent Difference (%RPD)

$$\%RPD = \frac{|D_1 - D_2|}{\frac{D_1 + D_2}{2}} * 100$$

Where:
D1 = Sample result
D2 = Duplicate Result

Water Sample Concentration

$$C_{(ug/L)} = \frac{\mu g}{L_{dig}} * \frac{V_{dig}}{V_{samp}}$$

Where:
$\mu g/L_{dig}$ = ICP result including all dilution factors
V_{dig} = final digestate volume in mLs
V_{samp} = sample volume in mLs

Soil/Sediment Sample Concentration

$$C_{(mg/Kg)} = \frac{\mu g}{L_{dig}} * \frac{V_{dig}}{g_{samp}} * \frac{100}{\%\,solids}$$

Where:
$\mu g/L_{dig}$ = ICP result including all dilution factors
V_{dig} = final digestate volume in Liters
g_{samp} = sample weight in grams

Title: Determination of Mercury by Cold Vapor Analysis (CLP SOW ISM01.2)

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1.0 Scope and Application

This SOP describes the laboratory procedure for the analysis of total mercury in samples taken from hazardous waste sites using a cold vapor technique with atomic absorption (AA).

1.1 Analytes, Matrix(s), and Reporting Limits

This procedure may be used for a variety of matrices including: water, sediment, sludge and soil.

For aqueous samples, the contract required quantitation limit (CRQL) is 0.2 ug/L, and for soils, the CRQL is 0.1 mg/kg.

2.0 Summary of Method

2.1 Water

A measured volume of sample is acid digested with concentrated sulfuric, nitric acids, and potassium permanganate for two hours in a block digester maintained at a temperature of 95°C. After digestion, hydroxylamine hydrochloride is added to each digestate in order to reduce excess permanganate. The digestate is placed on a closed-system mercury autoanalyzer and stannous chloride is added to each sample. The elemental mercury released is measured spectrophotometrically at a wavelength of 253.7 nm. The concentration is calculated from the response of the sample absorbance applied against the calibration curve.

2.2 Soil/Sediment

A weighed portion of solid sample is acid digested with aqua regia for 2 minutes at a temperature of 95°C then digested with potassium permanganate for 30 minutes at a temperature of 95°C. Hydroxylamine hydrochloride is added to each digestate in order to reduce excess permanganate. The digestate is placed on a closed-system mercury autoanalyzer and stannous chloride is added to each sample. The elemental mercury released is measured spectrophotometrically at a wavelength of 253.7 nm. The concentration is calculated from the response of the sample absorbance applied against the calibration curve.

This procedure is based on CLP SOW ISM01.2, Exhibit D (Mercury).

3.0 Definitions

A list of terms and definitions are provided in Appendix A.

4.0 Interferences

4.1 Water

Some seawaters and wastewaters that are high in chlorides exhibit a positive interference; during the oxidation step chlorides are converted to free chlorine, which will also absorb radiation at 253 nanometers (nm). To ensure free chlorine is absent before the mercury is reduced and swept into the cell use an excess of hydroxylamine HCl reagent (25mL) and additional amounts of permanganate [as much as 25 milliliters (mL)].

Possible interference from sulfide is eliminated by the addition of potassium permanganate. Copper has also been reported to interfere; however, per the CLP SOW, copper concentrations as high as 10mg/L have not shown an effect on recovery of mercury from spiked samples.

Samples that contain high concentrations of oxidizable organic materials (high COD values) may not be completely oxidized by this procedure. If this occurs, the recovery of organic mercury will be low. To eliminate the problem, reduce the weight of the original samples or increase the amount of potassium persulfate (and stannous chloride) used in the digestion.

4.2 Soil/Sediment

The same types of interferences noted for water samples are possible with sediments.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added. Protective clothing such as a lab coat, safety glasses and latex gloves must be worn while performing this procedure.

5.2 Primary Materials Used

Table 2, Section 18.0 lists of the materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the MSDS. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

6.0 Equipment and Supplies

Catalog numbers listed in this SOP are subject to change at the discretion of the vendor. Analysts are cautioned to be sure equipment used meets the specification of this SOP.

6.1 Miscellaneous

- Block digester; Environmental Express
- Polyethylene Digestion Vessels; 100 mL; Environmental Express
- Volumetric Pipettes

- Top Loading Balance

6.2 Analytical System

- Mercury Auto-Analyzer; Teledyne Leeman Labs Hydra AA.

7.0 Reagents and Standards

7.1 Reagents

- Reagent Water, ASTM Type II
- Sulfuric Acid, concentrated - Reagent grade; JT Baker or equivalent
- Nitric Acid, concentrated - Reagent grade; JT Baker or equivalent
- Hydrochloric Acid, concentrated - Reagent grade; JT Baker or equivalent
- Hydroxylamine Hydrochloride; Reagent grade; JT Baker or equivalent
- Potassium Permanganate; Reagent grade; JT Baker or equivalent
- Potassium Persulfate; Reagent grade; JT Baker or equivalent
- Stannous Chloride; Reagent grade; JT Baker or equivalent
- Sodium Chloride; Reagent grade; JT Baker or equivalent

Sodium Chloride Hydroxylamine Hydrochloride: Dissolve 240 grams of Hydroxylamine Hydrochloride and 240 grams of sodium chloride in 2 L of reagent water. Assign an expiration date of 6 months and store this solution at room temperature.

Potassium Permanganate ($KMNO_4$): 5% solution w/v: Dissolve 100 grams of Potassium Permanganate in 2 L of reagent water. Assign an expiration date of 6 months and store this solution at room temperature.

Aqua Regia: Carefully add three volumes of concentrated hydrochloric acid to one volume of concentrated nitric acid. Assign an expiration date of 6 months and store this solution at room temperature.

Potassium Persulfate – 5% solution w/v: Dissolve 100 grams of Potassium Persulfate in 2L of reagent water. Assign an expiration date of 6 months and store this solution at room temperature.

Stannous Chloride Solution: Add 100 g of stannous chloride to 1 L of 10% hydrochloric acid. Assign an expiration date of 6 months and store this solution at room temperature.

7.2 Standards

Purchase stock standard solutions from commercial vendors and from these prepare intermediate and working standard solutions are prepared by diluting volumes of stock standards with acidified reagent water in volumetric flasks to obtain the appropriate concentration. Assign expiration

dates according to expiration date of the parent standard. Prepare standard solutions as needed or on the expiration date, whichever occurs first.

- Primary Source Mercury Stock Standard (1000 mg/L): Purchase from Spex or equivalent.
- Second Source Mercury Stock Standard (1000 mg/L): Purchase from Inorganic Ventures.

Mercury Intermediate Standard (10,000 ug/L): Add 1mL of the 1000 mg/L primary source stock standard solution and 0.15 mL of concentrated nitric acid to a 100 mL volumetric flask that contains approximately 80 mL reagent water. Adjust to volume with reagent water. Store this solution at room temperature.

Mercury Daily Working Standard (100 ug/L): Add 10 mL of the intermediate standard and 1.5 mL of concentrated nitric acid to a 1000 mL volumetric flask that contains approximately 800 mL reagent water. Adjust to volume with reagent water. Use secondary dilutions of the working standard for the calibration curve, continuing calibration verification (CCV) standards, and the Contract Required Quantitation Limit (CRQL) Check Standard (CRI). Store this solution at room temperature and prepare fresh daily.

- ICV Solution: Obtain from EPA and use as per EPA instructions. Concentration and preparation at discretion of EPA CLP Program.

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection so these procedures are not included in this SOP. Listed below are the laboratory recommended minimum sample size, preservation and holding time requirements:

Matrix	Sample Container	Minimum Sample Size	Preservation	Holding Time[1]	Reference
Water[2]	Glass or polyethylene container	100 mL	pH <2 with nitric acid. Chill to <4°C (±2°C).	26 days from Validated Time of Sample Receipt (VTSR)	ISM01.2
Soil	Glass or polyethylene container		Chill to <4°C (±2°C).	26 days from Validated Time of Sample Receipt (VTSR)	ISM01.2

[1]Holding time is determined from validated time of sample receipt (VTSR)

For the determination of dissolved metals, the sample must be filtered through a 0.45 micrometer (um) pore diameter membrane filter at the time of collection or as soon as possible. Use a portion of the sample to rinse the filter flask, discard this portion, and collect the required volume of filtrate. Preserve the filtrate with nitric acid to pH less than or equal to 2 immediately after filtration.

Unless otherwise specified by client or regulatory program, after analysis, samples and extracts are retained for a minimum of 60 days after provision of the project report and then disposed of in accordance with applicable regulations.

9.0 Quality Control

9.1 Sample QC

The laboratory prepares the following quality control samples with each batch of samples.

QC Item	Frequency	Acceptance Criteria
Method Blank (MB)	1 in 20 or fewer samples	See Table 2
Matrix Spike(s) MS/MSD	Client Request	See Table 2
Sample Duplicate (SD)	Client Request	See Table 2

9.2 Instrument QC

The following instrument QC is performed:

QC Item	Frequency	Acceptance Criteria
Initial Calibration (ICAL)	Initially; when ICV or CCV fail	See Section 10.0
Second Source Calibration Verification (ICV)	Once, after each ICAL	See Section 10.0
Initial Calibration Blank (ICB)	Once, after each ICV	See Section 10.0
Continuing Calibration Verification (CCV)	Daily, every 10 samples, end of sequence	See Section 10.0
Continuing Calibration Blank (CCB)	Daily, every 10 samples, end of sequence	See Section 10.0

10.0 Procedure

10.1 Instrument Operating Conditions

Set up the instrument according to the instructions provided by the instrument manufacturer.

Turn on the instrument lamp, gas and pump and let the instrument warm up for 15 minutes. Fill the rinse bath with 10% hydrochloric acid solution and check all tubing connections. Reset the calibration curve. Check the stannous chloride reductant reservoir and fill as needed. Check and record the intensity of the 0.2 ug/L standard. When applicable, record sample intensity and reference intensities and verify against previous day. Perform maintenance to increase intensities if needed.

10.2 Instrument Calibration

10.2.1 Initial Calibration (ICAL)

Calibrate the instrument daily, or after initial calibration (ICV) or continuing calibration (CCV) failure.

Prepare fresh calibration standards with each calibration performed using at least 5 standards and a blank (6 total) by making successive dilutions of the working standard (100ug/L). One of the calibration standards must be at or below the contract required quantitation limit (CRQL). The recommended formulation and final concentrations of the calibration standards are provided in Appendix B.

Digest and analyze the standards following the procedures given in section 7.2.

The data system prepares a standard curve using linear regression by plotting the instrument response of the calibration standards against the true value concentration. The correlation coefficient must be greater than or equal to 0.995.

Check the calibration equation to establish the representativeness of the data that were used to produce the calibration equation. This check involves the re-fitting of the non-blank calibration data back to the calibration equation or the comparison of the calculated concentration of each of the standards against the expected concentration of the associated standard. If the Percent Differences for each of the standards do not fall within ±30%, the calibration equation is not acceptable, recalibrate the instrument.

Check the y-intercept from the linear regression initial calibration equation to ensure it is not below the low standard. If the y-intercept is not below the low standard, the calibration fails. Repeat the calibration. No samples may be analyzed until this criterion is met.

10.2.2 Second Source Calibration Verification (ICV)

Immediately after calibration, check the accuracy of the calibration with the ICV standard provided by the EPA. Digest and analyze the ICV following the procedure described in sections 10.3 and 10.4.

The percent recovery of the ICV must be within 85-115%. If this criterion is not met, correct the problem, recalibrate and repeat the ICV verification.

10.2.3 Continuing Calibration Verification (CCV)

To verify accuracy of the calibration during the analytical sequence, analyze a CCV standard at the beginning of the sequence, after the last sample and at a frequency not to exceed 1 hour. The concentration of the CCV standard must be at the mid-level concentration of the calibration curve.

Prepare the CCV using the same source standard as used for initial calibration at a concentration of 5 ug/L. See the table for the preparation of calibration standards for the formulation. Prepare, digest and analyze the CCV following the procedure described in sections 10.3 and 10.4.

The percent recovery of the CCV should be within 85-115%. If this criterion is not met, correct the problem, recalibrate and repeat the ICV verification. If criterion is not met, correct the problem and reanalyze all samples since the last compliant CCV.

10.2.4 Initial and Continuing Calibration Blanks (ICB/CCB)

Analyze calibration blanks immediately after every ICV and CCV during the analytical sequence. The absolute value of the ICB/CCB must be less than or equal to the CRQL. If it is not, correct the problem, recalibrate and reanalyze all samples since the last compliant calibration.

10.2.5 Troubleshooting

Check the following items in case of calibration failures:

- ICAL Failure – Perform instrument maintenance, change pump tubing, adjust the lamp, clean the sipper tip, replace the drying tube, clean or replace the optical cell. Re-pour curve standards and restart calibration.

- CCV Failure – Perform instrument maintenance, change pump tubing, adjust the lamp, clean the sipper tip, replace the drying tube, clean or replace the optical cell. Re-pour CCV standard and restart calibration and analytical sequence.

10.3 Sample Preparation

10.3.1 Water Sample and Standard Preparation (7470A, Revision 1, September 1994)

Transfer 50 mL of each sample into prepared digestion vessels. Use 50 mL of reagent water for the MB and calibration blanks. Add 0.5mL of the calibration source working standard solution (100 ug/L) to the sample selected as the matrix spike.

To prepare the preparation blank, and calibration blanks, add 50 mL of reagent water to a labeled digestion vessel(s).

To prepare the ICV, transfer 5 mL of the ICV solution provided by the EPA and 1 mL of 2% nitric acid solution into a prepared digestion vessel then adjust to 50 mL with reagent water.

To prepare the CCV transfer 50 mL of CCV solutions into a prepared digestion vessel.

Add 2.5 mL of concentrated sulfuric acid, 1.25 mL of concentrated nitric acid, and 7.5 mL of potassium permanganate solution to each digestion vessel and let the bottles sit for 15 minutes. During this time-frame the solution in the digestion vessels should turn and remain purple. If after 15 minutes, the solution is not purple, add more potassium permanganate (~1.25 mL). If additional amounts of potassium permanganate are needed, ensure that equal amounts are added to all standards, blanks and samples.

Add 4 mL of potassium persulfate solution to each digestion vessel and heat the vessels for two hours in a block digester maintained at 95°C (+/-3°C). After the time period has elapsed, allow the digestion vessel to cool then add 3 mL of hydroxylamine hydrochloride solution to each vessel in order to reduce the excess permanganate. Swirl to ensure that any soluble residue dissolves back into solution.

NOTE: At this point, samples can remain at room temperature for up to 48 hours prior to analysis but it is recommended that analysis be performed as soon as possible.

Transfer each solution to individual autoanalyzer tubes in preparation for analysis.

10.3.2 Solid Sample Preparation (Manual)

Measure 0.50-0.60 g of sample into a prepared digestion vessel then add 5.0 mL of reagent water to the vessel. Use 5.0 mL of reagent water for the method blanks. Add 0.5 mL of the calibration source mercury working standard solution (100ug/L) to the sample selected as the matrix spike.

Add 5 mL of aqua regia to each digestion vessel. Heat the vessels in a hot block digester maintained at 95°C (+/-3°C) for 2 minutes. After two minutes, remove from heat and allow the vessels to cool. Add 45 mL of reagent water and 15 mL of potassium permanganate solution. Swirl to mix. Heat in a hot block digester maintained at 95°C (+/-3°C) for 30 minutes. Remove from heat, allow the vessels to cool and add 6 mL of hydroxylamine hydrochloride solution to reduce the excess permanganate. Swirl each vessel to ensure that any soluble residue dissolves back into solution.

Add 45 mL of reagent water to each vessel and then transfer the solutions to individual autoanalyzer tubes in preparation for analysis. NOTE: All standards and samples must be at the same final volume.

NOTE: At this point, samples can remain at room temperature for up to 48 hours prior to analysis but it is recommended that analysis be performed as soon as possible.

10.4 Sample Analysis

On the PC connected to the instrument select the autosampler template and enter the sample Ids in the order of analysis. Place the samples, calibration blanks, calibration standards, and performance check standards in the position on the autosampler rack that corresponds to their assigned position in the autosampler template. Place the autosampler rack in the autosampler tray and initiate the software macro to begin analysis.

An example analytical sequence that includes initial calibration (ICAL) is provided below.

Injection Number	Lab Description
1	Calibration Blank
2	0.2 Calibration Standard
3	0.5 Calibration Standard
4	1.0 Calibration Standard
5	5.0 Calibration Standard
6	10.0 Calibration Standard
7	ICV
8	ICB
9	CCV
10	CCB
11-20	Samples
21	CCV
22	CCB

NOTE: In addition to the beginning and end of the analytical sequence, analyze a CCV throughout the analytical sequence at a frequency not to exceed 1 hour.

Enter the sample ID's into the data acquisition program in the order the samples were placed in the autosampler and initiate the analytical sequence.

11.0 Calculations / Data Reduction

11.1 Calculations

Unless otherwise noted all calculations are performed by the instrument processing software and the TALS LIMS system.

See Appendix C.

11.2 Data Review

11.2.1 Primary Review

Evaluate the results of the instrument performance check samples and field and QC samples against the established acceptance criteria. If criteria are not met, perform corrective action. If any data is reported outside criteria, initiate a nonconformance memo (NCM).

Upload the data into TALS. Enter the worksheet and batch information in the TALS batch. Set results to primary and secondary as appropriate, check QC linkages then set the TALS batch to first level review.

11.2.2 Secondary Review

Review project documents such as the Project Plan (PP), Project Memo or any other document/process used to communicate project requirements to ensure those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Verify that the acceptance criteria for the calibration and QC items listed in Table 1 were met. If the results do not fall within the established limits verify the recommended corrective actions were performed. If not, initiate corrective actions and/or verify an NCM was created to document the criteria exception. Verify analytical results are qualified accordingly and the TALS batch information is complete. Set samples to 2nd level review.

Run the LIMS QC Checker, investigate and correct any problems found. Run and review the deliverable. Fix any problems found then set the method chain to lab complete.

11.2.3 Data Reporting

The report format, application of data qualifiers and creation of the data deliverable is performed by the LIMS using the formatter set by the project manager during log-in. The LIMS formatter for CLP SOW is designed to match the reporting specifications given in the CLP SOW.

Records of electronic and hardcopy data are maintained as described in laboratory SOP BR-QA-014.

12.0 <u>Method Performance</u>

12.1 Method Detection Limit (MDL)

A Method Detection Limit (MDL) must be determined on each instrument used for analysis for each matrix and non-prepared analyses prior to initial use of the method and annually thereafter.

Refer to laboratory SOP BR-QA-005 for the laboratory's procedure for method detection limit studies.

12.2 Demonstration of Capabilities (DOC)

Perform a method demonstration of capability at initial set-up and when time there is a significant change in instrumentation or procedure.

Each analyst that performs the analytical procedure must complete an initial demonstration of capability (IDOC) prior to independent analysis of client samples. Each analyst must demonstrate on-going proficiency (ODOC) annually thereafter. DOC procedures are further

described in the laboratory's quality system manual (QAM) and in the laboratory SOP for employee training.

12.3 Training Requirements

Any employee that performs any portion of the procedure described in this SOP must have documentation in their employee training file that they have read this version of this SOP.

Instrument analysts, prior to independent analysis of client samples, must also have documentation of demonstration of initial proficiency (IDOC) and annual on-going proficiency (ODOC) in their employee training files.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability).

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to laboratory SOP BR-LP-001.

15.0 References / Cross-References

- CLP SOW ISM01.2 For Inorganic Superfund Methods, Multi-Media, Multi-Concentration, January 2010.
- Laboratory SOP BR-QA-005, Procedures for the Determination of Limits of Detection (LOD), Limits of Quantitation (LOQ) and Reporting Limits (RL).
- Laboratory SOP BR-QA-011 Employee Training
- Laboratory SOP BR-LP-011 Hazardous Waste
- Laboratory SOP BR-QA-014 Laboratory Records
- Laboratory Quality Assurance Manual (QAM)

16.0 Method Modifications

Not applicable.

17.0 Attachments

- Table 1: Primary Materials Used
- Table 2: QC Summary & Recommended Corrective Action
- Appendix A: Terms and Definitions
- Appendix B: Standard Preparation Tables
- Appendix C: Equations

18.0 Revision History

Not applicable. First version.

Table 1: Primary Materials Used

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Mercury (1,000 PPM in Reagent)	Oxidizer Corrosive Poison	0.1 Mg/M3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 PPM-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Permanganate	Oxidizer	5 Mg/M3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Table 2: QC Summary, Frequency, Acceptance Criteria and Recommended Corrective Action (ISM01.2 Hg)

QC Item	Frequency	Acceptance Criteria	Recommended Corrective Action[1]
ICAL	Prior to each analytical sequence	Linear Regression: r ≥ 0.995, the results for each calibration level should be within 30% D of the true value.	Correct problem, reanalyze, repeat calibration.
ICV	After each initial calibration	(% R) 85-115%	Correct problem, verify second source standard. If that fails, repeat calibration..
ICB	After each ICV	Target Analyte <CRQL	Correct problem and reanalyze
CCV	On each analytical sequence before sample analysis, every 10 samples and at the end of the analytical sequence	(% R) 85-115%	Correct problem. Repeat calibration and reanalyze all samples since last successful calibration.
CCB	After each CCV	Target Analyte <CRQL	Correct problem and reanalyze
MB	One per preparation batch of 20 or fewer samples	Target Analyte < CRQL	Correct problem. Redigest and reanalyze MB and associated samples if samples are not >10X contaminant concentration in MB.
MS	One per batch of twenty samples or less	(% R) 75-125	Evaluate data to determine if outage is related to analytical error or matrix effect. Flag data if original sample results is <4X spike added amount.
DP	One per batch of twenty samples or less	<20%	Evaluate data to determine source of difference between results. Flag Data.

[1]The recommended corrective action may include some or all of the items listed in this column. The corrective action taken may be dependent on project data quality objectives and/or analyst judgment but must be sufficient to ensure that results will be valid. If corrective action is not taken or is not successful, data must be flagged with appropriate qualifiers.

Appendix A: Terms and Definitions

Acceptance Criteria: specified limits placed on characteristics of an item, process or service defined in requirement documents.

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 which are due to sampling and analytical operations; a data quality indicator.

Analyte: The specific chemicals or components for which a sample is analyzed. (EPA Risk Assessment Guide for Superfund, OSHA Glossary).

Batch: environmental samples that are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria. An analytical batch is composed of prepared environmental samples (extracts, digestates and concentrates), which are analyzed together as a group.

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 the standards.

Calibration Curve: the graphical relationship between the known values or a series of calibration standards and their instrument response.

Calibration Standard: A substance or reference used to calibrate an instrument.

Continuing Calibration Verification (CCV): a single or multi-parameter calibration standard used to verify the stability of the method over time, usually from the same source as the calibration curve.

Corrective Action: the action taken to eliminate the cause of an existing nonconformity, defect or other undesirable occurrence in order to prevent recurrence.

Data Qualifier: a letter designation or symbol appended to an analytical result used to convey information to the data user. (Laboratory)

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

Intermediate Standard: a solution made from one or more stock standards at a concentration between the stock and working standard. Intermediate standards may be certified stock standard solutions purchased from a vendor and are also known as secondary standards.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Matrix Spike (MS): a field sample to which a known amount of target analyte(s) is added.

Matrix Spike Duplicate (MSD): a second replicate matrix spike

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which relative uncertainty is ±100%. The MDL represents a range where qualitative detection occurs. Quantitative results are not produced in this range.

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Precision: the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Quality Control Sample (QC): a sample used to assess the performance of all or a portion of the measurement system.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample.

Stock Standard: a solution made with one or more neat standards usually with a high concentration. Also known as a primary standard. Stock standards may be certified solutions purchased from a vendor.

Appendix B: Standard Preparation Tables

The standard formulations contained in this Appendix are recommended and are subject to change. If the concentration of the stock standard is different than those noted in this table, adjust the standard preparation formulation accordingly. Unless otherwise specified, prepare the standard solutions using Class A volumetric glassware. Unless otherwise specified for a standard solution, assign an expiration date of 6 months from date of preparation unless the parent standard expires sooner in which case use the earliest expiration date. See laboratory SOP BR-QA-002 *Standard Preparation* for further guidance.

Intermediate Calibration Standards (10,000 ug/L)

Parent Standard	Vendor	Stock Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
Mercury	SPEX	1000	1.0	100	10000

Add the mercury standard and 0.15 mL of concentrated HNO_3 to a 100 mL volumetric flask that contains approximately 80 mL of reagent water. Adjust to final volume with reagent water.

Working Calibration Standards (100 ug/L)

Parent Standard	Vendor	Parent Standard Concentration (ug/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
Intermediate Calibration	Laboratory Prepared	10000	10.0	1000	100

Add the mercury standard and 1.5 mL of concentrated HNO_3 to a 1000 mL volumetric flask that contains approximately 800 mL of reagent water. Adjust to final volume with reagent water.

Intermediate ICV Standard (10,000 ug/L)

Parent Standard	Vendor	Stock Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
Mercury	Inorganic Ventures	1000	1.0	100	10000

Add the mercury standard and 0.15 mL of concentrated HNO_3 to a 100 mL volumetric flask that contains approximately 80 mL of reagent water. Adjust to final volume with reagent water.

Working ICV Standard (30 ug/L)

Parent Standard	Vendor	Parent Standard Concentration (ug/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
Intermediate ICV	Laboratory Prepared	10000	1.5	500	30

Add the mercury standard and 0.75 mL of concentrated HNO_3 to a 500 mL volumetric flask that contains approximately 300 mL of reagent water. Adjust to final volume with reagent water.

Mercury Calibration Standard(s): CAL Levels 1- 6

Parent Standard	Calibration Standard	Parent Standard Concentration (ug/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration* (ug/L)
Reagent Water	Blank	0	50	50	0
Intermediate Calibration	Level 1	100	0.1	50	0.2
Intermediate Calibration	Level 2	100	0.25	50	0.5
Intermediate Calibration	Level 3	100	0.5	50	1
Intermediate Calibration	Level 4	100	2.5	50	5
Intermediate Calibration	Level 5	100	5.0	50	10

**The final concentration is achieved after digestion.*

Appendix C: Equations

Percent Recovery (%R)

$$\text{Percent Recovery (\%R)} = \frac{C_s}{C_n} \times 100\%$$

Where:
C_s = Concentration of the Spiked Field or QC Sample
C_n = Nominal Concentration of Spike Added

Percent Recovery (%R) for MS/MSD

$$\text{Percent Recovery (\%R) for MS/MSD} = \frac{C_s - C_u}{C_n} \times 100\%$$

Where:
C_s = Concentration of the Spiked Sample
C_u = Concentration of the Unspiked Sample
C_n = Nominal Concentration of Spike Added

Relative Percent Difference (%RPD)

$$\text{Relative Percent Difference (\%RPD)} = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100\%$$

Where:
C_1 = Measured Concentration of First Sample
C_2 = Measured Concentration of Second Sample

Water Sample Concentration

$$C_{(ug/L)} = \frac{\mu g}{L_{dig}} * \frac{V_{dig}}{V_{samp}}$$

Where:
$\mu g/L_{dig}$ = Instrument result adjusted for dilution factors
V_{dig} = Final digestate volume
V_{samp} = Sample volume

Solid Sample Concentration

$$C_{(mg/Kg\ \ drywt.)} = \frac{\mu g}{L_{dig}} * \frac{V_{dig}}{g_{samp}} * \frac{100}{\%\ \ solids}$$

Where:

$\mu g/L_{dig}$ = Instrument result adjusted for dilution factors
V_{dig} =Final digestate volume
g_{samp} = Sample weight in grams
% Solids = Percent solids to nearest 0.1%

Title: DETERMINATION OF PESTICIDES BY GC/ECD (CLP SOW SOM01.2)

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1.0 Scope and Application

This SOP describes the laboratory procedure used to determine the concentration of chlorinated pesticides using dual column Gas Chromatography with Electron Capture Detectors (GC/ECD). This SOP is applicable to the analytical procedure.

1.1 Analytes, Matrices, and Reporting Limits

This procedure may be used for a variety of matrices including: water, soil, and sediment.

The list of target compounds that can be determined from this method along with the Contract Required Quantitation Limit (CRQL) are provided in Table 1.

NOTE: There are two isomers of heptachlor epoxide, the endo-epoxy isomer (Isomer A) and the exo-epoxy isomer (Isomer B). The two isomers are separable using current GC capillary columns, but only the exo isomer (Isomer B) is of environmental significance. Isomer B is the isomer used as an analytical standard, and it is the isomer identified, quantitated in sample analysis and reported on the appropriate forms as heptachlor epoxide.

2.0 Summary of Method

After extraction and cleanup, extracts are analyzed by injecting a 2 uL aliquot into a dual capillary column gas chromatograph equipped with electron capture detectors (GC/ECD).

This SOP is based on the following reference methods:

- Exhibits B & D, Analytical Methods for the Analysis Pesticides, USEPA CLP SOW for Organic Analysis, SOM01.1, May 2005.
- USEPA CLP SOW Clarifications to SOM01.1, November 7, 2005 and September 26, 2006.
- USEPA CLP SOW Modifications Updating SOM01.1 to SOM01.2, October 5, 2006 (Updated 02-12-2007) Amended 04-11-2006.
- Section 8.3.4 General Analytical Requirements NJDEP USEPA Contract, Laboratory Program Analysis.

3.0 Definitions

A list of terms and definitions are provided in Appendix A.

4.0 Interferences

Method Interferences

Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing equipment. These contaminants can lead to elevated baselines and discrete artifacts that appear in gas chromatograms. These materials are demonstrated to be free of interferences by the analysis of method blanks. Interferences from phthalate esters can also pose a problem for the chlorinated pesticides analysis. To avoid this type of interference, the use of plastics in the laboratory must be minimized.

Matrix Interferences

Matrix interferences may be caused by contaminants that are co-extracted with the samples. The extent of the interference will vary by matrix and are minimized using the various cleanup procedures described in this SOP.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

The gas chromatograph contains zones that have elevated temperatures. The analyst must be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.2 Primary Materials Used

Table 2 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the MSDS. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

6.0 Equipment and Supplies

Catalog numbers listed in this SOP are subject to change at the discretion of the vendor. Analysts are cautioned to be sure equipment used meets the specification of this SOP.

6.1 Miscellaneous

Autosampler Vials, National Scientific or equivalent.

Hydrogen Generator: Whatman.

Volumetric Syringes, Class “A” (10µl, 25µl, 50µl, 100µl, 250µl and 500µl), Hamilton or equivalent.

6.2 Analytical System

Computer Hardware/Software: GC Acquisition Platform - VAX 4505 (GVAX) Multichrom V2.11. Data Processing - Hewlett-Packard 9000-series computers, an HP 9000 K200 (Chemsvr5)/ HP-UX 10.20 and Target V3.5 or higher.

GC/ECD: with dual columns, dual ECDs, and auto-sampler capable of a 2-µl injection split onto two columns: HP 5890 with Leap Technology CTC A200SE and A200S Fisons autosamplers, Agilent Technologies 6890N with 7683 Series injector, or equivalent.

GC Columns: A dual fused silica capillary column system that will provide simultaneous primary and confirmation analyses.

- RTX - CLPesticides (30m x 0.32 mm ID x 0.25um), Restek # 11139 (or)
- RTX - CLPesticides (30m x 0.32 mm ID x 0.32um), Restek # 11141.
- RTX - CLPesticides II, (30m x 0.32 mm ID x 0.25um), Restek # 11324.

Equivalent columns may be used so long as elution orders are documented and compound separations are maintained.

7.0 Reagents and Standards

7.1 Reagents

- Hexane, Ultra-Resi Analyzed, JT Baker or equivalent.

7.2 Standards

Purchase stock standard solutions from commercial vendors and from these prepare calibration and working standards by diluting a known volume of stock standard in an appropriate solvent to the final volume needed to achieve the desired concentration. The recommended formulation for each standard used in this procedure is provided in Appendix B along with the recommended source materials, expiration dates and storage conditions.

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection so these procedures are not included in this SOP. Sampling requirements may be found in the published reference method.

Listed below are minimum sample size, preservation and holding time requirements:

Matrix	Sample Container	Minimum Sample Size	Preservation	Holding Time1	Reference
Water	Amber Glass	Two 1 L for samples One 1 L per MS/MSD	4°C (±2°C)	Extraction: 5 days from VTSR Analytical: 40 days	CLP SOW
Solid	Amber Glass	Two 125 mL for samples One 125 mL per MS/MSD	4°C (±2°C)	Extraction: 10 days Analytical: 40 days	CLP SOW
Extract	Amber vial	NA	chilled to <4°C	Analytical: 40 days	CLP SOW

1Extraction holding time is determined from the date sample were received by the laboratory (VTSR); analytical holding time is determined from date of initiation of extraction.

For the USEPA CLP contract samples are kept for 60 days from validation and extracts are retained for a minimum of 365 days after provision of the project report and then disposed of in accordance with applicable regulations. For all other projects, unless otherwise specified by the client, samples and extracts are retained for a minimum of 30 days after provision of the project report and then disposed of in accordance with applicable regulations.

9.0 Quality Control

9.1 Sample QC

The laboratory prepares the following quality control samples with each batch of samples.

QC Item	Frequency	Acceptance Criteria
Method Blank (MB)	1 in 20 or fewer samples	See Table 4
Laboratory Control Sample (LCS)	1 in 20 or fewer samples	See Table 3A
Matrix Spike(s) MS/MSD	1 in 20 or fewer samples	See Table 3B
Sample Duplicate (SD)	Client Request	Client Defined

The method blank is analyzed on each GC/ECD system used to analyze associated samples.

All extracts including the MB and the LCS undergo sulfur cleanup. When it is necessary to do additional sulfur cleanups on one or more of the extracts a sulfur cleanup blank (PSBLK##) is performed with those extracts.

9.2 Instrument QC

The following instrument QC is performed:

QC Item	Frequency	Acceptance Criteria
Initial Calibration (ICAL)	Initially; when CCV or PEM fail	See Section 10 and Table 3
Continuing Calibration Verification (CCV or PEM)	Daily, every 12 hour window, end of sequence	See Section 10 and Table 3
Retention Time Windows	Method Defined	See Table 1
Instrument Blanks	As needed in the analytical sequence	

10.0 Procedure

10.1 Instrument Operating Conditions

Instrument Set-Up and Operating Conditions

Install a five meter deactivated guard column to the injection port, and using a glass "Y" connect the guard column to the separate analytical columns. Attach the analytical columns to each Electron Capture Detector (ECD).

The following are example instrument conditions used for analysis:

Carrier Gas:	Hydrogen (Hydrogen Generator)
Column Flow:	2.0 mL/min.
Make-up Gas:	Argon/Methane
Make-up Gas Flow:	120 mL/min.
Injector Temperature:	225°C
Detector Temperature	300°C

Injection Technique:	on-column
Injection volume:	2 µL
Injector:	CTC autosampler
Initial Temperature:	120°C
Initial Hold Time:	1 minute
Temperature Program:	16°C /min. to 210°C
	6°C /min. to 245°C
	12.5°C/min to 300°C. Hold for 4 minutes.

Once instrument conditions are set for an initial calibration, the same instrument conditions must be used for subsequent analysis of associated standards and samples.

10.2 Instrument Calibration

10.2.1 Initial Calibration (ICAL)

Calibrate the GC using five different concentrations of the single component pesticides, Toxaphene and the surrogate compound in order to determine the instrument's sensitivity and linearity. The recommended concentration for each calibration level is provided in Appendix A. Perform initial calibration upon initial award of the contract, whenever major instrument maintenance or modification is performed (for example, column replacement, baking or replacement of ECD), or if the calibration verification technical acceptance criteria are not met.

Set up the GC/ECD system as described in Section 10.1.

Prepare the calibration standards using the formulations provided in Appendix B then allow the standards to warm to ambient temperature prior to analysis.

Analyze the calibration standards in the sequence specified in the following table.

Calibration Sequence (CLP SOM01.2 Sequence 1)

Calibration Standard	EPA Sample Number
Instrument Blank	PIBLK##
Resolution Check	RESC##
Performance Evaluation Mixture (PEM)	PEM##
Toxaphene CS1	TOXAPH1##
Toxaphene CS2	TOXAPH2##
Toxaphene CS3	TOXAPH3##
Toxaphene CS4	TOXAPH4##
Toxaphene CS5	TOXAPH5##
CS1 Individual Standard Mix C	INDC1##
CS2 Individual Standard Mix C	INDC2##
CS3 Individual Standard Mix C	INDC3##
CS4 Individual Standard Mix C	INDC4##
CS5 Individual Standard Mix C	INDC5##
Instrument Blank	PIBLK##
PEM	PEM##

NOTE: The order of the analytical sequence is prescribed by the SOW and may not be modified.

NOTE: Two calibration sequence options are provided in the CLP SOW. The laboratory uses the calibration option that includes the single mixture (INDC).

The laboratory's data processing system measures the RT of each single component pesticide for each of the five calibration standards (Individual Standard Mix C). For Toxaphene, it measures the RTs for the 5 quantitation peaks chosen. The mean absolute RT ($\overline{RT}$) is calculated for each single component pesticide, surrogate and Toxaphene quantitation peaks as the average of the five values. The RT window is calculated for each single component pesticide, surrogate and Toxaphene quantitation peaks using the RT windows given in Table 1.

The data processing system also determines the linearity of the instrument by calculating the Percent Relative Standard Deviation (%RSD) of the Calibration Factors (CFs) for all single component pesticides, surrogates and the five quantitation peaks chosen for Toxaphene.

The laboratory's preferred method to calculate the CF is peak height but the SOW allows the CF to be calculated either from peak height or peak area. For instance, the SOW specifies that the linearity of one individual component may be calculated in peak area and another individual component may be calculated in peak height. For example, it is acceptable to calculate the linearity of DDT using peak height and to calculate the linearity of DDD using peak area. It is also permitted to choose peak area for all quantitation peaks chosen for Toxaphene. However, the SOW does not allow the calculation of the CF for one individual component in peak area and height. For example, you cannot calculate the CF for the CS1 standard of Aldrin in peak height and calculate the CF for CS3 of Aldrin in peak area. For Toxaphene, it is not permitted to calculate the CF of peak 1 in peak height and peak 4 in peak area. Whether peak area or height is used, the option chosen must remain consistent for all calculations for that analyte.

The data processing system calculates the breakdown of DDT, the breakdown of endrin and the combined breakdown in the PEM. The data system calculates the percent difference for each pesticide and surrogate in the PEM. The resolution between the analytes in the Resolution Check, PEM, and CS3 Individual Standard Mixtures are calculated and entered into the data processing system.

The equations for the calculation of the calibration factor (CF), mean calibration factor, Percent Relative Standard Deviation, percent breakdown, percent difference and resolution are provided in Appendix C for reference.

ICAL Acceptance Criteria :

The acceptance criteria described in this section apply independently to each GC column. The acceptance criteria must be met prior to sample analysis. If criteria are not met, identify and correct the problem prior to further analysis.

The initial calibration standard sequence must be analyzed in the order specified in the calibration sequence table.

The resolution between two adjacent peaks in the Resolution Check Mixture must be greater than or equal to 80.0% for all analytes on both columns.

All single component pesticides and surrogates in the PEMs must be greater than or equal to 90.0% resolved on each column.

The absolute RTs of the single component pesticides and surrogates in the PEMs must be within the established RT window.

The Percent Difference between the calculated amount and nominal amount for each of the single component pesticides and surrogates in the PEMs must be less than 25.0%.

The percent breakdown of DDT and Endrin in PEMs must each be less than or equal to 20.0%. The combined breakdown of DDT and Endrin must be less than or equal to 30.0%.

The %RSD of the CFs for each single component pesticide must be less than or equal to 20.0%, except for alpha-BHC and delta-BHC. The %RSD for alpha-BHC and delta-BHC must be less than 25.0%. The %RSD of the CFs for TCX and DCB (surrogates) must be less than or equal to 30.0%. Up to two single component pesticides (not surrogates) per column may exceed 20.0% RSD (25.0% for alpha-BHC and delta-BHC) but they must be less than or equal to 30.0% RSD. The %RSD of the CFs for Toxaphene must be less than or equal to 30.0%.

The resolution between any two adjacent peaks in the CS3 Individual Standard Mixture C must be at least 80.0% on both columns.

All instrument blanks must meet the following criteria:

- The instrument blank must be analyzed at the original concentration.
- The instrument blank must meet the acceptance criteria for sample analysis.
- The concentration of each target analyte in the instrument blanks must be less than the CRQL on each chromatographic column.
- The RT for each surrogate must be within the established RT window.

10.2.2 Calibration Verification (CCV)

The ICAL and instrument performance are evaluated with instrument blanks (PIBLKs), PEMs and the CS3 Individual Standard Mixtures. Calibration verification consists of a PIBLK and PEM or a PIBLK and the CS3 Individual Standard Mixture. Sample data must be bracketed by acceptable analyses of instrument blanks, PEMs and the CS3 Individual Standard Mixture.

Prepare the standards as needed and allow them to warm to ambient temperature prior to analysis.

Bracket one end of a 12-hour window with a PIBLK and PEM standard. Bracket the other end of the 12-hour window with a PIBLK and an Individual Standard Mix CS3.

For the 12-hour period immediately following the ICAL, the PIBLK and the PEM that are analyzed in the last two steps of the initial calibration sequence may bracket the front end of the 12-hour period. The injection of the PIBLK begins the 12-hour period. Inject a PIBLK and the Individual Standard Mix CS3 immediately after the 12-hour period. Continue to use this progression until any of the technical acceptance criteria for the PIBLKs, PEMs or Individual Standard Mix CS3s fail. No more than 14 hours may elapse from the injection beginning the opening CCV and the injection of the closing CCV. If Toxaphene is detected in a sample, analyze a Toxaphene CCV standard within 72 hours of the analyte detection in the sample and in a valid 12-hour period.

If the instrument sits idle for more than 12 hours, start a new analytical window with the analysis of a PIBLK and a PEM.

The data processing system performs all calculations. The equations for the calculation of the calibration factor (CF), mean calibration factor, relative standard deviation, percent breakdown, percent difference and resolution are provided in Appendix C for reference.

CCV Acceptance Criteria:

The acceptance criteria listed below applies independently to each column. The acceptance criteria must be met prior to analysis of field and QC samples.

The PEMs, Individual Standard Mixtures and PIBLKs must be analyzed at the required frequency.

All single component pesticides and surrogates in the PEMs used to demonstrate calibration verification must be greater than or equal to 90.0% resolved. The resolution between any two adjacent peaks in the Individual Standard Mix CS3 must be at least 80.0% on both columns.

The absolute RT for the single component pesticides and surrogates in the PEMs and CS3 Individual Standard Mixture must be within the RT windows.

The percent difference between the calculated amount and nominal amount for each single component pesticide and surrogates in the PEM used to demonstrate calibration verification must less than or equal to 25.0%.

The percent breakdown of DDT and Endrin in the PEM must each be less than or equal to 20.0% on each column. The combined breakdown must be less than or equal to 30.0% on each column.

The percent difference between the CF of each single component pesticide and surrogates in the Individual Standard Mixture CS3, and the mean calibration factor from the initial calibration must less than or equal to 20.0%. The percent difference between the CF of each quantitation peak of Toxaphene and the mean calibration factor from the initial calibration must be less then or equal to 20.0%.

All instrument blanks must meet the following criteria:

- The instrument blank must be analyzed at the original concentration.
- The instrument blank must meet the acceptance criteria for sample analysis.
- The concentration of each target analyte in the instrument blanks must be less than the CRQL on each chromatographic column.
- The RT for each surrogate must be within the established RT window.

10.3 Troubleshooting:

Check the following items in case of calibration failures:

- ICAL Failure – Perform injection port maintenance, install new guard column, check detector ends to see if detector jet has slipped. In extreme cases, install new columns, particularly if the chromatography has degraded as evidenced by peak shapes.
- CCV Failure – Perform Injection port maintenance; if injection port maintenance does not restore CCV, install a new guard column and remove one or more loops from each analytical column.

- Needle crushed during injection - Replace the needle and check the injection port for obstructions and check the autosampler for misalignment.
- Auto-sampler failure - Reset the auto-sampler.
- Power failure - Reset run in Multichrom and re-acquire or re-initiate run sequence.

10.4 Sample Preparation

Before field and QC samples and required blanks can be analyzed, ensure that the instrument meets criteria for initial calibration and calibration verification. Analyze all samples and standards under the same instrument conditions using the same on-column injection volume of 2.0 uL.

10.4.1 Extract Screening and Guidance for Dilution

Screen all extracts on a designated screen instrument prior to instrument analysis to determine the presence of sulfur and to assess target analyte concentrations. Use the results of the screen to determine the approximate dilution factor (DF) required to get the largest peak within the calibration range. If sulfur is found in the extract, repeat sulfur cleanup. Refer to the extraction SOPs for the cleanup procedure.

To prepare the extract for the screen, perform a 1:10 dilution in hexane by adding 50uL of sample extract to 450uL of hexane into an autosampler vial.

If the concentration of any single target analyte is greater than the concentration of the high standard (CS5) of the initial calibration range on **both** columns, dilute the extract such that the concentration of the pesticide compounds in the diluted extract is between the low standard (CS1) and the high standard (CS5) for the lower column concentration of the two analyses.

If the concentration of any Toxaphene peak used for quantitation is greater than the concentration of the corresponding Toxaphene peak in the high standard (CS5), dilute the extract so that the concentration of the same peak is between the mid standard (CS3) and the high standard (CS5).

If a dilution is performed solely to bring a peak within calibration range or to get the Toxaphene pattern on scale, the results for both the greater and the less concentrated extracts must be reported.

If the dilution factor is greater than 10, analyze the extract 10 times more concentrated than the diluted sample extract and report both sets of data. If the dilution factor is less than 10, analyze the extract undiluted and report both sets of data.

If the concentration of any target analyte is above the high calibration standard (CS5) after a dilution of 1:100,000 contact the project manager for further instruction.

10.5 Sample Analysis

Analytical Sequence

Load the extracts and standards into the autosampler and enter the sample ID's into the data acquisition program in the same order that the extracts and standards were placed in the autosampler. Start the analytical sequence and acquire the data.

When ICAL is needed, analyze the samples using the following analytical sequence:

Injection #	Material Injected
1-13	First 13 steps of initial calibration sequence 1 (See Section 10.2.1)
14	PIBLK at end of initial calibration sequence 1
15	PEM at end of initial calibration sequence 1
16	First sample if using initial calibration sequence 1
1st injection past 12 hours	PIBLK
2nd injection past 12 hours	Individual Standard Mixture C

When ICAL is not needed, analyze the samples using the following analytical sequence:

Injection #	Material Injected
1-2	PIBLK
3	PEM
4	Sample extract(s) (12 hour window counted from the injection of the first PIBLK injection to the injection of the PIBLK that ends the window.)
1st injection past 12 hours	PIBLK
2nd injection past 12 hours	Individual Standard Mixture C

The sequence above provides the minimum requirements. Additional standards may be run at the discretion of the laboratory. However, the standards must satisfy all criteria in order to continue the sequence.

11.0 Calculations / Data Reduction

11.1 Qualitative Identification

The data processing system identifies the target analytes by comparing the retention time of the peaks to the retention time windows established in the of the initial calibration standards. All tentative identifications made by the computer are reviewed and either accepted or rejected by the primary analyst and/or the analyst that performs secondary data review.

Single component analytes are identified when peaks are observed in the RT window for the analyte on both GC columns. The data system uses a set of 3-5 major peaks for Toxaphene. RT windows for each peak are determined in the initial calibration. Identification of Toxaphene in the sample is based on pattern recognition and if the 3-5 major peaks chosen are within the established RT windows on both GC columns. If Toxaphene is detected in a sample, analyze a Toxaphene CS3 standard in a valid analytical sequence within 72 hours of detection in the sample.

11.2 Quantitative Identification

The data system performs quantitation for all analytes (including Toxaphene) and surrogates for each GC column based on the mean calibration factor from the most recent initial calibration.

The quantitation of Toxaphene is accomplished by comparing the height or area (See section 10.2.1) of each of the 3-5 major peaks in the sample with the same peaks from initial calibration. The concentration of each peak is determined then a mean concentration is determined for each column. The lower of the two concentrations (between columns) is reported on the Form I.

The data system adjusts calculated sample results to account for dilution and percent moisture. The data system also calculates the percent recovery for the surrogates for each GC column as well as the relative percent difference between results on each GC column. Although the data system performs the calculations, equations for the calculation of sample concentration is provided for reference in Appendix C.

11.3 Calculations

See Appendix C.

11.4 Data Review

11.4.1 Primary Review

Confirm quantitative and qualitative identification criteria using the criteria provided in Section 11.1 and Section 11.2.

Check sample information and preparation information from sample log-in and preparation upon initial processing. Perform necessary manual integrations and identifications.

Evaluate the results of the instrument performance check samples, field and QC samples against the acceptance criteria given in Table 4. Perform the recommended corrective action as necessary. If corrective action is not taken or is not successful, initiate a nonconformance report (NCR) to document the situation.

Perform the following checks:

If the samples required GPC cleanup, ensure the GPC system used met the acceptance criteria for calibration and verification. See the extraction SOP for criteria.

If samples received Florisil cleanup, ensure the technical acceptance criteria for Florisil cartridge lot verification were met. See the extraction SOP for criteria.

Verify the samples were extracted and analyzed within holding time.

Verify that samples were associated with a method blank and an LCS that met acceptance criteria.

Verify that the method blank was analyzed on each instrument on which associated samples were analyzed. Additionally, ensure the method blank was subject to sulfur cleanup along with the associated samples, or a sulfur cleanup blank was performed. The surrogate recovery for the method blank was between 30-150%.

- Ensure the RT for each surrogate is within the RT window and the percent recovery for each surrogate in samples is within 30-150%*. **Up to one surrogate may fail criteria per column and the surrogate recovery limits are not applicable to samples that were diluted.*

Compare results from each column to verify confirmation of each target analyte.

Ensure a Toxaphene standard CS3 was analyzed within 72 hours of detection of Toxaphene in any field sample.

If any single component pesticide concentration (on column) is greater than or equal to 5.0 ng/uL (or 125ng/uL for toxaphene) for both columns, contact the project manager to determine whether or not GC/MS confirmation is required.

Evaluate the results of samples analyzed immediately after high concentration samples for signs of carry-over. Reanalyze the sample if carry over is suspected.

Dilute and reanalyze samples whose results exceed the calibration range. The diluted analysis should result in a determination within the upper half of the calibration curve.

- Check to ensure an appropriate technical reason code is provided for each manual integration. Acceptable technical reason codes are provided in laboratory SOP BR-QA-006 *Manual Integration Requirements*.

- Generate a "before" and "after" chromatogram for every manual integration performed on an instrument performance check standard (ICAL, ICV, CCV), QC sample (MB, LCS) and for any manual integration performed on any surrogate in any field sample. Additionally, all "before" and "after" chromatograms for target analytes in field sample analyses will be supplied for clients requesting this documentation.

- Generate the Manual Integration Summary Report. Document your review of manual integrations on the summary report and sign the summary report.

- Generate a quantitation and chromatogram report for the calibration, calibration check standards, associated summary forms, and compile the package.

11.4.2 Secondary Data Review

Check each qualitative identification and spot check quantitative values using the criteria provided in Section 11.1 and Section 11.2.

If manual integrations were performed:

- Review each manual integration to verify that the integration is consistent and compliant with the requirements specified in laboratory SOP BR-QA-006 *Manual Integration Requirements*. If a problem is found, immediately consult with the primary analyst or notify the Technical Director or QA Manager. Check that each manual integration is included in the manual integration summary and that each instance has an associated manual integration code. Also, check to ensure that a "before and after" report is present for each manual integration of reported analyte.

- Reintegration (by secondary data reviewers) should not be performed except in limited circumstances such as when the primary analyst who performed the initial integration is not available to correct any errors found during secondary review. If reintegration is performed,

each integration performed by the secondary reviewer must be reviewed by a peer analyst or the department supervisor to verify the integration is consistent and compliant with the requirements specified in laboratory SOP BR-QA-006 *Manual Integration Requirements*.

Verify that the performance criteria for the QC items listed in Table 3 were met. If the results do not fall within the established limits verify that the recommended corrective actions were performed. If corrective action was not taken or was unsuccessful, ensure that the situation is documented with a nonconformance report (NCR) and ensure that the data is qualified accordingly. Report the nonconformance in the narrative note program.

If the percent difference of the concentrations between the 2 columns is greater than 25%, flag the results with a "P" data qualifier.

11.5 Data Reporting

11.5.1 Data Reporting & Order of Deliverables

Evaluate each chromatogram to verify qualitative and quantitative identification of target compounds. Exhibit B of the CLP SOW specifies that the laboratory report estimated values qualified with a "J" data qualifier when the retention time (RT) data indicate the presence of a compound that meets the identification criteria and the result is less than the CRQL but greater than zero. For instance, if the CRQL is 5.0 ug/L and a concentration of 3.0 ug/L is found, the results is reported as 3.0J. However, results between zero and the CRQL should not be reported if the presence of the peak is considered to be from instrument noise or other interference.

Review all samples, standards, and QC samples against the acceptance criteria provided in this SOP. Generate and arrange the pesticide data following the requirements specified in the Table 5.0. If the results do not fall within the criteria, perform corrective action. If corrective action is not taken, or is unsuccessful, document the situation with a nonconformance report and qualify the data using an appropriate data qualifier (See Appendix A for data qualifier definitions). For additional guidance regarding the laboratory's protocol and required elements for each level of data review (primary, secondary, and tertiary) refer to laboratory SOP BR-QA-019 *Data Review.*

If the sample was analyzed at multiple dilutions, report the result from the appropriate dilution (i.e. no target analyte above calibration range and the result for the analyte for which the dilution was performed is in the upper half of the calibration range). Provide results for the undiluted or more concentrated analyses when requested.

Review project documents such as the environmental test request (ETR) analytical worksheets, Project Plan (PP), Project Memo or any other document/process used to communicate project requirements to ensure those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Generate the summary forms and compile with the data report in the deliverable format specified by the laboratory PM and release the report to the report management group. For USEPA contract, forms and data should be arranged in chronological order by column. Sample data should be arranged in increasing order by Client ID. Refer to the CLP SOW for further guidance.

Retain, manage and archive electronic and hardcopy data as specified in laboratory SOP BR-QA-014 *Laboratory Records*.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

A Method Detection Limit (MDL) must be determined on each instrument used for analysis for each matrix prior to initial use of the method. The MDLs are verified annually with an MDL Verification Check sample that is subject to the same extraction and cleanup procedures as used for field samples. The procedure and acceptance criteria for MDL studies and MDL verification are given in laboratory SOP BR-QA-005 *Determination of LOD, LOQ & RL*.

12.2 Demonstration of Capabilities (DOC)

Perform a method demonstration of capability at initial set-up and when there is a significant change in instrumentation or procedure.

Each analyst that performs the analytical procedure must complete an initial demonstration of capability (IDOC) prior to independent analysis of client samples. Each analyst must demonstrate on-going proficiency (ODOC) annually thereafter. DOC procedures are further described in the laboratory's quality system manual (QAM) and in the laboratory SOP BR-QA-011 *Procedures for Employee Training & Demonstration of Proficiency.*

12.3 Training Requirements

Any employee that performs any portion of the procedure described in this SOP must have documentation in their employee training file that they have read this version of this SOP.

Instrument analysts, prior to independent analysis of client samples, must also have documentation of demonstration of initial proficiency (IDOC) and annual on-going proficiency (ODOC) in their employee training files.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to BR-EH-001 *Hazardous Waste*. The following waste streams are produced when this method is carried out.

Vials containing sample extracts: Satellite container: 15 gallon bucket connected to a fume hood.
Solvent Waste: Satellite container: 1 L glass bottle located in fume hood.

15.0 References / Cross-References

- Exhibits B & D, Pesticides USEPA CLP SOW for Organic Analysis, SOM01.1, May 2005.
- USEPA CLP SOW Clarifications to SOM01.1, November 7, 2005 and September 26, 2006.
- USEPA CLP SOW Modifications Updating SOM01.1 to SOM01.2, October 5, 2006 (Updated 02-12-2007) Amended 04-11-2006.
- Laboratory SOP BR-QA -019 *Data Review*
- Laboratory SOP BR-QA-011 *Procedures for Employee Training & Demonstration of Proficiency.*
- Laboratory SOP BR-QA-014 *Laboratory Records*
- Laboratory SOP BR-QA-002 *Standard Preparation*
- Laboratory SOP BR-QA-006 *Manual Integration Requirements*
- Laboratory SOP BR-QA-005 *Determination of LOD, LOQ & RL*.
- Laboratory SOP BR-EH-001 *Hazardous Waste*
- Laboratory Quality Assurance Manual (QAM)
- Corporate Environmental Health and Safety Manual (CW-E-M-001)

16.0 Method Modifications

Modification Number	Method Reference	Modification
1	NJDEP	Per client request, the laboratory may report a lower CRQL than specified in the CLP SOW. See Table 1.

17.0 Attachments

- Table 1: Target Compound List and Reporting Limit
- Table 2: Primary Materials Used
- Table 3A: LCS Recovery Limits
- Table 3B: MS/MSD Recovery and Precision Limits
- Table 4: QC Summary and Recommended Corrective Action
- Table 5: Pesticide Data Reporting Requirements
- Appendix A: Terms and Definitions
- Appendix B: Standard Preparation Tables
- Appendix C: Equations

18.0 Revision History

Revision 1, Dated 05/23/08:

- SOP updated to the new TestAmerica format
- Updated Table 1 for Low Level Water CRQL limits
- Analytical Standard Table updated to include component information – Appendix B
- Form names added to Table 5: Pesticide Data Reporting Requirements.

Table 1: Target Compound List, CRQL, and RT Windows

Analyte	Contract Required Quantitation Limit			Retention Time Windows
	LL Water ug/L	Water ug/L	Solid ug/Kg	
alpha-BHC	0.0050	0.050	1.7	±0.05
beta-BHC	0.0050	0.050	1.7	±0.05
delta-BHC	0.0050	0.050	1.7	±0.05
gamma-BHC (Lindane)	0.0050	0.050	1.7	±0.05
Heptachlor	0.0050	0.050	1.7	±0.05
Aldrin	0.0050	0.050	1.7	±0.05
Heptachlor epoxide	0.0050	0.050	1.7	±0.07
Endosulfan I	0.0050	0.050	1.7	±0.07
Dieldrin	0.010	0.10	3.3	±0.07
4,4-DDE	0.010	0.10	3.3	±0.07
Endrin	0.010	0.10	3.3	±0.07
4,4-DDD	0.010	0.10	3.3	±0.07
Endosulfan II	0.010	0.10	3.3	±0.07
Endosulfan sulfate	0.010	0.10	3.3	±0.07
4,4-DDT	0.010	0.10	3.3	±0.07
Methoxychlor	0.050	0.50	17	±0.07
Endrin ketone	0.010	0.10	3.3	±0.07
Endrin aldehyde	0.010	0.10	3.3	±0.07
alpha-Chlordane	0.0050	0.050	1.7	±0.07
gamma-Chlordane	0.0050	0.050	1.7	±0.07
Toxaphene	0.50	5.0	170	±0.07
TCX (Surrogate)	NA	NA	NA	±0.05
DCB (Surrogate)	NA	NA	NA	±0.10

[1] Reporting Limits represent those that can be achieved in a blank matrix. Individual reporting limits will vary based upon sample matrix, target analyte concentration, co-extracted interferences, and dry weight of samples.

Table 2: Primary Materials Used

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Table 3A: Laboratory Control Sample Recovery Limits

Analyte	Recovery Limits (%R)
	Water/Soil
gamma-BHC	50-120
Heptachlor epoxide	50-150
Dieldrin	30-130
4,4'-DDE	50-150
Endrin	50-120
Endosulfan sulfate	50-120
gamma-Chlordane	30-130

Table 3B: MS/MSD Recovery and Precision Limits

Analyte	Recovery Limits (%R)	RPD	Recovery Limits (%R)	RPD
	Water	Water	Solid	Solid
gamma-BHC	56-123	0-15	46-127	0-50
Heptachlor	40-131	0-20	35-130	0-31
Aldrin	40-120	0-22	34-132	0-43
Dieldrin	52-126	0-18	31-134	0-38
Endrin	56-121	0-21	42-139	0-45
4,4'-DDT	38-127	0-27	23-134	0-50

Table 4: QC Summary and Recommended Corrective Action

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action[1]
Initial Calibration	Initially, prior to sample analysis; when calibration verification standards indicate calibration relationship is no longer valid; after major instrument maintenance	See Section 10.2	Correct problem and repeat initial calibration.
Calibration Verification	To open and close 12 hour sample windows.	See Section 10.3	Correct problem, reanalyze CCV and all associated samples since last successful CCV.
Method Blank	One per extraction batch (Not to exceed 20 field samples) Bracketed by 12 hour windows	Target analytes must be < CRQL Surrogate recovery: 30-150% [Not advisory] Analyzed on each GC/ECD system used to analyze field samples. RT of surrogates must be within RT windows	Correct problem, re-extract and reanalyze with all associated samples.
Sulfur Blank	Whenever a subset of samples within an extraction batch receives sulfur clean up.	Target analytes must be < CRQL Surrogate recovery: 30-150% [Not advisory] Analyzed on each GC/ECD system used to analyze field samples. RT of surrogates must be within RT windows	Correct problem, re-extract and reanalyze with all associated samples.
Instrument Blank	First analysis in 12-hour analytical sequence; preceding CCVs Preceding and following acceptable sample analyses.	Target analytes must be < CRQL Analyzed on each GC/ECD system used to analyze field samples. RT of surrogates must be within RT windows Requirements apply independently to each column	Correct problem and reanalyze with all associated samples.
LCS	One per extraction batch	%R within control limits given in Table 3A Surrogate recovery: 30-150% [Not advisory] RT of surrogates must be within RT windows Requirements apply independently to each column	Correct problem, re-extract and reanalyze with all associated samples.
MS/MSD	One per sample set of 20 field samples analyzed at the most concentrated analysis of parent. Note: Results can be reported from over-range response.	%R & %RPD within advisory limits given in Table 3B RT of surrogates must be within RT windows	Evaluate circumstances. Assay spike formulations.
Surrogate Spike	All field and QC samples	%R 30-150 for all field and QC samples *Up to one surrogate may fail criteria per column in samples.*	Correct problem, re-extract and reanalyze if sufficient sample is available.

[1]*The recommended corrective action may include some or all of the items listed in this column. The corrective action taken may be dependent on project data quality objectives and/or analyst judgment but must be sufficient to ensure that results will be valid. If corrective action is not taken or is not successful, data must be flagged with appropriate qualifiers.*

Table 5: Pesticide Data Reporting Requirements.

Section	Order of Forms and Raw Data Required
Quality Control (QC) Summary	Surrogate Recovery Summary (FORM II PEST-1(2N), PEST-2 (2P))
	Matrix Spike/Matrix Spike Duplicate Recovery (Form III PEST-1(3G), PEST-2(3H)).
	Laboratory Control Sample Summary (Form III PEST-3(3L), PEST-4(3M)).
	Method Blank Summary (Form IV PEST(4E)). *Forms arranged in chronological order by date of analysis of method blank.*
Sample Data (*Arrange sample data in order of increasing EPA sample number, considering both letters and numbers)*	Target Compound Results (Form I PEST(1G)) followed by the raw data (chromatogram and quantitation report) for pesticide samples. (column 1 and column 2)
Standard Data (*Forms arranged by instrument in chronological order)*	Initial Calibration of Single Component Analytes (Form VI PEST-1(6J), PEST-2(6K)) for all columns, instruments, in chronological order by GC column and instrument.
	Toxaphene Initial Calibration (Form VI PEST-3(6L), PEST-4(6M)) for all columns, instruments, in chronological order by GC column and instrument.
	Analyte Resolution Check Summary (Form VI PEST-5(6R,6T)) for all columns, instruments, in chronological order by GC column and instrument.
	Performance Evaluation Mixture (PEM) (Form VI PEST-6(6U)) for all columns, instruments, in chronological order by GC column and instrument.
	Individual Standard Mixture C (Form VI PEST-9(6X), PEST-10(6Y)) for all columns, instruments, in chronological order by GC column and instrument.
	Continuing Calibration Verification Summary (Form VII PEST-1(7J)) for all performance evaluation mixtures and instrument blanks, for all columns, instruments, in chronological order by GC column and instrument.
	Continuing Calibration Verification Summary (Form VII PEST-2(7K), PEST-3(7L)) for all mid-point concentrations of Individual Standard Mixture C and instrument blanks, for all columns, instruments, in chronological order by GC column and instrument.
	Analytical Sequence (Form VIII PEST(8G)) for all columns, instruments, in chronological order by GC column and instrument.
	Florisil Cartridge Check (Form IX PEST-1(9A)) for all lots of cartridges used to process samples in the SDG, using Individual Standard Mixture C.
	GPC Calibration Verification (Form IX PEST-2(9B)) for all GPC columns in chronological order by calibration verification date.
	Identification Summary for Single Component Analytes (Form X PEST-1(10A)) and Identification Summary for Toxaphene (Form X PEST-2(10B)) for all samples with positively identified pesticides, in order by increasing EPA Sample Number.

Table 5: Continue

Raw QC Data	Method Blank and Instrument Blank data arranged in chronological order by extraction date.
	Tabulated Results (Form I PEST(1G)) followed by chromatograms and quantitation reports for each GC column.
	Pesticides LCS data
	Tabulated Results (Form I PEST(1G)) for both GC columns followed by chromatograms and quantitation reports.
	Pesticides Matrix Spike/Matrix Spike Duplicate Data
	Tabulated Results (Form I PEST(1G)) for both GC columns followed by chromatograms and quantitation reports.
	Raw GPC Permeation Chromatograph (GPC) data
	GPC calibration. UV traces, chromatograms, quantitation reports arranged in chronological order by GPC blank and GPC check along with the chromatogram and quantitation report for the midpoint of the calibration (Standard Mixture C and Toxaphene) used to analyze the GPC check.
	Raw Florisil data
	Chromatograms and quantitation reports arranged in chronological order by Florisil cartridge check analyses and the associated standard associated with the check (Individual Standard Mixture C and the 2,4,5-Trichlorophenol solution.
Miscellaneous (Sample Preparation Section)	Copies of run logs, Manual Integration Summary Reports, Extraction Benchsheets, GPC runlogs, preservation logs, screen data

Appendix A: Terms & Definitions

Acceptance Criteria: specified limits placed on characteristics of an item, process or service defined in requirement documents.

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 which are due to sampling and analytical operations; a data quality indicator.

Aliquot: A measured portion of a field sample, standard, or solution taken for sample preparation and/or analysis.

Analyte: The specific chemicals or components for which a sample is analyzed. (EPA Risk Assessment Guide for Superfund, OSHA Glossary).

Batch: environmental samples that are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria. An analytical batch is composed of prepared environmental samples (extracts, digestates and concentrates), which are analyzed together as a group.

Breakdown: A measure of the decomposition of certain analytes (DDT and Endrin) into by-products.

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 the standards.

Calibration Curve: the graphical relationship between the known values or a series of calibration standards and their instrument response.

Calibration Factor: A measure of the Gas Chromatographic response of a target analyte to the mass injected.

Calibration Standard: A substance or reference used to calibrate an instrument.

Continuing Calibration Verification (CCV): a single or multi-parameter calibration standard used to verify the stability of the method over time. Usually from the same source as the calibration curve.

Corrective Action: the action taken to eliminate the cause of an existing nonconformity, defect or other undesirable occurrence in order to prevent recurrence.

Data Qualifier: a letter designation or symbol appended to an analytical result used to convey information to the data user. (Laboratory)

The EPA-defined qualifiers that are routinely used for this test method are:

U: Compound analyzed for but not detected at a concentration at or above the reporting limit.

J: Estimated Value

- Result is less than the CRQL but above the adjusted MDL
- RT data indicates the presence of a pesticide that meets the identification criteria and the result is less than the CRQL but above zero.

P: There is greater than 25% difference for detected concentrations between two GC columns

C: Positive result whose identification has been confirmed by GC/MS

B: Compound is found in the sample and the associated method blank.

E: Compound whose response exceeds the upper limit of the calibration range.

D: Concentration identified from a dilution analysis.

X,Y,Z: Laboratory defined flags that may be used alone or combined as needed. If used, provide a description of the flag in the project narrative.

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

Instrument Blank: a blank designed to determine the level of contamination associated with the analytical instruments.

Intermediate Standard: a solution made from one or more stock standards at a concentration between the stock and working standard. Intermediate standards may be certified stock standard solutions purchased from a vendor and are also known as secondary standards.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Matrix Spike (MS): a field sample to which a known amount of target analyte(s) is added.

Matrix Spike Duplicate (MSD): a second replicate matrix spike

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which relative uncertainty is ±100%. The MDL represents a range where qualitative detection occurs. Quantitative results are not produced in this range.

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Precision: the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Quality Control Sample (QC): a sample used to assess the performance of all or a portion of the measurement system.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample.

Stock Standard: a solution made with one or more neat standards usually with a high concentration. Also known as a primary standard. Stock standards may be certified solutions purchased from a vendor.

Surrogate: a substance with properties that mimic the analyte of interest but that are unlikely to be found in environmental samples.

Appendix B: Standard Preparation Tables

The standard formulations contained in this Appendix are recommended and are subject to change. If the concentration of the stock standard is different than those noted in this table, adjust the standard preparation formulation accordingly. Unless otherwise specified, prepare the standard solutions in hexane using Class A volumetric glassware and Hamilton syringes. Unless otherwise specified for a standard solution, assign an expiration date of 6 months from date of preparation unless the parent standard expires sooner in which case use the earliest expiration date. See laboratory SOP BR-QA-002 *Standard Preparation* for further guidance.

INTERMEDIATE STANDARDS

Toxaphene Stock Solution (50 mg/L)

Parent Standard	Vendor	Component	Stock Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
Toxaphene	Restek #32005	Toxaphene	1000	1.0	20	50

TCX/DCB Surrogate Stock (5/10 mg/L)

Parent Standard	Vendor	Component	Stock Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
TCX Solution	Ultra #IST-440	TCX	2000	0.10	40	5.0
DCB solution	Ultra #PPS-150	DCB	1000	0.40	40	10

CALIBRATION STANDARDS

Instrument Blank Surrogate Spike Solution

Parent Standard	Vendor	Component	Stock Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
TCX/DCB Stock	Laboratory Prepared	TCX	5.0	0.8	200	20
		DCB	10			40

Performance Evaluation Mix (PEM)

Parent Standard	Vendor	Component	Stock Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
Pesticide Performance Evaluation Mix	Ultra #CLP-250	alpha-BHC	10-250	0.030	30	10-250
		beta-BHC				
		gamma-BHC				
		4,4'-DDT				
		Endrin				
		Methoxychlor				
		TCX				
		DCB				

Individual Standard Mix CS5 (Single Component Pesticides)

Parent Standard	Vendor	Component	Stock Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
TCX Stock	Laboratory Prepared	TCX	4.0	2.0	100	80
DCB Stock	Laboratory Prepared	DCB	8.0	2.0		160
Organochlorine Pest Mix AB#2	Restek #32292	Aldrin	8.0	1.0		80
		alpha-BHC	8.0			80
		beta-BHC	8.0			80
		delta-BHC	8.0			80
		gamma-BHC	8.0			80
		alpha-chlordane	8.0			80
		gamma-chlordane	8.0			80
		4,4'-DDD	16			160
		4,4'-DDE	16			160
		4,4'-DDT	16			160
		Dieldrin	16			160
		endosulfan I	8.0			80
		endosulfan II	16			160
		endosulfan sulfate	16			160
		endrin	16			160
		endrin aldehyde	16			160
		endrin ketone	16			160
		heptachlor	16			160
		heptachlor epoxide	16			160
		methoxychlor	80			800

Calibration Standards CS4-CS1 (Single Component Pesticides)

Parent Standard	Calibration Standard	Parent Standard Concentration (ug/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
Individual Standard Mix CS5	Individual Standard Mix CS4	80-800	20	40	40-400
Individual Standard Mix CS5	Individual Standard Mix CS3	80-800	10	40	20-200
Individual Standard Mix CS5	Individual Standard Mix CS2	80-800	5.0	40	10-100
Individual Standard Mix CS5	Individual Standard Mix CS1	80-800	2.5	40	5-50

Toxaphene Standard Mix CS5

Parent Standard	Vendor	Component	Stock Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
TCX Stock	Laboratory Prepared	TCX	4.0	2.0	100	80
DCB Stock	Laboratory Prepared	DCB	8.0	2.0		160
Toxaphene Stock	Laboratory Prepared	Toxaphene	50	16		8000

Toxaphene Calibration Standards CS4-CS1

Parent Standard	Calibration Standard	Parent Standard Concentration (ug/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
Toxaphene Standard Mix CS5	Toxaphene Standard Mix CS4	8000	20	40	4000
Toxaphene Standard Mix CS5	Toxaphene Standard Mix CS3	8000	10	40	2000
Toxaphene Standard Mix CS5	Toxaphene Standard Mix CS2	8000	5.0	40	1000
Toxaphene Standard Mix CS5	Toxaphene Standard Mix CS1	8000	2.5	40	500

Final Concentration of Prepared Calibration Standards in Extract

Analyte	CS1 (ng/mL)	CS2 (ng/mL)	CS3 (ng/mL)	CS4 (ng/mL)	CS5 (ng/mL)
TCX (surrogate)	5	10	20	40	80
DCB (surrogate) Pesticides	10	20	40	80	160
alpha-BHC	5	10	20	40	80
beta-BHC	5	10	20	40	80
delta-BHC	5	10	20	40	80
gamma-BHC	5	10	20	40	80
Heptachlor	5	10	20	40	80
Aldrin	5	10	20	40	80
Heptachlor epoxide	5	10	20	40	80
Endosulfan I	5	10	20	40	80
Dieldrin	10	20	40	80	160
4-4'-DDE	10	20	40	80	160
Endrin	10	20	40	80	160
Endosulfan II	10	20	40	80	160
4-4'-DDD	10	20	40	80	160
Endosulfan sulfate	10	20	40	80	160
4,4'-DDT	10	20	40	80	160
Methoxychlor	50	100	200	400	800
Endrin ketone	10	20	40	80	160
Endrin aldehyde	10	20	40	80	160
gamma-Chlordane	5	10	20	40	80
alpha-Chlordane	5	10	20	40	80
Toxaphene	500	1000	2000	4000	8000

APPENDIX C: EQUATIONS

These equations were taken from reference method SOM01.0 and from SW-846 8000B, Test Methods for Evaluation of Solid Waste Revision 2, December 1996. USEPA.

Resolution

$$\%\,\text{Resolution} = \frac{(H - V)}{H} \otimes 100$$

Where:

V = Height of the valley between the two peaks measured from the drawn baseline to the floor of the valley between the two peaks.

H = Height of the shorter of the adjacent peaks.

Absolute Retention Times

$$\overline{RT} = \frac{\sum_{i=1}^{n} RT_i}{n}$$

Where:

$\overline{RT}$ = Mean Absolute Retention Time of analyte

RT_i = Absolute Retention Time of analyte

n = Number of measurements

Percent Breakdown

$$\%\,\text{Breakdown of DDT} = \frac{\text{amount found (ng) (DDE + DDD)}}{\text{amount (ng) of DDT injected}} \otimes 100$$

$$\%\,\text{Breakdown of Endrin} = \frac{\text{amount found (ng) (endrin aldehyde + endrin ketone)}}{\text{amount (ng) of endrin injected}} \otimes 100$$

$$\text{Combined \% Breakdown} = \%\,\text{Breakdown DDT} + \%\,\text{Breakdown Endrin}$$

Calibration Factor (CF_i)

$$CF = \frac{\text{Peak Area (or Height) of the Compound in the Standard}}{\text{Mass Injected (ng)}}$$

Mean Calibration Factor ($\overline{CF}$)

$$\overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

Where:
CF_i = Calibration Factor
n = Number of Calibration Standards

Standard Deviation of the Calibration Factor (SD)

$$SD = \sqrt{\frac{\sum_{i=1}^{n} \left(CF_i - \overline{CF}\right)_2}{n-1}}$$

Where:
CF_i = Calibration Factor
$\overline{CF}$ = Mean Calibration Factor
n = Number of calibration levels

Percent Relative Standard Deviation (RSD) of the Mean Calibration Factor

$$\%RSD = \frac{SD}{\overline{CF}} \otimes 100$$

Where:
SD = Standard Deviation of Calibration Factors
$\overline{CF}$ = Mean Calibration Factor

Percent Difference (%D)

Percent Difference (%D): Used for Calibration Verification Standards

$$\%D = \frac{CF_v - \overline{CF}}{\overline{CF}} \otimes 100$$

Where:
CF_v = Calibration Factor from the Continuing Calibration Verification (CCV)

Percent Difference (%D): Used for PEM standards

$$\%D = \frac{C_{calc} - C_{nom}}{C_{nom}} \otimes 100$$

Where:
C_{calc} = Calculated concentration
C_{nom} = Nominal concentration

Percent Difference (%D): Used for Form X

$$\%D = \frac{Conc_H - Conc_L}{Conc_L} \otimes 100$$

Where:
$Conc_H$ = Higher of the two concentrations
$Conc_L$ = Lower of the two concentrations

Percent Recovery (%R)

$$\%R = \frac{C_s}{C_n} \otimes 100$$

Where:
C_s = Concentration of the Spiked Field or QC Sample
C_n = Nominal Concentration of Spike Added

Percent Recovery (%R) for MS/MSD

$$\%R = \frac{C_s - C_u}{C_n} \otimes 100$$

Where:
C_s = Concentration of the Spiked Sample
C_u = Concentration of the Unspiked Sample
C_n = Nominal Concentration of Spike Added

Relative Percent Difference (RPD)

$$RPD = \frac{|MSR - MSDR|}{1/2(MSR + MSDR)} \otimes 100$$

Where:
MSR = Matrix Spike Recovery
MSDR = Matrix Spike Duplicate Recovery

Sample Concentration

Water

$$\text{Concentration}_{\text{sample}}(\text{ug/L}) = \left(\frac{A_x}{\overline{CF}}\right)\left(\frac{DF}{V_i}\right)\left(\frac{V_t}{V_o}\right)\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_1\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_2 K\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_n$$

Where:
A_x = Peak area or peak height of the compound to be measured
$\overline{CF}$ = Mean Calibration Factor determined from the initial calibration for the compound to be measured, in height/ng
DF = Dilution Factor
V_i = Volume of extract injected in uL
V_t = Volume of extract produced by the preparation process (extraction and concentration), and before cleanup, in uL
V_o = Volume of the original water sample extracted in mL. Note: for instrument and sulfur blanks assume a volume of 1000mL
CV_{out} = Volume of extract produced by a cleanup process (cleanup and concentration), in uL
CV_{in} = Volume of extract subjected to a cleanup process, in uL
E = The efficiency of the cleanup process expressed as a fraction of material that passes through or is not mechanically lost during the cleanup step (e.g. 50% efficiency must be expressed as 0.50)

Soil/Sediment

$$\text{Concentration}_{\text{sample}}(\text{ug/kg}) = \left(\frac{A_x}{\overline{CF}}\right)\left(\frac{DF}{V_i}\right)\left(\frac{V_t}{W_t \otimes D}\right)\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_1\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_2 K\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_n$$

Where:
A_x = Peak area or peak height of the compound to be measured
$\overline{CF}$ = Mean Calibration Factor determined from the initial calibration for the compound to be measured, in height/ng
DF = Dilution Factor
V_i = Volume of extract injected in uL
V_t = Volume of extract produced by the preparation process (extraction and concentration), and before cleanup, in uL
W_t = Weight of the original soil sample extracted in g.
CV_{out} = Volume of extract produced by a cleanup process (cleanup and concentration), in uL
CV_{in} = Volume of extract subjected to a cleanup process, in uL
E = The efficiency of the cleanup process expressed as a fraction of material that passes through or is not mechanically lost during the cleanup step (e.g. 50% efficiency must be expressed as 0.50)

$$D = \frac{100 - \%\text{Moisture}}{100}$$

Water Adjusted CRQL

$$\text{Adjusted CRQL} = (\text{Contract CRQL})\left(\frac{V_x}{V_o}\right)\left(\frac{V_t}{V_y}\right)(DF)\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_1\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_2 K\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_n$$

Where:
Contract CRQL = The CRQL value reported in Exhibit C – Pesticide (ug/L)
V_x = Contract sample volume (1000 mL)
V_o = Volume of the original water sample extracted in mL. Note: for instrument and sulfur blanks assume a volume of 1000mL
V_t = Volume of concentrated extract, in uL
V_y = Contract concentrated extract volume (10,000 uL)
DF = Dilution Factor
CV_{out} = Volume of extract produced by a cleanup process (cleanup and concentration), in uL
CV_{in} = Volume of extract subjected to a cleanup process, in uL
E = The efficiency of the cleanup process expressed as a fraction of material that passes through or is not mechanically lost during the cleanup step (e.g. 50% efficiency must be expressed as 0.50)

Soil/Sediment Adjusted CRQL

$$\text{Adjusted CRQL} = (\text{Contract CRQL})\left(\frac{V_x}{V_s \otimes D}\right)\left(\frac{V_t}{V_y}\right)(DF)\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_1\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_2 K\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_n$$

Where:
Contract CRQL = The CRQL value reported in Exhibit C – Pesticide (ug/Kg)
W_x = Contract sample weight (30 g)
W_s = Weight of sample extracted in grams (g)
$D = \frac{100 - \%\text{Moisture}}{100}$
V_t = Volume of concentrated extract, in uL
V_y = Contract concentrated extract volume (10,000 uL)
DF = Dilution Factor
CV_{out} = Volume of extract produced by a cleanup process (cleanup and concentration), in uL
CV_{in} = Volume of extract subjected to a cleanup process, in uL
E = The efficiency of the cleanup process expressed as a fraction of material that passes through or is not mechanically lost during the cleanup step (e.g. 50% efficiency must be expressed as 0.50)

Title: DETERMINATION OF AROCLORS BY GC/ECD (CLP SOW SOM01.2)

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1.0 Scope and Application

This SOP describes the laboratory procedure used to determine the concentration of Aroclors using dual column Gas Chromatography with Electron Capture Detectors (GC/ECD). This SOP is applicable to the analytical procedure.

1.1 Analytes, Matrices, and Reporting Limits

This procedure may be used for a variety of matrices including: water, soil, and sediment.

The list of target compounds that can be determined from this method along with the Contract Required Quantitation Limit (CRQL) are provided in Table 1. Recovery and precision limits for the laboratory control sample (LCS) and matrix spikes (MS/MSD) are provided in Table 3A and Table 3B, Section 18.0.

2.0 Summary of Method

After extraction and cleanup, extracts are analyzed by injecting a 2 uL aliquot into a dual capillary column gas chromatograph equipped with electron capture detectors (GC/ECD).

This SOP is based on:

- Exhibits B & D, Analytical Methods for the Analysis Aroclors, USEPA CLP SOW for Organic Analysis, SOM01.1, May 2005.
- USEPA CLP SOW Clarifications to SOM01.1, November 7, 2005 and September 26, 2006.
- USEPA CLP SOW Modifications Updating SOM01.1 to SOM01.2, October 5, 2006 (Updated 02-12-2007) Amended 04-11-2006.

3.0 Definitions

A list of terms and definitions are provided in Appendix A.

4.0 Interferences

Method Interferences

Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing equipment. These contaminants can lead to elevated baselines and discrete artifacts that appear in gas chromatograms. These materials are demonstrated to be free of interferences by the analysis of method blanks. Interferences from phthalate esters can also pose a problem for the chlorinated pesticides analysis. To avoid this type of interference, the use of plastics in the laboratory must be minimized.

Matrix Interferences

Matrix interferences may be caused by contaminants that are co-extracted with the samples. The extent of the interference will vary by matrix and are minimized using the various cleanup procedures described in this SOP.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

The gas chromatograph contains zones that have elevated temperatures. The analyst must be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.2 Primary Materials Used

Table 2, Section 18.0 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the MSDS. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

6.0 Equipment and Supplies

Catalog numbers listed in this SOP are subject to change at the discretion of the vendor. Analysts are cautioned to be sure equipment used meets the specification of this SOP.

6.1 Miscellaneous

Autosampler Vials, National Scientific or equivalent.

Hydrogen Generator: Whatman.

Volumetric Syringes, Class “A” (10µl, 25µl, 50µl, 100µl, 250µl and 500µl), Hamilton or equivalent.

6.2 Analytical System

Computer Hardware/Software: GC Acquisition Platform - VAX 4505 (GVAX) Multichrom V2.11. Data Processing - Hewlett-Packard 9000-series computers, an HP 9000 K200 (Chemsvr5)/ HP-UX 10.20 and Target V3.5 or higher.

GC/ECD: with dual columns, dual ECDs, and auto-sampler capable of a 2-µl injection split onto two columns: HP 5890 with Leap Technology CTC A200SE and A200S Fisons autosamplers, Agilent Technologies 6890N with 7683 Series injector, or equivalent.

GC Columns: A dual fused silica capillary column system that will provide simultaneous primary and confirmation analyses.

- RTX-5 (30m x 0.25 mm ID x 0.25um), Restek # 10223.
- RTX-35 (30m x 0.25 mm ID x 0.25um), Restek # 10423.

Equivalent columns may be used so long as elution orders are documented and compound separations are maintained.

7.0 Reagents and Standards

See Appendix B for standard formulations used for analysis.

7.1 Reagents

Hexane, Ultra-Resi Analyzed, JT Baker or equivalent.

7.2 Standards

Purchase stock standard solutions from commercial vendors and from these prepare calibration and working standards by diluting a known volume of stock standard in an appropriate solvent to the final volume needed to achieve the desired concentration. The recommended formulation for each standard used in this procedure is provided in Appendix B along with the recommended source materials, expiration dates and storage conditions.

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection so these procedures are not included in this SOP. Sampling requirements may be found in the published reference method.

Listed below are minimum sample size, preservation and holding time requirements:

Matrix	Sample Container	Minimum Sample Size	Preservation	Holding Time1	Reference
Water	Amber Glass	Two 1 L for samples One 1 L per MS/MSD	4°C (±2°C)	Extraction: 5 days from VTSR Analytical: 40 days	CLP SOW
Solid	Amber Glass	Two 125 mL for samples One 125 mL per MS/MSD	4°C (±2°C)	Extraction: 10 days Analytical: 40 days	CLP SOW
Extract	Amber vial	NA	chilled to <4°C	Analytical: 40 days	CLP SOW

1Extraction holding time is determined from the date sample were received by the laboratory (VTSR); analytical holding time is determined from date of initiation of extraction.

Unless otherwise specified by client or regulatory program, after analysis, samples and extracts are retained for a minimum of 365 days after provision of the project report and then disposed of in accordance with applicable regulations.

9.0 Quality Control

9.1 Sample QC

The laboratory prepares the following quality control samples with each batch of samples.

QC Item	Frequency	Acceptance Criteria
Method Blank (MB)	1 in 20 or fewer samples	See Table 4
Laboratory Control Sample (LCS)	1 in 20 or fewer samples	See Table 3A
Matrix Spike(s) MS/MSD	1 in 20 or fewer samples	See Table 3B
Sample Duplicate (SD)	Client Request	Client Defined

A method blank (MB) and laboratory control sample (LCS) are prepared with each extraction batch. Matrix spikes (MS/MSD) are prepared with each extraction batch of every 20 or fewer field samples when sufficient sample volume is available. Sample duplicates (SD) and/or client-specific MS/MSD are performed per client request. The method blank is analyzed on each GC/ECD system used to analyze associated samples.

All extracts undergo sulfur cleanup in the extraction procedure. At times it is necessary to do an additional sulfur cleanup on one or more of the extracts. When part of a set of samples is subjected to additional sulfur cleanup, a sulfur cleanup blank (PSBLK##) is prepared and analyzed in order to determine the level of contamination associated with the sulfur cleanup procedure.

9.2 Instrument QC

The following instrument QC is performed:

QC Item	Frequency	Acceptance Criteria
Initial Calibration (ICAL)	Initially; when CCV fails	See Section 10 and Table 4
Continuing Calibration Verification (CCV or PEM)	Daily, every 12 hour window, end of sequence	See Section 10 and Table 4
Retention Time Windows	Method Defined	See Table 1

Instrument blanks (PIBLK##) are analyzed during the analytical sequence to determine the level of contamination associated with the instrumental analysis.

10.0 <u>Procedure</u>

10.1 Instrument Operating Conditions

Instrument Set-Up and Operating Conditions

Install a five meter deactivated guard column to the injection port, and using a glass “Y” connect the guard column to the separate analytical columns. Attach the analytical columns to each Electron Capture Detector (ECD).

The following are example instrument conditions used for analysis:

Carrier Gas:	Hydrogen (Hydrogen Generator)
Column Flow:	2.0 mL/min.
Make-up Gas:	Argon/Methane
Make-up Gas Flow:	120 mL/min.
Injector Temperature:	225°C
Detector Temperature	300°C

Injection Technique:	on-column
Injection volume:	2 µL
Injector:	CTC auto sampler or 7683B Injector
Initial Temperature:	120°C
Initial Hold Time:	1 minute
Temperature Program:	16°C/min. to 210°C,6°C/min. to 245°C, 12.5°C/min to 300°C. Hold for 4 minutes.

10.2 Instrument Calibration

10.2.1 Initial Calibration (ICAL)

Calibrate the GC/ECD at a minimum of five concentrations using AR1660 (a mixture of Aroclor 1016 and Aroclor 1260) to determine instrument sensitivity and linearity. The recommended concentration levels are provided in Appendix B. For pattern recognition use a single mid-point standard for the calibration of Aroclor 1221, 1232, 1242, 1248, 1254, 1262, and 1268. Perform initial calibration upon initial award of the contract, whenever major instrument maintenance or modification is performed (for example, column replacement, baking or replacement of ECD), or if the calibration verification technical acceptance criteria are not met. Also, if any Aroclor other than AR1660 is detected in a sample, perform a five-point calibration for that Aroclor and re-analyze all samples with that Aroclor prior to reporting any results.

Calibration Procedure

Set up the GC/ECD system as described in Section 10.1. Prepare the calibration standards and instrument blank using the instructions provided in Appendix B. Allow the standards to warm to ambient temperature prior to analysis. Analyze the standards in the initial calibration sequence below.

Initial Calibration Sequence	EPA Sample Number
Instrument Blank	AIBLK##
Aroclor 1221 CS3	AR12213##
Aroclor 1232 CS3	AR12323##
Aroclor 1242 CS3	AR12423##
Aroclor 1248 CS3	AR12483##
Aroclor 1254 CS3	AR12543##
Aroclor 1262 CS3	AR12623##
Aroclor 1268 CS3	AR12683##
Aroclor 1660* CS1	AR16601##
Aroclor 1660 CS2	AR16602##
Aroclor 1660 CS3	AR16603##
Aroclor 1660 CS4	AR16604##
Aroclor 1660 CS5	AR16605##
Instrument Blank	AIBLK##

*Combination of Aroclor 1016 and Aroclor 1260

Retention Time Windows

During the initial calibration sequence the data system determines absolute retention times for each of the 5 peaks chosen for quantitation of each Aroclor analyzed as a single point calibration

standard. For Aroclors with 5 calibration levels, including each surrogate, the mean retention time is calculated for each quantitation peak chosen.

The acceptance criteria described in this section apply independently to each GC column. The acceptance criteria must be met prior to sample analysis. If criteria are not met, identify and correct the problem prior to further analysis.

- The initial calibration sequence must be analyzed at the frequency and the order specified in Section 10.2.1, at the concentrations specified in Appendix B.

- The chromatograms of the standards analyzed during the initial calibration sequence must display the peaks chosen for quantitation at greater than 25% and less than 100% of full scale. If a chromatogram is replotted electronically to meet the above requirements, the scaling factor must be displayed on the chromatogram.

- The %RSD of the CFs for each Aroclor peak and each surrogate must be less than or equal to 20% on each chromatographic column.

- All instrument blanks must meet the following criteria:

  - The instrument blank must be analyzed at the original concentration.
  - The instrument blank must meet the acceptance criteria for sample analysis.
  - The concentration of each target analyte in the instrument blanks must be less than the CRQL on each chromatographic column.
  - The RT for each of the surrogates must be within the RT window on both GC columns.

10.3 Calibration Verification (CCV)

Frequency of Calibration Verification

Analyze an instrument blank (AIBLK) and AR1660 CS3 (AR16603 ##) standard mixture at one end of a 12-hour period during which sample data is collected. Analyze a second AIBLK and AR1660 CS3 standard mixture at the other end of the 12-hour period. Field and QC samples must be bracketed by acceptable analyses of the instrument blank and CS3 standard mixture. If any other Aroclor is detected within the 12-hour period during which field and QC sample data are collected, and the 12-hour time period for the five-point initial calibration of the detected Aroclor has elapsed, then analyze an instrument blank and a CS3 standard of the detected Aroclor(s) to bracket both ends of the 12-hour window. If the opening CCV (AIBLK and CS3) does not meet acceptance criteria, then establish a new five-point initial calibration for the detected Aroclor(s) prior to further analysis.

For the 12-hour period following the initial calibration sequence, the analysis of an AIBLK signals the start of the 12-hour window. Analyze an AR1660 CS3 standard immediately after the AIBLK. Field and QC samples may then be injected for 12 hours from the injection of the AIBLK. The first injection immediately after the 12-hour window must be an AIBLK and the AR1660 CS3 standard. The analyses of the AIBLK and the CS3 standard are used to initiate the subsequent 12-hour window if they meet acceptance criteria. The subsequent 12-hour window must also be bracketed by acceptable analyses of the AIBLK and AR1660 CS3 standard. This progression may continue to define the analytical windows until acceptance criteria are not met or until an Aroclor has been detected in a sample for which the corresponding CS3 standard was not analyzed.

If the instrument is idle for more than 12 hours since the injection of the AIBLK that bracketed the end of the previous 12-hour window, analyze an acceptable AIBLK and AR1660 CS3 standard mixture to begin the new analytical sequence.

No more than 14 hours may elapse from the injection beginning the opening CCV (AIBLK) and the injection ending the closing CCV (Aroclor standard). All analytical sequences must end with a valid CCV.

Procedure for Calibration Verification

Allow the standards to warm to ambient temperature prior to analysis. Analyze the instrument blank and CS3 Standard Mixtures at the required frequencies.

Acceptance Criteria for Calibration Verification

The acceptance criteria listed below applies independently to each column. The acceptance criteria must be met prior to analysis of field and QC samples.

- The AR1660 standard and the standards of other Aroclors detected in the field samples must be analyzed at the appropriate frequency (See 10.3).

- The absolute retention time of each of the Aroclor peaks and the surrogates must be within the established retention time windows as determined from the initial calibration.

- For the opening CCV, the CFs for each Aroclor peak and surrogate calculated from the CCV standard must not exceed a difference of ± 15% when compared to the average CFs from the initial calibration. For the closing CCV, the CFs for each Aroclor peak and surrogate must not exceed a difference of ± 50% when compared to the average CFs from the initial calibration. If the closing standard is ± 15% or less, it can be used as the opening CCV for the next 12 hour window.

If the AR1660 does not meet the acceptance criteria, the standard may be immediately re-injected. If the second injection of the standard meets the acceptance criteria then sample analysis may continue. If the second injection fails, perform corrective action and repeat initial calibration.

10.4 Troubleshooting:

Check the following items in case of calibration failures:

- ICAL Failure – Perform injection port maintenance, install new guard column, check detector ends to see if detector jet has slipped. In extreme cases, install new columns, particularly if the chromatography has degraded as evidenced by peak shapes.
- CCV Failure – Perform Injection port maintenance; if injection port maintenance does not restore CCV, install a new guard column and remove one or more loops from each analytical column.
- Needle crushed during injection - Replace the needle and check the injection port for obstructions and check the autosampler for misalignment.
- Auto-sampler failure - Reset the auto-sampler.
- Power failure - Reset run in Multichrom and re-acquire or re-initiate run sequence.

10.5 Sample Preparation

Before field and QC samples and required blanks can be analyzed, ensure that the instrument meets criteria for initial calibration and calibration verification. Analyze all samples and standards under the same instrument conditions (See Section 10.1) using the same on-column injection volume of 2.0 uL.

Extract Screening and Guidance for Dilution

Prepare the extracts at a 1:10 dilution for screening. Screen all extracts on a designated screen instrument prior to instrument analysis to determine the presence of sulfur and to assess target analyte concentrations. Use the results of the screen to determine the approximate dilution factor (DF) required to get the largest peak within the calibration range. If sulfur is found in the extract, repeat sulfur cleanup following the procedure given in laboratory SOP LM-OP-SOM1.0-PCB.

- If the concentration of the largest Aroclor peak is greater than the concentration of the same peak in the high standard (CS5) of the initial calibration range on **both** columns, dilute the extract such that the concentration of the highest Aroclor peak in the diluted extract is between the low standard (CS1) and the high standard (CS5) for the lower column concentration of the two analyses. When diluted, the Aroclor must be reported at greater than 25.0% of full scale, but less than 100.0% of full scale.

- If a dilution based on preliminary screening is performed, report the results for the more and less concentrated extracts. If the dilution factor is greater than 10, analyze the extract 10 times more concentrated than the diluted sample extract and report both sets of data. If the dilution factor is less than 10, analyze the extract undiluted and report both sets of data. Analyze the MS/MSD at the same concentration as the most concentrated extract for which the original (parent) sample results will be reported.

- If the concentration of any target analyte is above the high calibration standard (CS5) after a dilution of 1:100,000 contact the project manager for further instruction.

10.6 Sample Analysis

Analytical Sequence

Analyze the samples using the following analytical sequence:

Injection #	Material Injected
1-12	First 12 steps of the initial calibration (See Section 10.2.1)
13	Instrument Blank (AIBLK)
14	AR1660 standard (CS3)
15	First sample
1st injection past 12 hour	After last sample, Instrument Blank
2nd injection past 12 hour	AR1660 standard (CS3) (and other Aroclor standards as needed depending on positive results found in sample analyses)

If the instrument has been calibrated and a new analytical window is created without the need to recalibrate the instrument, the following sequence should be used to analyze the samples.

Injection #	Material Injected
1-2	Instrument Blank (AIBLK)
3	AR1660 standard (CS3) (and other Aroclor standards as needed depending on positive results found in sample analyses)
4	Sample extract(s) (12 hour window counted from the injection of the first PIBLK injection to the injection of the PIBLK that ends the window.)
1st injection past 12 hours	Instrument Blank (AIBLK)
2nd injection past 12 hours	AR1660 standard (CS3) (and other Aroclor standards as needed depending on positive results found in sample analyses)

The above analysis sequences show only the minimum required standards. More standards may be run at the discretion of the laboratory. However, the standards must satisfy all criteria in order to continue the sequence.

Load the extracts and standards into the autosampler and enter the sample ID's into the data acquisition program in the same order that the extracts and standards were placed in the autosampler. Start the analytical sequence and acquire the data.

11.0 Calculations / Data Reduction

11.1 Qualitative Identification

The data system tentatively identifies and quantitates analyte peaks by comparing the retention time of the peaks to the retention time windows and the calibration factors (CFs) established during initial calibration. Identification of Aroclors in samples is based on pattern recognition in conjunction with the elution of the chosen sample peaks within the RT windows on both GC columns. The identification of Aroclors may be complicated by environmental alteration and by the presence of coeluting analytes or matrix interferences. Because of these alterations, Aroclors in samples may give patterns similar to, but not identical to the standards. If more than one Aroclor is observed in a sample, different peaks must be chosen to quantitate each Aroclor. A peak common to both Aroclors present in the sample must not be used to quantitate either compound. When an Aroclor other than AR1660 is detected in the sample, analyze a five-point calibration curve specific to that Aroclor and re-analyze all samples that contain that Aroclor.

11.2 Quantitative Identification

The data system performs quantitation for all analytes and surrogates for each GC column based on the mean calibration factor from the most recent initial calibration. The quantitation of each Aroclor is accomplished by comparing the height or area (See section 10.2.1) of each of the 3-5 major peaks in the sample with the same peaks from initial calibration. The concentration of each peak is determined then a mean concentration is determined for each column. The lower of the two concentrations (between columns) is reported on the Form I.

The data system adjusts calculated sample results to account for dilution and percent moisture. The data system also calculates the percent recovery for the surrogates for each GC column as well as the relative percent difference between results on each GC column. Although the data system performs the calculations, equations for the calculation of sample concentration are provided for reference in Appendix C.

11.3 Calculations

See Appendix C.

11.4 Data Review

11.4.1 Primary Review

Confirm quantitative and qualitative identification criteria using the criteria provided in Section 11.1 and Section 11.2.

The samples were extracted and analyzed within holding time. Check sample information and preparation information from sample log-in and preparation upon initial processing. Perform necessary manual integrations and identifications.

Evaluate the results of the instrument performance check samples, field and QC samples against the acceptance criteria given in Section 18 Table 4. Perform the recommended corrective action as necessary. If corrective action is not taken or is not successful, initiate a nonconformance report (NCR) to document the situation.

Samples were associated with a method blank and an LCS that met acceptance criteria.

The method blank was analyzed on each instrument on which associated samples were analyzed. Additionally, the method blank was subject to sulfur cleanup along with the associated samples, or a sulfur cleanup blank was performed. The surrogate recovery for the method blank was between 30-150%.

The RT for each surrogate is within the RT window.

The percent recovery for each surrogate in samples is within 30-150%*. **Up to one surrogate may fail criteria per column and the surrogate recovery limits are not applicable to samples that were diluted.*

Compare results from each column to verify confirmation of each target analyte.

If an individual peak concentration (on column) for an Aroclor is greater than 10 ng/uL for both columns, contact the project manager to determine whether or not GC/MS confirmation is required.

Evaluate the results of samples analyzed immediately after high concentration samples for signs of carry-over. Reanalyze the sample if carry over is suspected.

Dilute and reanalyze samples whose results exceed the calibration range. The diluted analysis should result in a determination within the upper half of the calibration curve.

Check to ensure an appropriate technical reason code is provided for each manual integration. Acceptable technical reason codes are provided in laboratory SOP BR-QA-006 *Manual Integration Requirements*.

Generate a “before” and “after” chromatogram for every manual integration performed on an instrument performance check standard (ICAL, ICV, CCV), QC sample (MB, LCS) and for any manual integration performed on any surrogate in any field sample. Additionally, all “before” and

"after" chromatograms for target analytes in field sample analyses will be supplied for clients requesting this documentation.

Generate the Manual Integration Summary Report. Document your review of manual integrations on the summary report and sign the summary report.

Generate a quantitation and chromatogram report for the calibration, calibration check standards, associated summary forms, and compile the package.

11.4.2 Secondary Data Review

Check each qualitative identification and spot check quantitative values using the criteria provided in Section 11.1 and Section 11.2.

If manual integrations were performed:

- Review each manual integration to verify that the integration is consistent and compliant with the requirements specified in laboratory SOP BR-QA-006 *Manual Integration Requirements*. If a problem is found, immediately consult with the primary analyst or notify the Technical Director or QA Manager. Check that each manual integration is included in the manual integration summary and that each instance has an associated manual integration code. Also, check to ensure that a "before and after" report is present for each manual integration of reported analyte.

- Reintegration (by secondary data reviewers) should not be performed except in limited circumstances such as when the primary analyst who performed the initial integration is not available to correct any errors found during secondary review. If reintegration is performed, each integration performed by the secondary reviewer must be reviewed by a peer analyst or the department supervisor to verify the integration is consistent and compliant with the requirements specified in laboratory SOP BR-QA-006 *Manual Integration Requirements*.

Verify that the performance criteria for the QC items listed in Tables and 4 were met. If the results do not fall within the established limits verify that the recommended corrective actions were performed. If corrective action was not taken or was unsuccessful, ensure that the situation is documented with a nonconformance report (NCR) and ensure that the data is qualified accordingly. Report the nonconformance in the narrative note program.

If the percent difference of the concentrations between the 2 columns is greater than 25%, flag the results with a "P" data qualifier.

11.5 Data Reporting

Data Reporting & Order of Deliverables

Evaluate each chromatogram to verify qualitative and quantitative identification of target compounds. Exhibit B of the CLP SOW specifies that the laboratory report estimated values qualified with a "J" data qualifier when the retention time (RT) data indicate the presence of a compound that meets the identification criteria and the result is less than the CRQL but greater than zero. For instance, if the sample quantitation limit is 5.0 ug/L but a concentration of 3.0 ug/L is calculated, the laboratory should report the results as 3.0J. However, the laboratory is further instructed to not report the estimated value if the presence of the peak is considered to be from instrument noise or other interference.

Review all samples, standards, and QC samples against the acceptance criteria provided in this SOP. Generate and arrange the Aroclor data following the requirements specified in the Table 5.0. If the results do not fall within the criteria, perform corrective action. If corrective action is not taken, or is unsuccessful, document the situation with a nonconformance report and qualify the data using an appropriate data qualifier (See Appendix A for data qualifier definitions). For additional guidance regarding the laboratory's protocol and required elements for each level of data review (primary, secondary, and tertiary) refer to laboratory SOP LP-QA-003 *Data Review*.

Generate a report that is legible, labeled and complete in CLP SOW Format. Forms and data should be arranged in chronological order by column. Sample data should be arranged in increasing order by Client ID.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

A Method Detection Limit (MDL) must be determined on each instrument used for analysis for each matrix prior to initial use of the method. The MDLs are then verified annually with an MDL Verification Check sample that is subject to the same extraction and cleanup procedures as used for field samples. Some regulatory programs may require that the MDL study be repeated annually, but this is not a requirement of the CLP SOW. The procedure and acceptance criteria for MDL studies and MDL verification are given in laboratory SOP BR-QA-005 *Determination of LOD, LOQ & RL.*

12.2 Demonstration of Capabilities (DOC)

Perform a method demonstration of capability at initial set-up and when there is a significant change in instrumentation or procedure.

Each analyst that performs the analytical procedure must complete an initial demonstration of capability (IDOC) prior to independent analysis of client samples. Each analyst must demonstrate on-going proficiency (ODOC) annually thereafter. DOC procedures are further described in the laboratory's quality system manual (QAM) and and in the laboratory SOP BR-QA-011 *Procedures for Employee Training & Demonstration of Proficiency.*

12.3 Training Requirements

Any employee that performs any portion of the procedure described in this SOP must have documentation in their employee training file that they have read this version of this SOP.

Instrument analysts, prior to independent analysis of client samples, must also have documentation of demonstration of initial proficiency (IDOC) and annual on-going proficiency (ODOC) in their employee training files.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to BR-EH-001 *Hazardous Waste*. The following waste streams are produced when this method is carried out.

- Vials containing sample extracts: Satellite container: 15 gallon bucket connected to a fume hood.
- Solvent Waste: Satellite container: 1 L glass bottle located in fume hood.

15.0 References / Cross-References

- Exhibits B & D, Analytical Methods for the Analysis of Trace Concentrations of Aroclors, USEPA CLP SOW for Organic Analysis, SOM01.1, May 2005.
- USEPA CLP SOW Clarifications to SOM01.1, November 7, 2005 and September 26, 2006.
- USEPA CLP SOW Modifications Updating SOM01.1 to SOM01.2, October 5, 2006 (Updated 02-12-2007) Amended 04-11-2006.
- Laboratory SOP BR-EX-013 *Extraction and Cleanup Procedure for the Determination of Aroclors (CLP SOW SOM01.2)*
- Laboratory SOP BR-EX-025 *Extraction and Cleanup Procedures for the Determination of Low Level Aroclors (CLP SOW SOM01.2)*
- Laboratory SOP BR-QA-005 *Determination of LOD, LOQ & RL.*
- Laboratory SOP BR-QA-011 *Procedures for Employee Training & Demonstration of Proficiency.*
- Laboratory SOP BR-EH-011 *Hazardous Waste.*
- Laboratory SOP BR-QA-014 *Laboratory Records.*
- Laboratory SOP BR-QA-006 *Procedures & Documentation Requirements for Manual Integration.*
- Laboratory Quality Assurance Manual (QAM).

16.0 Method Modifications

None.

17.0 Attachments

- Table 1: Target Compound List and Reporting Limit
- Table 2: Primary Materials Used
- Table 3A: LCS Recovery Limits
- Table 3B: MS/MSD Recovery and Precision Limits
- Table 4: QC Summary and Recommended Corrective Action
- Table 5: Aroclor Data Reporting Requirements
- Appendix A: Terms and Definitions
- Appendix B: Standard Preparation Tables
- Appendix C: Equations

18.0 Revision History

BR-GC-012, Revision 1:

- SOP updated to the new TestAmerica format
- Updated Table 1 for Low Level Water CRQL limits
- Updated sample container and sample size requirements
- Analytical Standard Table updated to include component information – Appendix B
- Form names added to Table 5: Aroclor Data Reporting Requirements.

Table 1: Target Compound List, CRQL, and RT Windows

Analyte	Contract Required Quantitation Limit			RT Window
	LL Water ug/L	Water ug/L	Solid ug/Kg	
Aroclor-1016	0.10	1.0	33	±0.07
Aroclor-1221	0.10	1.0	33	±0.07
Aroclor-1232	0.10	1.0	33	±0.07
Aroclor-1242	0.10	1.0	33	±0.07
Aroclor-1248	0.10	1.0	33	±0.07
Aroclor-1254	0.10	1.0	33	±0.07
Aroclor-1260	0.10	1.0	33	±0.07
Aroclor-1262	0.10	1.0	33	±0.07
Aroclor-1268	0.10	1.0	33	±0.07
TCX (Surrogate)	NA	NA	NA	±0.05
DCB (Surrogate)	NA	NA	NA	±0.10

[1] Reporting Limits represent those that can be achieved in a blank matrix. Individual reporting limits will vary based upon sample matrix, target analyte concentration, co-extracted interferences, and dry weight of samples.

Table 2: Primary Materials Used

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Table 3A: LCS Control Limits

Analyte	Recovery Limit (%R)
	Water/Solid
AR1016	50-150
AR1260	50-150

Table 3B: MS/MSD Control Limits

Analyte	Recovery Limits (%R)	% RPD
	Water/Solid	Water/Solid
AR1016	29-135	0-15
AR1260	29-135	0-20

Table 4: QC Summary and Recommended Corrective Action

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action[1]
Initial Calibration	Initially, prior to sample analysis; when calibration verification standards indicate calibration relationship is no longer valid; after major instrument maintenance	See Section 10.2	Correct problem and repeat initial calibration.
Calibration Verification	To open and close 12 hour sample windows.	See Section 10.3	Correct problem, reanalyze CCV and all associated samples since last successful CCV.
Method Blank	One per extraction batch (Not to exceed 20 field samples)	Target analytes must be < CRQL Surrogate recovery: 30-150% [Not advisory] Analyzed on each GC/ECD system used to analyze field samples. RTs within established windows	Correct problem, re-extract and reanalyze with all associated samples.
Sulfur Blank	Whenever a subset of samples within an extraction batch receives sulfur clean up.	Target analytes must be < CRQL Surrogate recovery: 30-150% [Not advisory] Analyzed on each GC/ECD system used to analyze field samples. RTs within established windows	Correct problem, re-extract and reanalyze with all associated samples.
Instrument Blank	First analysis in 12-hour analytical sequence Preceding and following acceptable sample analyses.	Target analytes must be < CRQL RTs within established windows (Requirements apply independently to each GC column)	Correct problem and reanalyze with all associated samples.
LCS	One per extraction batch	%R within control limits given in Table 3A Surrogate recovery: 30-150% [Not advisory] RTs within established windows (Requirements apply independently to each GC column)	Correct problem, re-extract and reanalyze with all associated samples.
MS/MSD	One per sample set of 20 field samples analyzed at the most concentrated analysis of parent. Note: Results can be reported from over-range response.	%R & %RPD within advisory limits given in Table 3B RTs within established windows	Evaluate circumstances. Assay spike formulations.
Surrogate Spike	All field and QC samples	%R 30-150 for all field and QC samples *Up to one surrogate may fail criteria per column in samples.*	Correct problem, re-extract and reanalyze if sufficient sample is available

[1]*The recommended corrective action may include some or all of the items listed in this column. The corrective action taken may be dependent on project data quality objectives and/or analyst judgment but must be sufficient to ensure that results will be valid. If corrective action is not taken or is not successful, data must be flagged with appropriate qualifiers.*

Table 5: Aroclor Data Reporting Requirements.

Section	Order of Forms and Raw Data Required
Quality Control (QC) Summary	Surrogate Recovery Summary (FORM II ARO-1(2Q), ARO-2 (2R))
	Matrix Spike/Matrix Spike Duplicate Recovery (Form III ARO-1(3J), ARO-2(3K)).
	Laboratory Control Sample Summary (Form III ARO-3(3N), ARO-4(3P)).
	Method Blank Summary (Form IV ARO(4F)). *Forms arranged in chronological order by date of analysis of method blank.*
Sample Data (*Arrange sample data in order of increasing EPA sample number, considering both letters and numbers)*	Target Compound Results (Form I ARO(1H)) followed by the raw data (chromatogram and quantitation report) for Aroclor samples. (column 1 and column 2)
Standard Data (*Forms arranged by instrument in chronological order)*	Initial Calibration Data (Form VI ARO-1(6N), ARO-2(6P), and ARO-3(6Q)) for all columns, instruments, in chronological order by GC column and instrument.
	Continuing Calibration Verification Summary (Form VII ARO(7N)) for all columns, instruments, in chronological order by GC column and instrument.
	Analytical Sequence (Form VIII ARO(8H)) for all columns, instruments, in chronological order by GC column and instrument.
	Identification Summary for Multicomponent Analytes (Form X ARO(10C)) for all samples with positively identified Aroclors, in order by increasing EPA Sample Number.
Raw QC Data	**Blank data arranged in chronological order by extraction date.**
	Tabulated Results (Form I ARO(1H)) followed by chromatograms and quantitation reports for each GC column.
	Aroclors LCS data
	Tabulated Results (Form I ARO(1H)) for both GC columns followed by chromatograms and quantitation reports.
	Matrix Spike/Matrix Spike Duplicate Data
	Tabulated Results (Form I ARO(1H)) for both GC columns followed by chromatograms and quantitation reports.
	Raw GPC Permeation Chromatograph (GPC) data
	GPC calibration. UV traces, chromatograms, quantitation reports arranged in chronological order by GPC blank along with the chromatogram and quantitation report for the midpoint of the calibration used to analyze the GPC check, Forms VI, VII, VIII
Miscellaneous (Sample Preparation Section)	Copies of run logs, Manual Integration Summary Reports, Extraction Benchsheets, GPC runlogs, preservation logs, screen data

Appendix A: Terms & Definitions

Acceptance Criteria: specified limits placed on characteristics of an item, process or service defined in requirement documents.

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 which are due to sampling and analytical operations; a data quality indicator.

Aliquot: A measured portion of a field sample, standard, or solution taken for sample preparation and/or analysis.

Analyte: The specific chemicals or components for which a sample is analyzed. (EPA Risk Assessment Guide for Superfund, OSHA Glossary).

Batch: environmental samples that are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria. An analytical batch is composed of prepared environmental samples (extracts, digestates and concentrates), which are analyzed together as a group.

Breakdown: A measure of the decomposition of certain analytes into by-products.

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 the standards.

Calibration Curve: the graphical relationship between the known values or a series of calibration standards and their instrument response.

Calibration Factor: A measure of the Gas Chromatographic response of a target analyte to the mass injected.

Calibration Standard: A substance or reference used to calibrate an instrument.

Continuing Calibration Verification (CCV): a single or multi-parameter calibration standard used to verify the stability of the method over time. Usually from the same source as the calibration curve.

Corrective Action: the action taken to eliminate the cause of an existing nonconformity, defect or other undesirable occurrence in order to prevent recurrence.

Data Qualifier: a letter designation or symbol appended to an analytical result used to convey information to the data user. (Laboratory)

The EPA-defined qualifiers that are routinely used for this test method are:

U: Compound analyzed for but not detected at a concentration at or above the reporting limit.

J: Estimated Value
- Result is less than the CRQL but above the adjusted MDL
- RT data indicates the presence of a pesticide that meets the identification criteria and the result is less than the CRQL but above zero.

P: There is greater than 25% difference for detected concentrations between two GC columns
C: Positive result whose identification has been confirmed by GC/MS
B: Compound is found in the sample and the associated method blank.
E: Compound whose response exceeds the upper limit of the calibration range.
D: Concentration identified from a dilution analysis.
X,Y,Z: Laboratory defined flags that may be used alone or combined as needed. If used, provide a description of the flag in the project narrative.

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

Instrument Blank: a blank designed to determine the level of contamination associated with the analytical instruments.

Intermediate Standard: a solution made from one or more stock standards at a concentration between the stock and working standard. Intermediate standards may be certified stock standard solutions purchased from a vendor and are also known as secondary standards.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Matrix Spike (MS): a field sample to which a known amount of target analyte(s) is added.

Matrix Spike Duplicate (MSD): a second replicate matrix spike

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which relative uncertainty is ±100%. The MDL represents a range where qualitative detection occurs. Quantitative results are not produced in this range.

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Precision: the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Quality Control Sample (QC): a sample used to assess the performance of all or a portion of the measurement system.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample.

Stock Standard: a solution made with one or more neat standards usually with a high concentration. Also known as a primary standard. Stock standards may be certified solutions purchased from a vendor.

Surrogate: a substance with properties that mimic the analyte of interest but that are unlikely to be found in environmental samples.

Appendix B: Standard Preparation Tables

The standard formulations contained in this Appendix are recommended and are subject to change. If the concentration of the stock standard is different than those noted in this table, adjust the standard preparation formulation accordingly. Unless otherwise specified, prepare the standard solutions in hexane using Class A volumetric glassware and Hamilton syringes. Unless otherwise specified for a standard solution, assign an expiration date of 6 months from date of preparation unless the parent standard expires sooner in which case use the earliest expiration date. See laboratory SOP BR-QA-002 *Standard Preparation* for further guidance.

INTERMEDIATE STANDARDS

TCX/DCB Surrogate Stock (5/10 mg/L)

Parent Standard	Vendor	Component	Stock Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
TCX Solution	Ultra #IST-440	TCX	2000	0.10	40	5.0
DCB solution	Ultra #PPS-150	DCB	1000	0.40	40	10

Intermediate Calibration Standards (10 mg/L)

Parent Standard	Vendor	Component	Stock Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
AR 1660 (1016/1260)[1]	Restek #32039	Aroclor 1660	1000	0.20	20	10
AR1254	Restek #32011	Aroclor 1254	1000	0.20	20	10
AR1248	Restek #32010	Aroclor 1248	1000	0.20	20	10
AR1242	Restek #32009	Aroclor 1242	1000	0.20	20	10
AR1232	Restek #32008	Aroclor 1232	1000	0.20	20	10
AR1221	Restek #32007	Aroclor 1221	1000	0.20	20	10
AR1262	Restek #32409	Aroclor 1262	1000	0.20	20	10
AR1268	Restek # 32410	Aroclor 1268	1000	0.20	20	10

[1] *Standard is a mix of 1016/1260. Concentration shown is the concentration of each Aroclor in the mixed standard.*

CALIBRATION STANDARDS

Instrument Blank Surrogate Spike Solution

Parent Standard	Vendor	Component	Stock Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
TCX/DCB Stock	Laboratory Prepared	TCX	5.0	0.8	200	20
		DCB	10			40

Aroclor 1221 CS5 Working Standard Solution (1.6 mg/L)

Parent Standard	Vendor	Component	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
AR1221	Restek #32007	Aroclor 1221	10	16	100	1.6
TCX/DCB Stock	Laboratory Prepared	TCX	5.0	1.6		0.08
		DCB	10			0.16

Aroclor 1221 CS4-CS1 Working Standard Solutions

Parent Standard	Calibration Standard	Parent Standard Concentration (ug/L)	Volume Added (mL)	Final Volume (mL)	Final Aroclor Concentration (ug/L)
AR1221 CS5	AR1221 CS4	1600	20	40	800
AR1221 CS5	AR1221 CS3	1600	10	40	400
AR1221 CS5	AR1221 CS2	1600	5.0	40	200
AR1221 CS5	AR1221 CS1	1600	2.5	40	100

Aroclor 1232 CS5 Working Standard Solution (1.6 mg/L)

Parent Standard	Vendor	Component	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
AR1232	Restek #32008	Aroclor 1232	10	16	100	1.6
TCX/DCB Stock	Laboratory Prepared	TCX	5.0	1.6		0.08
		DCB	10			0.16

Aroclor 1232 CS4-CS1 Working Standard Solutions

Parent Standard	Calibration Standard	Parent Standard Concentration (ug/L)	Volume Added (mL)	Final Volume (mL)	Final Aroclor Concentration (ug/L)
AR1232 CS5	AR1232 CS4	1600	20	40	800
AR1232 CS5	AR1232 CS3	1600	10	40	400
AR1232 CS5	AR1232 CS2	1600	5.0	40	200
AR1232 CS5	AR1232 CS1	1600	2.5	40	100

Aroclor 1242 CS5 Working Standard Solution (1.6 mg/L)

Parent Standard	Vendor	Component	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
AR1242	Restek #32009	Aroclor 1242	10	16	100	1.6
TCX/DCB Stock	Laboratory Prepared	TCX	5.0	1.6		0.08
		DCB	10			0.16

Aroclor 1242 CS4-CS1 Working Standard Solutions

Parent Standard	Calibration Standard	Parent Standard Concentration (ug/L)	Volume Added (mL)	Final Volume (mL)	Final Aroclor Concentration (ug/L)
AR1242 CS5	AR1242 CS4	1600	20	40	800
AR1242 CS5	AR1242 CS3	1600	10	40	400
AR1242 CS5	AR1242 CS2	1600	5.0	40	200
AR1242 CS5	AR1242 CS1	1600	2.5	40	100

Aroclor 1248 CS5 Working Standard Solution (1.6 mg/L)

Parent Standard	Vendor	Component	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
AR1248	Restek #32010	Aroclor 1248	10	16	100	1.6
TCX/DCB Stock	Laboratory Prepared	TCX	5.0	1.6		0.08
		DCB	10			0.16

Aroclor 1248 CS4-CS1 Working Standard Solutions

Parent Standard	Calibration Standard	Parent Standard Concentration (ug/L)	Volume Added (mL)	Final Volume (mL)	Final Aroclor Concentration (ug/L)
AR1248 CS5	AR1248 CS4	1600	20	40	800
AR1248 CS5	AR1248 CS3	1600	10	40	400
AR1248 CS5	AR1248 CS2	1600	5.0	40	200
AR1248 CS5	AR1248 CS1	1600	2.5	40	100

Aroclor 1254 CS5 Working Standard Solution (1.6 mg/L)

Parent Standard	Vendor	Component	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
AR1254	Restek #32011	Aroclor 1254	10	16	100	1.6
TCX/DCB Stock	Laboratory Prepared	TCX	5.0	1.6		0.08
		DCB	10			0.16

Aroclor 1254 CS4-CS1 Working Standard Solutions

Parent Standard	Calibration Standard	Parent Standard Concentration (ug/L)	Volume Added (mL)	Final Volume (mL)	Final Aroclor Concentration (ug/L)
AR1254 CS5	AR1254 CS4	1600	20	40	800
AR1254 CS5	AR1254 CS3	1600	10	40	400
AR1254 CS5	AR1254 CS2	1600	5.0	40	200
AR1254 CS5	AR1254 CS1	1600	2.5	40	100

Aroclor 1262 CS5 Working Standard Solution (1.6 mg/L)

Parent Standard	Vendor	Component	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
AR1262	Restek #32409	Aroclor 1262	10	16	100	1.6
TCX/DCB Stock	Laboratory Prepared	TCX	5.0	1.6		0.08
		DCB	10			0.16

Aroclor 1262 CS4-CS1 Working Standard Solutions

Parent Standard	Calibration Standard	Parent Standard Concentration (ug/L)	Volume Added (mL)	Final Volume (mL)	Final Aroclor Concentration (ug/L)
AR1262 CS5	AR1262 CS4	1600	20	40	800
AR1262 CS5	AR1262 CS3	1600	10	40	400
AR1262 CS5	AR1262 CS2	1600	5.0	40	200
AR1262 CS5	AR1262 CS1	1600	2.5	40	100

Aroclor 1268 CS5 Working Standard Solution (1.6 mg/L)

Parent Standard	Vendor	Component	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
AR1268	Restek #32410	Aroclor 1268	10	16	100	1.6
TCX/DCB Stock	Laboratory Prepared	TCX	5.0	1.6		0.08
		DCB	10			0.16

Aroclor 1268 CS4-CS1 Working Standard Solutions

Parent Standard	Calibration Standard	Parent Standard Concentration (ug/L)	Volume Added (mL)	Final Volume (mL)	Final Aroclor Concentration (ug/L)
AR1268CS5	AR1268CS4	1600	20	40	800
AR1268CS5	AR1268CS3	1600	10	40	400
AR1268CS5	AR1268CS2	1600	5.0	40	200
AR1268CS5	AR1268CS1	1600	2.5	40	100

Aroclor 1660 CS5 Working Standard Solution (1.6 mg/L)

Parent Standard	Vendor	Component	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
AR1660	Restek #32410	Aroclor 1660	10	16	100	1.6
TCX/DCB Stock	Laboratory Prepared	TCX	5.0	1.6		0.08
		DCB	10			0.16

Aroclor 1660 CS4-CS1 Working Standard Solutions

Parent Standard	Calibration Standard	Parent Standard Concentration (ug/L)	Volume Added (mL)	Final Volume (mL)	Final Aroclor Concentration (ug/L)
AR1660CS5	AR1660CS4	1600	20	40	800
AR1660CS5	AR1660CS3	1600	10	40	400
AR1660CS5	AR1660CS2	1600	5.0	40	200
AR1660CS5	AR1660CS1	1600	2.5	40	100

Final Concentration of Prepared Calibration Standards in Extract

Analyte	CS1 (ng/mL)	CS2 (ng/mL)	CS3 (ng/mL)	CS4 (ng/mL)	CS5 (ng/mL)
TCX (Surrogate)	5	10	20	40	80
DCB (Surrogate)	10	20	40	80	160
Aroclor 1660	100	200	400	800	1600
Aroclor 1221	100	200	400	800	1600
Aroclor 1232	100	200	400	800	1600
Aroclor 1242	100	200	400	800	1600
Aroclor 1248	100	200	400	800	1600
Aroclor 1254	100	200	400	800	1600
Aroclor 1262	100	200	400	800	1600
Aroclor 1268	100	200	400	800	1600

APPENDIX C: EQUATIONS

These equations were taken from reference method SOM01.0 and from SW-846 8000B, Test Methods for Evaluation of Solid Waste Revision 2, December 1996. USEPA.

Absolute Retention Times

$$\overline{RT} = \frac{\sum_{i=1}^{n} RT_i}{n}$$

Where:
$\overline{RT}$ = Mean Absolute Retention Time of analyte
RT_i = Absolute Retention Time of analyte
n = Number of measurements

Calibration Factor (CF_i)

$$CF = \frac{\text{Peak Area (or Height) of the Compound in the Standard}}{\text{Mass Injected (ng)}}$$

Mean Calibration Factor ($\overline{CF}$)

$$\overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

Where:
CF_i = Calibration Factor
n = Number of Calibration Standards

Standard Deviation of the Calibration Factor (SD)

$$SD = \sqrt{\frac{\sum_{i=1}^{n} \left(CF_i - \overline{CF}\right)^2}{n-1}}$$

Where:
CF_i = Calibration Factor
$\overline{CF}$ = Mean Calibration Factor
n = Number of calibration levels

Percent Relative Standard Deviation (RSD) of the Mean Calibration Factor

$$\%RSD = \frac{SD}{\overline{CF}} \otimes 100$$

Where:
SD = Standard Deviation of Calibration Factors
$\overline{CF}$ = Mean Calibration Factor

Percent Difference (%D)

Percent Difference (%D): Used for Calibration Verification Standards

$$\%D = \frac{CF_v - \overline{CF}}{\overline{CF}} \otimes 100$$

Where:
CF_v = Calibration Factor from the Continuing Calibration Verification (CCV)

Percent Difference (%D): Used for PEM standards

$$\%D = \frac{C_{calc} - C_{nom}}{C_{nom}} \otimes 100$$

Where:
C_{calc} = Calculated concentration
C_{nom} = Nominal concentration

Percent Difference (%D): Used for Form X

$$\%D = \frac{Conc_H - Conc_L}{Conc_L} \otimes 100$$

Where:
$Conc_H$ = Higher of the two concentrations
$Conc_L$ = Lower of the two concentrations

Percent Recovery (%R)

$$\%R = \frac{C_s}{C_n} \otimes 100$$

Where:
C_s = Concentration of the Spiked Field or QC Sample
C_n = Nominal Concentration of Spike Added

Percent Recovery (%R) for MS/MSD

$$\%R = \frac{C_s - C_u}{C_n} \otimes 100$$

Where:
C_s = Concentration of the Spiked Sample
C_u = Concentration of the Unspiked Sample
C_n = Nominal Concentration of Spike Added

Relative Percent Difference (RPD)

$$RPD = \frac{|MSR - MSDR|}{1/2(MSR + MSDR)} \otimes 100$$

Where:

MSR = Matrix Spike Recovery
MSDR = Matrix Spike Duplicate Recovery

Sample Concentration

Water

$$Concentration_{sample}(ug/L) = \left(\frac{A_x}{\overline{CF}}\right)\left(\frac{DF}{V_i}\right)\left(\frac{V_t}{V_o}\right)\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_1\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_2 K\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_n$$

Where:
A_x = Peak area or peak height of the compound to be measured
$\overline{CF}$ = Mean Calibration Factor determined from the initial calibration for the compound to be measured, in height/ng
DF = Dilution Factor
V_i = Volume of extract injected in uL
V_t = Volume of extract produced by the preparation process (extraction and concentration), and before cleanup, in uL
V_o = Volume of the original water sample extracted in mL. Note: for instrument and sulfur blanks assume a volume of 1000mL
CV_{out} = Volume of extract produced by a cleanup process (cleanup and concentration), in uL
CV_{in} = Volume of extract subjected to a cleanup process, in uL
E = The efficiency of the cleanup process expressed as a fraction of material that passes through or is not mechanically lost during the cleanup step (e.g. 50% efficiency must be expressed as 0.50)

Soil/Sediment

$$\text{Concentration}_{\text{sample}}\ (\text{ug/kg}) = \left(\frac{A_x}{\overline{CF}}\right)\left(\frac{DF}{V_i}\right)\left(\frac{V_t}{W_t \otimes D}\right)\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_1\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_2 K\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_n$$

Where:
A_x = Peak area or peak height of the compound to be measured
$\overline{CF}$ = Mean Calibration Factor determined from the initial calibration for the compound to be measured, in height/ng
DF = Dilution Factor
V_i = Volume of extract injected in uL
V_t = Volume of extract produced by the preparation process (extraction and concentration), and before cleanup, in uL
W_t = Weight of the original soil sample extracted in g.
CV_{out} = Volume of extract produced by a cleanup process (cleanup and concentration), in uL
CV_{in} = Volume of extract subjected to a cleanup process, in uL
E = The efficiency of the cleanup process expressed as a fraction of material that passes through or is not mechanically lost during the cleanup step (e.g. 50% efficiency must be expressed as 0.50)

$$D = \frac{100 - \%\text{Moisture}}{100}$$

Water Adjusted CRQL

$$\text{Adjusted CRQL} = (\text{Contract CRQL})\left(\frac{V_x}{V_o}\right)\left(\frac{V_t}{V_y}\right)(DF)\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_1\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_2 K\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_n$$

Where:
Contract CRQL = The CRQL value reported in Exhibit C – PCBs (ug/L)
V_x = Contract sample volume (1000 mL)
V_o = Volume of the original water sample extracted in mL. Note: for instrument and sulfur blanks assume a volume of 1000mL
V_t = Volume of concentrated extract, in uL
V_y = Contract concentrated extract volume (10,000 uL)
DF = Dilution Factor
CV_{out} = Volume of extract produced by a cleanup process (cleanup and concentration), in uL
CV_{in} = Volume of extract subjected to a cleanup process, in uL
E = The efficiency of the cleanup process expressed as a fraction of material that passes through or is not mechanically lost during the cleanup step (e.g. 50% efficiency must be expressed as 0.50)

Soil/Sediment Adjusted CRQL

$$\text{Adjusted CRQL} = (\text{Contract CRQL})\left(\frac{V_x}{V_s \otimes D}\right)\left(\frac{V_t}{V_y}\right)(DF)\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_1\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_2 K\left(\frac{CV_{out}}{CV_{in} \otimes E}\right)_n$$

Where:
Contract CRQL = The CRQL value reported in Exhibit C – PCBs (ug/Kg)
W_x = Contract sample weight (30 g)
W_s = Weight of sample extracted in grams (g)
$D = \frac{100 - \%\text{Moisture}}{100}$
V_t = Volume of concentrated extract, in uL
V_y = Contract concentrated extract volume (10,000 uL)
DF = Dilution Factor
CV_{out} = Volume of extract produced by a cleanup process (cleanup and concentration), in uL
CV_{in} = Volume of extract subjected to a cleanup process, in uL
E = The efficiency of the cleanup process expressed as a fraction of material that passes through or is not mechanically lost during the cleanup step (e.g. 50% efficiency must be expressed as 0.50)

Title: Sample Preparation and Cleanup Procedures for SVOCs (CLP SOW SOM01.2)

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1.0 Scope and Application

This SOP describes the laboratory procedures used for the extraction of water and soil/sediment samples and the procedures used for extract cleanup in preparation for analysis by Gas Chromatograph / Mass Spectrometry (GC/MS) to determine the presence and concentration of semivolatile organic compounds (SVOCs)

This SOP is applicable to hazardous waste samples for use in the EPA Contract Laboratory Program (CLP). The procedure may be used for other matrices or sample sites if the procedure meets the established data quality and performance objectives for the project.

1.1 Analytes, Matrix(s), and Reporting Limits

This procedure may be used for the following matrices: non-potable water and soil/sediment.

The analyte list and reporting limits are provided in laboratory SOPs for instrument analysis.

2.0 Summary of Method

Water Samples

1 L of sample is spiked with surrogate solution, acidified to pH 2.0, and extracted with methylene chloride using a continuous liquid-liquid extractor (CLLE). The extract is dried with anhydrous sodium sulfate, concentrated, and if necessary subjected to cleanup by Gel Permeation Chromatography (GPC). GPC cleanup is optional and may be performed when the presence of higher molecular weight compounds in the sample interfere with the analyses of target compounds. The final volume of the extract is 1 mL or if GPC was performed, the post-cleanup extract volume is 0.5 mL.

Solid/Sediment Samples

The extraction procedure for soils/sediment depends on the concentration of target analytes in sample. The medium-level extraction procedure is used when the results from screen analysis indicate that a dilution greater than 10 times the low soil CRQL would be necessary.

Low-Level Soil: 30 g of sample is mixed with anhydrous sodium sulfate, spiked with a solution of deuterated monitoring compounds (DMCs) and extracted with a 1:1 v/v acetone/methylene chloride solvent using ultrasonic extraction. The extract is concentrated to 10 mL then screened by the GC/MS analysis. If the on-column results of the screen analysis are less than 450 ng, GPC cleanup is performed and the post cleanup extract is concentrated to a final volume of 0.5 mL. If the on-column results of the screen analysis are greater than 450 ng the samples are re-extracted using the medium-level extraction procedure.

Medium-Level Soil: 1 g of sample is mixed with anhydrous sodium sulfate, spiked with a solution of deuterated monitoring compounds (DMCs) and extracted with methylene chloride solvent using ultrasonic extraction. GPC cleanup is performed and the post cleanup extract is concentrated to a final volume of 0.5 mL.

This SOP is based on the following reference method:

- SOM1.2 Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration, USEPA Contract Laboratory Program. June 2007.

NOTE: SOM01.2 is defined by the EPA as SOM1.1 SOW combined with the "Modifications Updating SOM01.1 to SOM01.2".

If the laboratory's procedure is modified from the reference method, a list of modifications will be provided in Section 16.0

3.0 Definitions

A list of terms and definitions are provided in Appendix A.

4.0 Interferences

- Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing equipment may cause discrete artifacts and elevated baselines in the Extracted Ion Current Profiles (EICPs). These materials are demonstrated to be free of interferences by the analysis of method blanks. To avoid this type of interference, minimize the use of plastics in the laboratory.

- Temperature stability is important to the GPC cleanup process, variations in temperature may cause retention times to shift and affect the basis of the preset "Dump" and "Collect" times. To prevent this, the GPC laboratory is to be maintained in a temperature range between 19 and 22°C.

- Non-target compounds co-extracted from the sample matrix can also cause interference, the extent of which will vary considerably depending on the nature of the samples. The extent of the interference will vary by matrix and are minimized using the various cleanup procedures described in this SOP.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

None

5.2 Primary Materials Used

Table 1 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the SDS. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section.

Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

6.0 Equipment and Supplies

Catalog numbers listed in this SOP are subject to change at the discretion of the vendor. Analysts are cautioned to be sure equipment used meets the specification of this SOP.

6.1 Continuous Liquid-Liquid Extraction

- Continuous Liquid-Liquid Extractor equipped with Teflon or glass connecting joints and stopcocks that do not require lubrication. (AMK LLL-1130 or equivalent).
- Evaporation flask. 500 mL (Kontes 570037-0500 or equivalent).
- Drying Adapter. (AMK LLL-1137 or equivalent)
- Jacketed Concentrator Tube. (AMK LLL-1136 or equivalent)
- Allihn Condenser. (AMK EX-03A or equivalent)
- Hot Water Bath with Circulation Pump, capable of temperature control ±5℃ (VWR Scientific Model# 1131 or equivalent)
- Class A Graduated Cylinder: 1 L capacity. Fisher Scientific
- Fiberglass Wool: 8 um, Fisher Scientific.
- pH Indicator Paper: Whatman.
- pH meter- Denver Instruments

6.2 Ultrasonic Extraction

- Ultrasonic disrupter, Vibra Cell 750-watt Model Dual Output with pulsing capability, 3/4" standard disrupter horn for low level extractions or a 1/8” disruptor horn for medium level extractions. Sonics and Materials Model Number VC750 or equivalent.
- 400 mL glass beaker. Fisher Scientific
- Sonication box. Sonics and Materials
- Glass Funnels - 100mm. Fisher Scientific.
- Filter paper- No. 54 Whatman 18.5cm, or equivalent
- pH meter- Denver Instruments

6.3 Extract Concentration (KD Apparatus)

- Concentrator tube, 10 mL graduated. ChemGlass Catalog Number CG-1316-11 or equivalent
- Snyder Column, Three ball macro AMK Catalog Number SC2-01 or equivalent
- Snyder Column, Two ball micro AMK Catalog Number SC3-01 or equivalent
- Evaporation Flask, 500 mL attached to concentrator tube with clip. AMK Catalog Number KDF-500 or equivalent
- Boiling Chips, silicon carbide, approximately 10/40 mesh, solvent extracted in methylene chloride. Troemner Catalog Number 133B or equivalent.
- Heating mantle rheostat controlled for water bath capable of temperature control (± 5℃). ChemGlass Catalog Number PL3122 or equivalent.
- Glass Water Bath, AMK Glass
- Solvent Vapor Recovery System, Kontes K-54000-1006, K-547300-000, Ace Glass Catalog Number 6614-30 or equivalent.

6.4 Miscellaneous

- Disposable glass Pasteur pipette and bulb. Fisher Scientific
- Top Loading balance: Capable of measuring to 0.01 gram accuracy. Mettler Model Number PM4800 or equivalent.
- Teflon and Stainless Steel Spatulas. Fisher Scientific
- Adjustable Pipette. Finnpipette or equivalent
- 0.5 mL – 10.0 mL Hamilton Gastight® syringes or equivalent.
- Class "A" Volumetric Flasks: 10 mL to 1000 mL, Fisher Scientific.
- Glass Scintillation Vials: 2, 4, 8, and 16 mL with Teflon lined septa and screw caps, Fisher Scientific.
- Centrifuge: Thermo.
- 50 mL Centrifuge Tubes: Fisher Scientific.
- Vortex mixer- Thermo
- Autovial Filter: Whatman.
- Aluminum Weigh Pans. Fisher Scientific

6.5 Gel Permeation Chromatography

- GPC System: J2 Scientific.
- Chromatographic Column: AMK Glass
- Bio Beads: J2 Scientific
- UV Detector: J2 Scientific.

7.0 <u>Reagents and Standards</u>

7.1 Reagents

- Sodium Sulfate (granular, anhydrous), Na_2SO_4. J.T. Baker or equivalent. Purify by heating at 400°C for at least 4 hours.
- Methylene Chloride (CH_2CL_2), Pesticide quality, J.T Baker or equivalent.
- Acetone, ($(CH_3)_2CO$), Pesticide quality. J.T. Baker or equivalent.
- Reagent Water- RO water filtered through a Nanopure System
- Sulfuric Acid, (H_2SO_4), J.T. Baker-Reagent grade.

7.2 Prepared Reagents

- <u>Methylene Chloride/Acetone (1:1)</u>: Mix 2 L methylene chloride with 2 L acetone in a 4 L amber bottle. Store the solution in a fume hood.

- <u>Sulfuric Acid Solution (1:1 v/v)</u>: Add 450 mL of reagent water to a 1 L amber glass bottle then slowly add 450 mL of concentrated sulfuric acid to the bottle.

7.3 Standards

Purchase stock standard solutions from commercial vendors. From these, prepare surrogate and spiking solutions by diluting known volumes of the stock standard solutions in an appropriate solvent using the formulations provided in Appendix B. Record the preparation of the standard in the LIMS. Unless otherwise specified in Appendix B, store the prepared solutions in glass

containers at a temperature of 4℃ (±2) and assign an expiration date of 6 months from date of preparation unless the parent standard expires sooner in which case use the earliest expiration date.

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection so these procedures are not included in this SOP. Listed below are the recommended minimum sample size needed for analysis and the requirements for preservation and holding times.

Matrix	Sample Container	Minimum Sample Size	Preservation	Holding Time[1]	Reference
Water	Glass	1 L	4℃ (±2℃)	5 Days VTSR	CLP SOW
Solid	Glass	80 g	4℃ (±2℃)	5 Days VTSR	CLP SOW

[1]Extraction holding time is determined from the date sample were received by the laboratory.

The laboratory routinely retains unused sample volumes in the laboratory for 30 days from date of data submission. For EPA CLP contract work, unused sample volume, partially used sample volume, used sample containers and empty sample containers are retained for 60 days after the date of data submission.

9.0 Quality Control

9.1 Sample QC

The laboratory prepares the following quality control samples with each batch of samples.

QC Item	Frequency	Acceptance Criteria
Method Blank (MB)	1 in 20 or fewer samples	See Analytical SOP
Matrix Spike(s) MS/MSD	Assigned by client per SDG	See Analytical SOP
Sample Duplicate (SD)	Client Request	See Analytical SOP

10.0 Procedure

10.1 Instrument Calibration and Equipment Preparation

Check and record the calibration of the pH meter and the balance each day of use, prior to use and record these checks in the logbooks established for this purpose.

Inspect the tip of the sonicator horn for excessive wear. If the sonicator is not self-tuning, check and record the tuning of the sonicator horn as follows:

1. Attach the converter to the bottom connector.

2. Set the pulsar switch to the off position, the output control to 10 (full power) and the % duty cycle to 50 (energy on 50% of time and off 50% of time).

3. Briefly depress the tune switch and rotate the tuning control clockwise or counterclockwise until a minimum reading of less than 20% is achieved on the power meter.

4. Re-attach the upper converter if using both converters and record the tune calibration in the logbook designated for this purpose.

Wash each piece of glassware and sample preparation equipment using the procedures described in laboratory SOP BR-EX-017. Label the equipment to clearly and unambiguously identify the sample ID during each step of the extraction procedure. Solvent will erase “sharpie” labeling, so caution must be taken to ensure markings are not obliterated during the procedure.

For each water sample: Add a plug of Pyrex glass wool to a drying adapter. Add a sufficient amount of purified sodium sulfate to each adapter such that the funnel is approximately ¾ full. Rinse the adapter with ~30 mL of acetone and ~30 mL of methylene chloride and discard the rinsate. Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL jacketed concentrator tube to a 500 mL evaporation flask. Add 1-2 boiling stones to K-D flask and then place under the adapter. Add 200 mL of methylene chloride to each CLLE.

For each solid sample: Add a Whatman No. 54 filter to a 100 mm glass funnel then add a sufficient amount of purified sodium sulfate to each funnel to fill the funnel ~ ¾ full. Rinse the funnel with ~30 mL of acetone and ~30 mL of methylene chloride and discard the rinsate. Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporation flask. Add 1-2 boiling stones to K-D flask and place the setup under a drying funnel.

10.2 Water Sample Preparation

Let each sample warm to ambient temperature.

Measure and record the pH of each sample with a pH meter. Adjust the sample pH to 2.0 with 1:1 sulfuric acid as needed.

Mark the meniscus of each sample on the sample container. Transfer the sample into a prepared CLLE. If an MS/MSD is requested, prepare 1 MS/MSD pair each for full scan and SIM analysis.

To prepare the method blank (MB) transfer 1 L of reagent water to a labeled CLLE.

Add an appropriate volume of surrogate and spike solution to field and QC samples. Refer to the Extraction Conditions Workbook or project notes to determine the type and volumes of surrogate and spiking solutions to add to each sample. Use the following specification for routine EPA CLP SOW work:

- Add 0.5 mL each of DMC surrogate and SIM DMC surrogate solution to each field and QC sample. Add 0.5 mL each of matrix spike solution to the full scan MS/MSD and add 0.5 mL of SIM matrix spike solution to the SIM MS/MSD. This spiking scheme results in the addition of 40 ug and 0.4 ug (SIM) of DMC to each sample.

- If the reporting sub list includes 1, 4 Dioxane add 0.5 mL of the 1,4-Dioxane surrogate solution to each field and QC sample.

Rinse each sample container with 60 mL of methylene chloride and transfer the rinsate into the corresponding CLLE to ensure complete transfer of sample.

Add a sufficient amount of methylene chloride to the extractor to ensure proper solvent cycling during the extraction. Attach the assembled drying flask and KD apparatus to the CLLE. Attach the hot water hose to the threaded jacket of the concentrator tube, set the temperature of the heater to 90-95℃ and turn the water heaters "on". Attach the cooling condenser to the CLLE and open the stopcock allowing the methylene chloride to siphon through the drying flask into the KD apparatus and concentrator tube.

After a few minutes check each CLLE to ensure the methylene chloride in the concentrator tube flask is bubbling and to ensure that there is continuous condensation of methylene chloride passing through the sample into the KD apparatus. Extract for 18 hours.

Measure and record the sample volume for each field sample by filling each sample container to the meniscus line with water then measure the volume using a Class A graduated cylinder. If the sample volume is less than 900 mL or if the sample has multiple phases notify the PM and wait for further instruction.

After the 18 hour time-frame is finished, close the stopcock and concentrate the extract to 1 mL using the techniques described in section 10.4. If GPC is needed, concentrate the extract to 10 mL, filter the sample and proceed to section 10.5.

10.3 Soil Sample Preparation

Mix each sample thoroughly with a spatula and discard any foreign objects such as sticks, leaves, and rocks. If freestanding water remains after mixing, decant the water.

pH Determination:

Add a magnetic stir bar to a clean 400 mL glass beaker. Place the beaker on the balance and tare the balance. Measure ~ 50 g of sample into the beaker and record or upload the sample weight into the worksheet. Add 50 mL of reagent water to the beaker and place the beaker on a stir plate to mix for 1 hour.

NOTE: If a limited sample mass was received, use a smaller 1:1 ratio of sample to reagent water and record the modification with a nonconformance memo (NCM).

Measure the pH with a pH meter and record the sample pH in the worksheet. If the pH of the sample is greater than 9 or less than 5, notify the Project Manager but do not adjust the pH of the sample.

Discard the portion of sample used for the pH determination.

Percent Moisture

The percent moisture of samples is determined by the wet chemistry department following the procedure given in laboratory SOP BR-WC-006.

Low Level Soil Extraction

Prepare a 400 mL glass beaker for each sample. Place the beaker on the top loading balance and tare the balance. Measure 30 g (± 1 gram) of sample into the beaker and upload the weight into the LIMS worksheet. Add a sufficient amount of purified anhydrous granulated sodium

sulfate to the sample to ensure a free-flowing mixture. If an MS/MSD is requested create 1 MS/MSD pair each for full scan and SIM analysis.

Add an appropriate volume of surrogate and spike solution to field and QC samples. Refer to the Extraction Conditions Workbook to determine the type and volumes of surrogate and spiking solutions to add to each sample. Use the following specification for routine EPA CLP SOW work:

- Add 0.5 mL each of DMC surrogate and SIM DMC surrogate solution to each field and QC sample. Add 0.5 mL each of matrix spike and SIM matrix spike solution to each MS/MSD. This spiking scheme results in the addition of 40 ug and 0.4 ug (SIM) of DMC to each sample.

NOTE: 1, 4 Dioxane is considered a poor performer in soils, if the reporting sub list for soils includes this analyte, contact the Organic or GC/MS Department Manager for further instructions.

After spiking, immediately add 100 mL of 1:1 acetone/methylene chloride solvent to each beaker.

Clean the tip of the sonicator horn using a Kimwipe wetted with acetone. Set the control to 10 (full power) and with the mode switch on “Pulse” (pulsing energy rather than continuous energy) and the percent duty cycle switch set to 50% (energy on 50% of time and off 50% of time).

Place a beaker in the sonicator box and place the bottom surface of the tip of the sonicator horn ~1/2 inch below the solvent, but above the sample.

Sonicate the sample for 3 minutes then decant the extract through the drying funnel. Repeat the extraction / decant two more times with fresh 100 mL portions of extraction solvent. Stir each sample with a clean spatula before each extraction to break up any large clumps and to ensure that the sample is free flowing.

After the third extraction, transfer the entire sample into the drying funnel then rinse the beaker with ~30 mL of extraction solvent, transferring the rinsate to the drying funnel. Let the solvent completely drain through the drying funnel into the K-D apparatus. Remove the drying funnel and discard the contents into the solid waste stream.

Concentrate the extract to 2-3 mL using the extraction techniques described in section 10.4. Filter the extract through a 0.45 um filter, collecting the filtrate in a 16 mL amber vial. Adjust the extract final volume to 10 mL. Transfer 100 uL of extract to an autosampler vial and give the vial to the GC/MS department for screen analysis. If the results of screen indicate medium level extraction is needed, proceed to the next section. Otherwise proceed to Section 10.5 for GPC cleanup.

Medium-Level Soil Extraction

Obtain a 40 mL vial for each sample that requires medium level extraction. Place the vial on the top loading balance and tare the balance. Measure 1 g of sample to the vial and upload the weight measurement into the LIMS worksheet. Add a sufficient amount of anhydrous granular sodium sulfate to the sample and mix. Use 1 g of sodium sulfate for the method blank.

Add an appropriate volume of surrogate and spike solution to field and QC samples. Refer to the Extraction Conditions Workbook to determine the type and volumes of surrogate and spiking solutions to add to each sample. Use the following specification for routine EPA CLP SOW work:

- Add 0.5 mL each of DMC surrogate to each field and QC sample. Add 0.5 mL each of matrix spike to each MS/MSD. This spiking scheme results in the addition of 40 ug and 0.4 ug of DMC to each sample.

After spiking, immediately add 8 mL of methylene chloride to each field sample, MB and any MS/MSD.

Insert a micro-tip ultrasonic probe on the sonicator and set the output control setting to 5 with continuous mode. Extract each sample for two minutes.

Filter each sample through a 0.45um filter collecting the filtrate in a 16 mL vial. Rinse the filter with 1 mL of methylene chloride combining the rinsate with the filtered extract. Adjust the extract volume to 10 mL and proceed to section 10.5.2 for GPC cleanup.

10.4 Extract Concentration Techniques

Macro Snyder Column (K-D)

Add one or two clean boiling chips to the K-D evaporation flask and attach a three-ball Snyder column to the flask. Add ~1 mL of methylene chloride to the top of the column then place the K-D apparatus in a hot water bath (60-70℃) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in hot water vapor.

Attach the solvent vapor recovery glassware to the Snyder column. Adjust the vertical position of the apparatus and check the water bath temperature. The water bath temperature should be between 54.8 – 74.8℃ when methylene chloride is the extraction solvent and 84-89℃ when hexane is the extraction solvent. Higher water bath temperatures may be used so long as the recovery of target analytes is not impacted. The boiling point of each solvent is provided in the following table:

Solvent	Boiling Point	Water Bath Temperature
Hexane	69℃	84 – 89℃
Methylene Chloride	39.8℃	54.8 – 74.8℃

Monitor the concentration and do not let the extract evaporate to dryness. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with solvent.

When the apparent volume of the extract reaches desired amount remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

Micro Snyder Column (K-D)

Add one or two clean boiling chips to the concentrator tube and attach a two ball micro-Snyder column to the tube. Place the concentrator tube into the water bath so that the concentrator tube is partially immersed in hot water. Adjust the vertical position of the concentrator tube and check the temperature of the water bath to ensure the proper temperature for the extract solvent.

Continuously monitor the distillation process to ensure sample extracts do not evaporate to dryness. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with solvent. Remove setup when desired sample volume is reached.

Nitrogen Blowdown

Nitrogen blow down may be used to concentrate extracts as needed.

Place the concentrator tube in a warm water bath maintained at a temperature of 35℃. Apply a steady stream of nitrogen until the desired final extract volume is achieved. Rinse the internal wall of the concentrator tube several times with the appropriate solvent during the evaporation and ensure the solvent level in the concentrator is positioned such to prevent water condensations. Monitor the concentration carefully and do not allow the extract to evaporate to dryness.

10.5 GPC Cleanup

10.5.1 GPC Calibration

Calibrate the GPC system prior to initial use, when the calibration fails to meet acceptance criteria, when the column is changed, when channeling occurs, once every 7 days or when the shift in retention time (RT) is greater than 5% when compared to the RTs in the last calibration UV traces.

Prepare the GPC column following the instructions provided in Appendix B.

Establish the flow rate by pumping methylene chloride through the GPC column for 5 minutes and collecting the eluate in a 25 mL volumetric flask and calculate the flow rate. The flow rate should be between 4.9 and 5.1 mL/minute.

Check the system pressure, the pressure should be less than 30 psi.

Load 10 mL of the stock standard GPC calibration solution onto the GPC system and determine the elution times for phthalate, methoxychlor, and perylene and set the dump and collect cycles on the GPC system.

- Determine a “DUMP” time that will remove > 85% of phthalate. Determine a “COLLECT” time so that > 95% of the methoxychlor is collected. Continue the collect time until just before the elution time of sulfur. Add 2 minutes to the collect time to account for sample volume between the UV detector and the collection vessel. Use a “WASH” time of 15 minutes beginning after the elution of perylene.

After setting the dump and collect times, inject 10 mL of GPC calibration solution onto the system collect the elutriate over the course of 10 minutes into a volumetric flask. Measure and record the volume of eluate collected and calculate the flow rate. The flow rate should be between 4.9 and 5.1 mL per minute. If it is not, adjust the pump speed and repeat the calibration procedure.

The UV trace of the GPC calibration must meet the following criteria:

- Peaks must be observed and the peaks should be symmetrical for each compound in the calibration solution.

- The peaks for corn oil and phthalate should exhibit greater than 85% resolution.
- The peaks for phthalate and methoxychlor should exhibit greater than 85% resolution.
- The peaks for methoxychlor and perylene should exhibit greater than 85% resolution.
- The peaks for perylene and sulfur must not be saturated and should exhibit greater than 90% resolution.
- The solvent flow rate should be between 4.9 and 5.1 mL/min.
- The column pressure should not exceed 30 psi.
- The retention times (RTs) for bis (2-ethylhexyl) phthalate and perylene must not vary more than ±5% between the first and second injections.

If these criteria are not met, identify and correct the problem. Corrective action typically requires preparation of a new GPC column.

After criteria are met, run a GPC blank consisting of 10 mL of methylene chloride through the system to verify it is clean. Concentrate the GPC blank to ~3-5 mL using macro snyder column technique. Exchange the blank into hexane and concentrate the blank to a final volume of 5 mL. Give the GPC blank to GC for analysis by GC/ECD. There should be no target analytes present in the GPC blank above the CRQL. If contamination is found, pump methylene chloride through the GPC system for 1-2 hours then analyze another GPC blank. Repeat this procedure until the GPC system is proven clean.

10.5.2 Sample Cleanup by GPC

Extracts with viscosity greater than 1:1 v/v glycerol / water must be diluted prior to GPC cleanup and soil extracts with more than 40 mg/mL of non-volatile residue must be diluted and processed through the GPC system as multiple fractions that are later recombined.

To determine the dissolved solids in soil extracts: Place an aluminum weigh pan on a calibrated top loading balance and tare the balance. Measure 100 uL of extract into the weigh pan and upload the measurement into the LIMS worksheet. Let the aliquot evaporate to dryness. Reweigh the pan, upload the weight measurement. Dissolved solids are calculated by the LIMS system. If the dissolved solids are greater than 40 mg/mL, split the sample for multiple GPC loops.

Prepare and label a collection vessel for each extract and place the collection vessels in the tray of the GPC system. Place the injection vessels in the autosampler and initiate the cleanup sequence. **NOTE: Place the MB at the end of the GPC sequence.** The GPC system loads 5 mL of each extract through the system using the collect and dump times previously established. After each sample loop, the GPC system rinses the loading port with methylene chloride to minimize cross-contamination.

When the GPC run is finished, concentrate the extract to ~3-5 mL using the macro snyder column technique. When apparent volume is reached, continue the concentration using micro snyder technique or nitrogen blow down to a post cleanup volume of 0.5 mL.

11.0 Calculations / Data Reduction

11.1 Calculations

The calculation for dissolved solids is performed by the laboratory's LIMS system or the EXCEL worksheet established for this purpose.

11.2 Data Review

Primary Review

Review project documents such as the Project Plan (PP), Project Memo or any other document/process used to communicate project requirements to ensure those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Enter the batch information into LIMS and complete the batch editor and worksheet for each extraction and cleanup batch performed. Initiate NCMs for any anomalies observed during the preparation process. Set the status of each batch to 1st level review.

Secondary Data Review

Review project documents such as the Project Plan (PP), Project Memo or any other document/process used to communicate project requirements and verify those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Check the batch editor and worksheet to verify the batch is complete and any outages are documented with an NCM along with the results of any corrective actions taken. Set the status of each batch to second level review.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

A Method Detection Limit (MDL) Study must be determined for each test method associated with this extraction procedure during initial method set-up or prior to the analysis of field samples. The MDLs are verified annually or after major instrument maintenance. The procedure for the determination of MDLs is described in laboratory SOP BR-QA-005.

12.2 Demonstration of Capabilities (DOC)

Each analyst must complete an Initial Demonstration of Capability prior to unsupervised performance of this method.

12.3 Training Requirements

Any employee that performs any portion of the procedure described in this SOP must have documentation in their employee training file that they have read this version of this SOP.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to BR-EH-001. The following waste streams are produced when this method is carried out.

- Organic Solvents - Satellite container: 55 gallon covered and vented drum.
- Extracted water samples - Satellite container: 55 gallon covered and vented drum.
- Vials containing extracts - Satellite container: 5 gallon covered bucket in fume hood.
- Methylene Chloride-Waste - Satellite Container: 55 Gallon Waste Drum
- Solid Waste-Satellite Container - Solid Waste 5 Gallon Plastic Bucket (inside fume hood)

15.0 References / Cross-References

- Exhibits B & D, USEPA CLP SOW for Organic Analysis, SOM01.1, May 2005.
- USEPA CLP SOW Clarifications to SOM01.1, November 7, 2005 and September 26, 2006.
- USEPA CLP SOW Modifications Updating SOM01.1 to SOM01.2, October 5, 2006 (Updated 02-12-2007) Amended 04-11-2006.

16.0 Method Modifications

Modification Number	Method Reference	Modification
1	10.3	SOW states to measure sample volume by pouring sample into a graduated Class A cylinder. Our lab practice is to mark the meniscus on the sample's bottle, decant the sample into extraction vessel, and fill the bottle back up with water to meniscus mark. After the bottle is filled to the mark it is transferred to a Class A Grad. cylinder to measure the sample volume.
2	10.3	When requested by client laboratory will spike the additional analyte 1, 4 Dioxane in addition to regular spiked analytes.

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17.0 Attachments

- Table 1: Primary Materials Used
- Appendix A: Terms and Definitions
- Appendix B: Standard Preparation Formulas

18.0 Revision History

BR-EX-015, Revision 2

- Title Page: Updated approval signatures and copyright date
- Updated MSDS to SDS.

BR-EX-015, Revision 1

- Title Page: Updated approval signatures.
- All Sections: Updated to reflect current practice; added instructions for exception analyte 1,4 Dioxane.
- Add language for LIMS
- Added Appendix B: Standard Preparation Formulas
- Added Appendix C: GPC Column Preparation.

Table 1: Primary Materials Used

Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Appendix A: Terms and Definitions

Acceptance Criteria: specified limits placed on characteristics of an item, process or service defined in requirement documents.

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 which are due to sampling and analytical operations; a data quality indicator.

Analyte: The specific chemicals or components for which a sample is analyzed. (EPA Risk Assessment Guide for Superfund, OSHA Glossary).

Batch: environmental samples that are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria. An analytical batch is composed of prepared environmental samples (extracts, digestates and concentrates), which are analyzed together as a group.

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 the standards.

Calibration Standard: A substance or reference used to calibrate an instrument.

Continuing Calibration Verification (CCV): a single or multi-parameter calibration standard used to verify the stability of the method over time. Usually from the same source as the calibration curve.

Corrective Action: the action taken to eliminate the cause of an existing nonconformity, defect or other undesirable occurrence in order to prevent recurrence.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

Intermediate Standard: a solution made from one or more stock standards at a concentration between the stock and working standard. Intermediate standards may be certified stock standard solutions purchased from a vendor and are also known as secondary standards.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Matrix Spike (MS): a field sample to which a known amount of target analyte(s) is added.

Matrix Spike Duplicate (MSD): a second replicate matrix spike

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Precision: the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Quality Control Sample (QC): a sample used to assess the performance of all or a portion of the measurement system.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample.

Stock Standard: a solution made with one or more neat standards usually with a high concentration. Also known as a primary standard. Stock standards may be certified solutions purchased from a vendor.

Surrogate: a substance with properties that mimic the analyte of interest but that are unlikely to be found in environmental samples.

Appendix B: Standard Preparation Formulas

Primary Source SOM DMC Surrogate

Stock Standard	Vendor	Component	Stock Standard Concentration (ug/mL)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/mL)
SOM DMC Acids	Absolute # 94448	2-Chlorophenol-d4	2000	5.0	125	80
		p-Cresol-d8				
		2,4-Dichlorophenol-d3				
		4,6-Dinitro-2-methylphenol-3,5-d2				
		2-Nitrophenol-d4				
		4-Nitrophenol-d4				
		Phenol-d6				
SOM DMC Base/Neutrals	Absolute # 94449	Acenaphthylene-d8	2000	5.0	125	80
		Anthracene-d10				
		Benzo(a)pyrene-d12				
		Bis(2-Chloroethyl) ether-d8				
		4-Chloroaniline-d4				
		Dimethyl phthalate-d6				
		Flurene-d10				
		Nitrobenzene-d5				
		Pyrene-d10				

Solvent: methanol

Primary Source SOM SIM DMC Surrogate

Stock Standard	Vendor	Component	Stock Standard Concentration (ug/mL)	Volume Added (uL)	Final Volume (mL)	Final Concentration (ug/mL)
2-Methylnaphthalene-d10	Cambridge Isotopes # DLM-1322	2-Methylnaphthalene-d10	200	800	200	0.8
Fluoranthene-d10	Restek # 562096	Fluoranthene-d10	1000	160		

Solvent: Methanol

Primary Source SOM BNA Matrix Spike

Stock Standard	Vendor	Component	Stock Standard Concentration (ug/mL)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/mL)
B/N Matrix Spike Mix	Restek #31084	1,4-Dichlorobenzene	5000	4.0	250	80
		N-Nitroso-di-n-propylamine				
		1,2,4-Trichlorobenzene				
		Acenaphthene				
		2,4-Dinitrotoluene				
		Pyrene				
Acid Matrix Spike Mix	Restek #31085	Phenol	7500	2.66		
		2-Chlorophenol				
		4-Chloro-3-methylphenol				
		4-Nitrophenol				
		Pentachlorophenol				

Solvent: Methanol

Primary Source SOM SIM BNA Matrix Spike

Stock Standard	Vendor	Component	Stock Standard Concentration (ug/mL)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/mL)
SOM BNA Matrix Spike	Laboratory	SOM BNA Matrix Spike	80	1.0	100	0.8

Solvent: Methanol

Primary Source 1, 4 Dioxane d8 Surrogate

Stock Standard	Vendor	Component	Stock Standard Concentration (ug/mL)	Volume Added (uL)	Final Volume (mL)	Final Concentration (ug/mL)
1, 4 Dioxane d8	Absolute #94158	1, 4 Dioxane d8	31,250	320	250	40

Solvent: Methanol

GPC Calibration Solution, Restek #54218

The GPC calibration solution is a whole volume standard solution purchased from a commercial vendor. The components of the calibration solution are provided in the following table:

Analyte	Concentration (mg/mL)
Corn Oil	25
Bis (2-ethylhexyl) phthalate	1.0
Methoxychlor	0.10
Perylene	0.02
Sulfur	0.08

Appendix C: GPC Column Preparation

Weigh 70 g of Bio Beads into a 1-quart amber glass container. Add ~300 mL of methylene chloride to the container and swirl to mix ensuring all beads are wet. Allow the beads to swell for a minimum of 2 hours. Ensure there is sufficient solvent to cover the beads during the entire time period.

With permanent marker, mark a 50cm length, centered on the column. Turn the GPC column upside down and remove the inlet bed support plunger. Position the outlet bed support plunger as close to the outlet end as possible, but no closer than 5 cm from the end of the column. Cap the end of the outlet tube and add a small amount of methylene chloride to the GPC column in order to minimize the formation of air bubbles at the base of the column packing.

After 2 hours is complete, swirl the bead / solvent slurry to achieve a homogenous mixture. Rinse a pre-baked funnel with methylene chloride and place it on top of the GPC column. Slowly pour the bead / solvent slurry into the GPC column, angling the funnel in such a manner that allows the bead slurry to slide down the side of the GPC column filling the column. Carefully remove the cap on the outlet tube and allow the solvent to drain into a solvent waste container.

Add methylene chloride to the column in an amount sufficient to rewet and compact the gel mixture. Continue to add portions of the slurry and when all of the bead slurry has been added, rinse the beaker with methylene chloride to complete the transfer, add the rinsate to the GPC column. DO NOT ALLOW THE PACKED COLUMN TO GO DRY. Rinse the column walls with methylene chloride. Loosen the seal of the inlet plunger and insert it into the column. Insert the line on the inlet side into a solvent waste container. Tighten the seal so that any beads on the glass surface are pushed forward but not so tight that the plunger cannot be pushed. *Caution: If there are beads between the seal and the glass, do not tighten this seal because doing so will damage the seal causing leaks.*

Push the plunger until it meets the gel, then compress the column bed ~4 cm. Cap the inlet line if it is necessary to prevent channeling and column dryness. Continue to compact the column until the frit on the bed support reaches the previously made 50 cm mark on the inlet side of the column. Quickly cap the inlet and outlet lines. Turn the packed column right side up. Remove the cap from the outlet line and place the line in the solvent waste container. Slowly apply pressure to the plunger and compact the column until the frit reached the 50 cm mark on the outlet side of the column. Quickly cap the outlet line.

Install the packed column on the GPC system following the manufacturer's instructions. Pump methylene chloride through the column for 1-2 hours. Check the column for signs of dryness or channeling. If channeling occurs, remove the gel from the column, re-swell and re-pack the column following the above procedure. If drying occurs, pump a sufficient amount of methylene chloride through the column until the column pressure remains constant and the column appears wet. Label the column with the date made and a unique sequential number. The column is ready for use after it has been calibrated and the calibration meets relevant acceptance criteria. If the GPC system is not in use place the column valves in the bypass position and check the GPC system program to ensure the column is identified as offline.

Title: Sample Preparation and Cleanup Procedures for Pesticides (CLP SOW SOM01.2)

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1.0 Scope and Application

This SOP describes the laboratory procedures used for the extraction of water and soil/sediment samples and the procedures used for extract cleanup in preparation for analysis by Gas Chromatograph / Electron Capture Detector (GC/ECD) to determine the presence and concentration of organochlorine pesticides.

This SOP does not include the procedure for the determination of percent solids. These procedures are described in laboratory SOPs BR-WC-006 and BR-EX-016, respectively.

This SOP is applicable to hazardous waste samples for use in the EPA Contract Laboratory Program (CLP). The procedure may be used for other matrices or sample sites if the procedure meets the established data quality and performance objectives for the project.

1.1 Analytes, Matrix(s), and Reporting Limits

This procedure may be used for the following matrices: non-potable water and soil/sediment.

The analyte list and reporting limits are provided in laboratory SOPs for instrument analysis.

2.0 Summary of Method

Water Sample:

1 L of sample is spiked with surrogate solution and serially extracted with methylene chloride using a separatory funnel. The extract is dried with anhydrous sodium sulfate, concentrated to 10 mL in hexane, of which 1 mL is subjected to Florisil cleanup (required) and sulfur cleanup as needed. GPC cleanup is optional. The final volume of the extract is 10 mL unless GPC is performed in which case the post-GPC extract volume is 5 mL.

Solid/Sediment Sample:

30 g of sample is mixed with anhydrous sodium sulfate, spiked with surrogate, and extracted with a 1:1 v/v acetone/methylene chloride solvent mixture using ultrasonic extraction. The extract is concentrated to 10 mL, filtered, and cleaned up by Gel Permeation Chromatography (GPC). After the GPC cleanup the extract is solvent exchanged into hexane and concentrated to a final volume of 5 mL. A 1 mL aliquot of post GPC extract is subjected to Florisil cleanup (required) and sulfur cleanup (as needed)

This SOP is based on the following reference method:

- SOM1.2 Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration, USEPA Contract Laboratory Program. June 2007.

NOTE: SOM01.2 is defined by the EPA as SOM1.1 SOW combined with the “Modifications Updating SOM01.1 to SOM01.2”.

If the laboratory’s procedure is modified from the reference method, a list of modifications will be provided in Section 16.0

3.0 Definitions

A list of terms and definitions are provided in Appendix A.

4.0 Interferences

- Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing equipment. These contaminants can lead to elevated baselines and discrete artifacts that appear in gas chromatograms. These materials are demonstrated to be free of interferences by the analysis of method blanks. Interferences from phthalate esters can also pose a problem for the chlorinated pesticides analysis. To avoid this type of interference, the use of plastics in the laboratory must be minimized.

- Temperature stability is important to the GPC cleanup process, variations in temperature may cause retention times (RT) to shift and affect the basis of the preset “Dump” and “Collect” times. To prevent RT shift, the temperature of the room should be maintained at a constant temperature.

- Non-target compounds co-extracted from the sample matrix can also cause interference, the extent of which will vary considerably depending on the nature of the samples. The extent of the interference will vary by matrix and are minimized using the various cleanup procedures described in this SOP.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

The use of separatory funnels to extract aqueous samples with methylene chloride creates excessive pressure very rapidly. Initial venting should be done immediately after the sample container has been sealed and inverted. Vent the funnel into the hood away from people and other samples. This is considered a high-risk activity, and a face shield must be worn over safety glasses or goggles when it is performed.

5.2 Primary Materials Used

Table 1 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the SDS. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

6.0 Equipment and Supplies

Catalog numbers listed in this SOP are subject to change at the discretion of the vendor. Analysts are cautioned to be sure equipment used meets the specification of this SOP.

6.1 Separatory Funnel Extraction

- Separatory Funnel, 2 Liter with PTFE stopcock and cap. Fisher Scientific or equivalent.
- Separatory Funnel Rotator
- Glass Funnel – 100 mm. Fisher Scientific or equivalent.
- Class A Graduated Cylinder: 1 L capacity. Fisher Scientific or equivalent.
- Fiberglass Wool: 8 um, Fisher Scientific or equivalent.
- pH meter- Denver Instrument or equivalent.

6.2 Ultrasonic Extraction

- Ultrasonic disrupter, Vibra Cell 750-watt Model Dual Output with pulsing capability, 3/4" standard disrupter horn for low level extractions. Sonics and Materials Model Number VC750 or equivalent.
- 400 mL glass beaker. Fisher Scientific
- Sonication box. Sonics and Materials
- Glass Funnels - 100mm. Fisher Scientific.
- Filter paper- No. 54 Whatman 18.5cm, or equivalent
- pH meter- Denver Instruments

6.3 Extract Concentration (KD Apparatus)

- Concentrator tube, 10 mL graduated. ChemGlass Catalog Number CG-1316-11 or equivalent
- Snyder Column, Three ball macro AMK Catalog Number SC2-01 or equivalent
- Snyder Column, Two ball micro AMK Catalog Number SC3-01 or equivalent
- Evaporation Flask, 500 mL attached to concentrator tube with clip. AMK Catalog Number KDF-500 or equivalent
- Boiling Chips, silicon carbide, approximately 10/40 mesh, solvent extracted in methylene chloride. Troemner Catalog Number 133B or equivalent.
- Heating mantle rheostat controlled for water bath capable of temperature control (± 5℃). ChemGlass Catalog Number PL3122 or equivalent.
- Glass Water Bath, AMK Glass
- Solvent Vapor Recovery System, Kontes K-54000-1006, K-547300-000, Ace Glass Catalog Number 6614-30 or equivalent.

6.4 Miscellaneous

- Disposable glass Pasteur pipette and bulb. Fisher Scientific
- Top Loading balance: Capable of measuring to 0.01 gram accuracy. Mettler Model Number PM4800 or equivalent.
- Teflon and Stainless Steel Spatulas. Fisher Scientific
- Adjustable Pipette. Finnpipette or equivalent
- 0.5 mL – 10.0 mL Hamilton Gastight® syringes or equivalent.
- Class “A” Volumetric Flasks: 10 mL to 1000 mL, Fisher Scientific.

- Glass Scintillation Vials: 2, 4, 8, and 16 mL with Teflon lined septa and screw caps, Fisher Scientific.
- Centrifuge: Thermo.
- 50 mL Centrifuge Tubes: Fisher Scientific.
- Vortex mixer- Thermo
- Autovial Filter: Whatman.
- Aluminum Weigh Pans. Fisher Scientific

6.5 Gel Permeation Chromatography

- GPC System: J2 Scientific.
- Chromatographic Column: AMK Glass
- UV Detector: J2 Scientific.

6.6 Florisil Cleanup Equipment

- Vacuum Manifold, Supelco - 24 Port
- Valve Liners, Supelco #57059

7.0 Reagents and Standards

Reagents

- Sodium Sulfate (granular, anhydrous), Na_2SO_4. J.T. Baker or equivalent. Purify by heating at 400°C for at least 4 hours.
- Methylene Chloride (CH_2C_{12}), Pesticide quality, J.T Baker or equivalent.
- Hexane, (C_6H_{14}), Pesticide quality. J.T. Baker or equivalent.
- Acetone, ($(CH_3)_2CO$), Pesticide quality. J.T. Baker or equivalent.
- Reagent Water- RO water filtered through a Nanopure System
- Sodium Hydroxide (NaOH), J.T. Baker- Reagent grade.
- Sulfuric Acid, (H_2SO_4), J.T. Baker-Reagent grade.
- Bio Beads: J2 Scientific
- Florisil Cartridge with PFTE tip, 1 g. Restek #24034

Methylene Chloride/Acetone (1:1): Mix 2 L methylene chloride with 2 L acetone. Transfer to a 4 L amber glass bottle and store in a fume hood.

Sulfuric Acid Solution (1:1 v/v): Slowly add 450 mL of concentrated sulfuric acid to 450 mL of reagent water. Store in a 1L amber glass bottle at ambient temperature.

10N Sodium Hydroxide (10N): Add 40 g of sodium hydroxide to a 100 mL volumetric flask that contains ~ 50 mL reagent water. Adjust to volume with reagent water. Store in a 150 mL amber glass jar.

If pre-activated copper is not available:

Activated Copper Powder: Add 5-8 g of copper powder to a 16 mL clear glass vial. Add 15-20 mL of concentrated hydrochloric acid to the vial. Cap the vial and vortex for 1 minute. Centrifuge for 1 minute. Decant and discard the acid. Repeat the acid wash 2-3 times with fresh portions of acid, discarding the acid each time. Rinse the copper powder two times following the same

procedure with reagent water, methanol, methylene chloride and hexane then dry the activated copper with nitrogen. In a separate vial, prepare a saturated sulfur solution by adding 0.5 g of sulfur to 10 mL of hexane then add ~0.25 g of the activated copper to the sulfur solution. If the copper turns black, the activated copper powder is adequate for use. If the activated copper powder does not turn black, discard the activated copper powder and remake.

7.1 Standards

Purchase stock standard solutions from commercial vendors. From these, prepare surrogate and spiking solutions by diluting known volumes of the stock standard solutions in an appropriate solvent using the formulations provided in Appendix B. Record the preparation of the standard in the LIMS. Unless otherwise specified in Appendix B, store the prepared solutions in glass containers at a temperature of 4℃ (±2) and assign an expiration date of 6 months from date of preparation unless the parent standard expires sooner in which case use the earliest expiration date.

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection so these procedures are not included in this SOP. Listed below are the recommended minimum sample size needed for analysis and the requirements for preservation and holding times.

Matrix	Sample Container	Minimum Sample Size	Preservation	Holding Time[1]	Reference
Water	Glass	1 L	4℃ (±2℃)	5 Days VTSR	CLP SOW
Solid	Glass	80 g	4℃ (±2℃)	5 Days VTSR	CLP SOW

[1]Extraction holding time is determined from the date sample were received by the laboratory.

The laboratory routinely retains unused sample volumes in the laboratory for 30 days from date of data submission. For EPA CLP contract work, unused sample volume, partially used sample volume, used sample containers and empty sample containers are retained for 60 days after the date of data submission.

9.0 Quality Control

The laboratory prepares the following quality control samples with each batch of samples.

QC Item	Frequency	Acceptance Criteria
Method Blank (MB)	1 in 20 or fewer samples	See Analytical SOP
Laboratory Control Sample (LCS)	1 in 20 or fewer samples	See Analytical SOP
Matrix Spike(s) MS/MSD	Assigned by client per SDG	See Analytical SOP
Sample Duplicate (SD)	Client Request	See Analytical SOP

10.0 Procedure

10.1 Instrument Calibration and Equipment Preparation

Check and record the calibration of the pH meter and the balance each day of use prior to use and record the calibration check in the logbook established for this purpose.

Inspect the tip of the sonicator horn for excessive wear. If the sonicator is not self-tuning, check and record the tuning of the sonicator horn as follows:

To perform the tune check:

1. Attach the converter to the bottom connector.

2. Set the pulsar switch to the off position, the output control to 10 (full power) and the % duty cycle to 50 (energy on 50% of time and off 50% of time).

3. Briefly depress the tune switch and rotate the tuning control clockwise or counterclockwise until a minimum reading of less than 20% is achieved on the power meter.

4. Re-attach the upper converter if using both converters and record the tune calibration in the logbook designated for this purpose.

Wash each piece of glassware and sample preparation equipment using the procedures described in laboratory SOP BR-EX-017. Label the equipment to clearly and unambiguously identify the sample ID during each step of the extraction procedure. Solvent will erase “sharpie” labeling, so caution must be taken to ensure markings are not obliterated during the procedure.

For each water sample: Add a plug of Pyrex glass wool to a 100 mm glass funnel. Add a sufficient amount of purified sodium sulfate to each funnel such that the funnel is approximately ¾ full. Rinse the funnel with ~30 mL of acetone and ~30 mL of methylene chloride, discard the rinsate. Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporation flask. Add 1-2 boiling stones to K-D flask and then place under a drying funnel.

For each soil sample: Add a Whatman No. 54 filter to a 100 mm glass funnel and add a sufficient amount of purified sodium sulfate to each funnel such that the funnel is approximately ¾ full. Rinse the funnel with ~30 mL of acetone and ~30 mL of methylene chloride, discard the rinsate. Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporation flask. Add 1-2 boiling stones to K-D flask and then place under a drying funnel.

10.2 Water Sample Preparation

Let each sample warm to ambient temperature.

Measure and record the pH of each sample with a pH meter. Adjust the sample pH to between 5 and 9 with 10N sodium hydroxide or 1:1 sulfuric acid, as necessary.

Mark the meniscus of each sample on the sample container. Transfer the sample into a prepared separatory funnel. Rinse each container with 60 mL of methylene chloride and transfer the rinsate into the corresponding separatory funnel to ensure complete transfer of sample.

To prepare the method blank (MB) and LCS, transfer 1 L of reagent water to labeled separatory funnels.

Add an appropriate volume of surrogate and spike solution to field and QC samples. Refer to the Extraction Conditions Workbook to determine the type and volumes of surrogate and spiking solutions to add to each sample. Use the following specification for routine EPA CLP SOW work:

- Add 3.0 mL surrogate solution to each field and QC sample. Add 1.0 mL of matrix spike solution to each MS/MSD and add 1.0 mL of LCS spike solution to the LCS.

Measure and record the sample volume for each field sample by filling each sample container to the meniscus line with water then measure the volume using a Class A graduated cylinder. If the sample volume is less than 900 mL or if the sample has multiple phases notify the PM and wait for further instruction.

Cap each separatory funnel and shake the funnel vigorously for 15-20 seconds with periodic venting into a fume hood to release excess pressure.

Caution*: Methylene chloride rapidly creates excessive pressure. After sealing the separatory funnel, shake once and immediately vent the sample into a fume hood. Venting must be performed into the fume hood in order to avoid exposure to solvent vapors.*

Place the separatory funnel on the mechanical rotator and rotate for 2 minutes then let the sample sit for 10 minutes to allow the solvent layer to separate. If an emulsion is present and the emulsion interface between layers is more than one-third the size of the solvent layer, drain the solvent into a labeled 50 mL centrifuge tube and centrifuge at full speed (3500 RPM) for ~10 minutes. After centrifugation, transfer the solvent back to the separatory funnel.

After the layers have separated decant the solvent portion into the drying funnel.

Repeat the extraction/decant process two more times using fresh 60 mL portions of methylene chloride each time.

If GPC cleanup is not needed, concentrate the extract to 10 mL in hexane using the techniques provided in section 10.4 then proceed to section 10.6 for Florisil cleanup.

If GPC cleanup is needed, concentrate the extract to 10 mL in methylene chloride then proceed to section 10.5 for GPC cleanup.

10.3 Soil Sample Preparation

Mix each sample thoroughly with a spatula and discard any foreign objects such as sticks, leaves, and rocks. If freestanding water remains after mixing, decant the water.

pH Determination:

Add a magnetic stir bar to a clean 400 mL glass beaker. Place the beaker on the balance and tare the balance. Measure ~ 50 g of sample into the beaker and record or upload the sample weight into the LIMS worksheet. Add 50 mL of reagent water to the beaker and place the beaker on a stir plate to mix for 1 hour.

NOTE: If a limited sample mass was received, use a smaller 1:1 ratio of sample to reagent water and record the modification with a nonconformance memo (NCM).

Measure the pH with a pH meter and record the sample pH in the worksheet. If the pH of the sample is greater than 9 or less than 5, notify the Project Manager but do not adjust the pH of the sample.

Discard the portion of sample used for the pH determination.

The percent moisture of samples is determined by the wet chemistry department following the procedure given in laboratory SOP BR-WC-006.

Use the percent moisture determination to determine the amount of sample for extraction. If the percent moisture of the sample is less than 65%, extract 30 g of sample; if the percent moisture is 65% or higher, extract 50 g.

Place a 400 mL glass beaker onto the calibrated top loading balance and tare the balance. Measure the appropriate amount of sample for extraction to within ± 1g into the beaker and upload the sample weight into the LIMS worksheet.

Mix the sample with a sufficient amount of purified anhydrous granulated sodium sulfate to ensure a free-flowing mixture.

Add an appropriate volume of surrogate and spike solution to field and QC samples. Refer to the Extraction Conditions Workbook to determine the type and volumes of surrogate and spiking solutions to add to each sample. Use the following specification for routine EPA CLP SOW work:

- Add 3.0 mL surrogate solution to each field and QC sample. Add 1.0 mL of matrix spike solution to each MS/MSD and add 1.0 mL of LCS spike solution to the LCS.

After spiking, immediately add 100 mL of 1:1 acetone/methylene chloride solvent to each beaker.

Clean the tip of the sonicator horn using a Kimwipe wetted with acetone. Set the control to 10 (full power) and with the mode switch on “Pulse” (pulsing energy rather than continuous energy) and the percent duty cycle switch set to 50% (energy on 50% of time and off 50% of time).

Place a beaker in the sonicator box and place the bottom surface of the tip of the sonicator horn ~1/2 inch below the solvent, but above the sample.

Sonicate the sample for 3 minutes then decant the extract through the drying funnel. Repeat the extraction / decant two more times with fresh 100 mL portions of extraction solvent. Stir each sample with a clean spatula before each extraction to break up any large clumps and to ensure that the sample is free flowing.

After the third extraction, transfer the entire sample into the drying funnel then rinse the beaker with ~30 mL of extraction solvent, transferring the rinsate to the drying funnel. Let the solvent completely drain through the drying funnel into the K-D apparatus. Remove the drying funnel and discard the contents into the solid waste stream.

Prior to GPC cleanup, concentrate the extract to 1 mL using the techniques described in section 10.4. Adjust the extract volume to 10 mL with methylene chloride then proceed to 10.5 for GPC

10.4 Extract Concentration Techniques

Macro Snyder Column (K-D)

Add one or two clean boiling chips to the K-D evaporation flask and attach a three-ball Snyder column to the flask. Add ~1 mL of methylene chloride to the top of the column then place the K-D apparatus in a hot water bath (60-70℃) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in hot water vapor.

Attach the solvent vapor recovery glassware to the Snyder column. Adjust the vertical position of the apparatus and check the water bath temperature. The water bath temperature should be between 54.8 – 74.8℃ when methylene chloride is the extraction solvent and 84-89℃ when hexane is the extraction solvent. Higher water bath temperatures may be used so long as the recovery of target analytes is not impacted. The boiling point of each solvent is provided in the following table:

Solvent	Boiling Point	Water Bath Temperature
Hexane	69℃	84 – 89℃
Methylene Chloride	39.8℃	54.8 – 74.8℃

Monitor the concentration and do not let the extract evaporate to dryness. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with solvent.

When the apparent volume of the extract reaches desired amount remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

Micro Snyder Column (K-D)

Add one or two clean boiling chips to the concentrator tube and attach a two ball micro-Snyder column to the tube. Place the concentrator tube into the water bath so that the concentrator tube is partially immersed in hot water. Adjust the vertical position of the concentrator tube and check the temperature of the water bath to ensure the proper temperature for the extract solvent.

Continuously monitor the distillation process to ensure sample extracts do not evaporate to dryness. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with solvent. Remove setup when desired sample volume is reached.

Nitrogen Blowdown

Nitrogen blow down may be used to concentrate extracts as needed.

Place the concentrator tube in a warm water bath maintained at a temperature of 35℃. Apply a steady stream of nitrogen until the desired final extract volume is achieved. Rinse the internal wall of the concentrator tube several times with the appropriate solvent during the evaporation and ensure the solvent level in the concentrator is positioned such to prevent water condensations. Monitor the concentration carefully and do not allow the extract to evaporate to dryness.

10.5 GPC Cleanup (Optional)

10.5.1 GPC Calibration

Calibrate the GPC system prior to initial use, when the calibration fails to meet acceptance criteria, when the column is changed, when channeling occurs, once every 7 days or when the shift in retention time (RT) is greater than 5% when compared to the RTs in the last calibration UV traces.

Prepare the GPC column following the instructions provided in Appendix B.

Establish the flow rate by pumping methylene chloride through the GPC column for 5 minutes and collecting the eluate in a 25 mL volumetric flask and calculate the flow rate. The flow rate should be between 4.9 and 5.1 mL/minute.

Check the system pressure, the pressure should be less than 30 psi.

Load 10 mL of the stock standard GPC calibration solution onto the GPC system and determine the elution times for phthalate, methoxychlor, and perylene and set the dump and collect cycles on the GPC system.

- Determine a “DUMP” time that will remove > 85% of phthalate. Determine a “COLLECT” time so that > 95% of the methoxychlor is collected. Continue the collect time until just before the elution time of sulfur. Add 2 minutes to the collect time to account for sample volume between the UV detector and the collection vessel. Use a “WASH” time of 15 minutes beginning after the elution of perylene.

After setting the dump and collect times, inject 10 mL of GPC calibration solution onto the system collect the elutriate over the course of 10 minutes into a volumetric flask. Measure and record the volume of eluate collected and calculate the flow rate. The flow rate should be between 4.9 and 5.1 mL per minute. If it is not, adjust the pump speed and repeat the calibration procedure.

The UV trace of the GPC calibration must meet the following criteria:

- Peaks must be observed and the peaks should be symmetrical for each compound in the calibration solution.
- The peaks for corn oil and phthalate should exhibit greater than 85% resolution.
- The peaks for phthalate and methoxychlor should exhibit greater than 85% resolution.
- The peaks for methoxychlor and perylene should exhibit greater than 85% resolution.
- The peaks for perylene and sulfur must not be saturated and should exhibit greater than 90% resolution.
- The solvent flow rate should be between 4.9 and 5.1 mL/min.
- The column pressure should not exceed 30 psi.
- The retention times (RTs) for bis (2-ethylhexyl) phthalate and perylene must not vary more than ±5% between the first and second injections.

If these criteria are not met, identify and correct the problem. Corrective action typically requires preparation of a new GPC column.

After criteria are met, run a GPC blank consisting of 10 mL of methylene chloride through the system to verify it is clean. Concentrate the GPC blank to ~3-5 mL using macro snyder column technique. Exchange the blank into hexane and concentrate the blank to a final volume of 5 mL. Give the GPC blank to GC for analysis by GC/ECD. There should be no target analytes present in the GPC blank above the CRQL. If contamination is found, pump methylene chloride through the GPC system for 1-2 hours then analyze another GPC blank. Repeat this procedure until the GPC system is proven clean.

10.5.2 Sample Cleanup by GPC

Filter each sample and QC extract through a 0.45 um filter collecting the filtrate in a 16 mL vial and adjust the extract volume to 10 mL. Transfer the extract to an injection vessel.

Extracts with viscosity greater than 1:1 v/v glycerol / water must be diluted prior to GPC cleanup and extracts with more than 40 mg/mL of non-volatile residue must be diluted and processed through the GPC system as multiple fractions that are later recombined.

To determine the dissolved solids in soil extracts: Place an aluminum weigh pan on a calibrated top loading balance and tare the balance. Measure 100 uL of extract into the weigh pan and upload the measurement into the LIMS worksheet. Let the aliquot evaporate to dryness. Reweigh the pan, upload the weight measurement. Dissolved solids are calculated by the LIMS system. If the dissolved solids are greater than 40 mg/mL, split the sample for multiple GPC loops.

Prepare and label a collection vessel for each extract and place the collection vessels in the tray of the GPC system. Place the injection vessels in the autosampler and initiate the cleanup sequence. **NOTE: Place the MB at the end of the GPC sequence.** The GPC system loads 5 mL of each extract through the system using the collect and dump times previously established. After each sample loop, the GPC system rinses the loading port with methylene chloride to minimize cross-contamination.

When the GPC run is finished, concentrate the extract to 5 mL using the macro snyder column technique. Use hexane as the exchange solvent and concentrate the extract to a final volume of 5 mL.

Proceed to Section 10.6 for Florisil cleanup.

10.6 Florisil Cleanup (Mandatory)

Attach the manifold to a vacuum pump with trap. Prepare a 10 mL concentrator tube for each extract. Place a Florisil cartridge into the manifold for each extract. Wash each cartridge with 90:10 v/v hexane/acetone. Place the concentrator tube under each manifold port.

Caution: Do not allow the cartridges to go dry after the wash.

Use a volumetric pipette to transfer 1.0 mL of the extract to the top frit of a Florisil cartridge. Elute the extract through the cartridge with 8 mL of 90:10 v/v hexane/acetone collecting the elutriate in the 10 mL concentrator tube. Rinse the cartridge twice with 1 mL of hexane – collect the rinsate

in the concentrator tube. Concentrate the extract to 1.0 mL. If sulfur cleanup is needed, proceed to the next section, otherwise proceed to Section 11.0.

Test each lot of Florisil cartridges prior to use of the lot and every 6 months.

To perform the test:

Prepare the 2,4,5 Trichlorophenol standard solution using the formulations provided in Appendix B and pull prepared standard Individual Standard Mixture C from the GC department. Add 0.5 mL of 2,4,5-trichlorophenol solution and 0.5 mL of to 4 mL of hexane. Concentrate the solution to 0.5 mL using micro snyder technique.

Take the solution through the cleanup process then concentrate the solution to 1.0 mL and give to the GC department for analysis. The lot of Florisil cartridges is deemed acceptable if the recovery of all of the pesticides in the solution is 80-120%, if the recovery of 2,4,5 trichlorophenol is less than 5%, and if there are no interfering peaks detected. If these criteria are not met, identify and correct the problem and repeat the performance check procedure. If necessary, discard the lot of cartridges tested and start over with a new lot.

10.7 Sulfur Cleanup

Add ~0.25 g, up to 2 g of activated copper granules to the 1 mL portion of extract that received Florisil cleanup. Extract and vortex the extract for one minute. If the copper changes color, draw off the extract with a disposable pipette, transfer the extract to a clean 8 mL vial and repeat the procedure. When the copper appears bright, the cleanup step is complete.

Each sample in the extraction batch including the MB is subject to the sulfur cleanup procedure.

NOTE: If all samples in the batch require sulfur cleanup, the MB and LCS in the extraction batch will also receive cleanup. If only a subset of samples in the extraction batch require sulfur cleanup, a sulfur blank is prepared and analyzed with those samples. To prepare the sulfur blank, transfer 1.4 mL of hexane to a clean 8 mL vial, add 0.6 mL of surrogate spike solution to the vial. Subject the sulfur cleanup blank to the same sulfur cleanup and analysis procedure as the field samples.

11.0 <u>Calculations / Data Reduction</u>

11.1 Calculations

The calculation for dissolved solids is performed by the laboratory's LIMS system or the EXCEL worksheet established for this purpose.

11.2 Data Review

<u>Primary Review</u>

Review project documents such as the Project Plan (PP), Project Memo or any other document/process used to communicate project requirements to ensure those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Enter the batch information into LIMS and complete the batch editor and worksheet for each extraction and cleanup performed. Initiate NCMs for any anomalies observed during the preparation process. Set the status of the batch to 1st level review.

Secondary Data Review

Review project documents such as the Project Plan (PP), Project Memo or any other document/process used to communicate project requirements and verify those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Check the batch editor and worksheet to verify the batch is complete and any outages are documented with an NCM along with the results of any corrective actions taken. Set the status of the batch to second level review.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

A Method Detection Limit (MDL) Study must be determined for each test method associated with this extraction procedure during initial method set-up or prior to the analysis of field samples. The MDLs are verified annually or after major instrument maintenance. The procedure for the determination of MDLs is described in laboratory SOP BR-QA-005.

12.2 Demonstration of Capabilities (DOC)

Each analyst must complete an Initial Demonstration of Capability prior to unsupervised performance of this method.

12.3 Training Requirements

Any employee that performs any portion of the procedure described in this SOP must have documentation in their employee training file that they have read this version of this SOP.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to BR-EH-001. The following waste streams are produced when this method is carried out.

- Organic Solvents - Satellite container: 55 gallon covered and vented drum.

- Extracted water samples - Satellite container: 55 gallon covered and vented drum.
- Vials containing extracts - Satellite container: 5 gallon covered bucket in fume hood.
- Methylene Chloride-Waste-Satellite Container: 55 Gallon Waste Drum
- Sulfuric Acid Waste-Satellite Container: 2.5L Waste Bottle Labeled with appropriate acid type (sulfuric).
- Solid Waste-Satellite Container: Solid Waste 5 Gallon Plastic Bucket (inside fume hood)

Transfer the waste stream(s) to the appropriate satellite container(s) located in your work area. Notify authorized personnel when it is time to transfer the contents of the satellite containers to the hazardous waste storage room for future disposal in accordance with Federal, State and Local regulations. The procedures for waste management are further given in laboratory SOP BR-EH-001.

15.0 References / Cross-References

- Exhibits B & D, Analytical Methods for the Analysis of Trace Concentrations of Volatile Organic Compounds, USEPA CLP SOW for Organic Analysis, SOM01.1, May 2005.
- USEPA CLP SOW Clarifications to SOM01.1, November 7, 2005 and September 26, 2006.
- USEPA CLP SOW Modifications Updating SOM01.1 to SOM01.2, October 5, 2006 (Updated 02-12-2007) Amended 04-11-2006.

16.0 Method Modifications

Modification Number	Method Reference	Modification
1	10.3	SOW states to measure sample volume by pouring sample into a graduated Class A cylinder. Our lab practice is to mark the meniscus on the sample's bottle, decant the sample into extraction vessel, and fill the bottle back up with water to meniscus mark. After the bottle is filled to the mark it is transferred to a Class A Grad. cylinder to measure the sample volume.

17.0 Attachments

- Table 1: Primary Materials Used
- Appendix A: Terms and Definitions
- Appendix B: Standard Preparation Formulas

18.0 Revision History

BR-EX-014, Revision 2:
- Title Page: Updated approval signatures.
- Updated MSDS to SDS.

BR-EX-014, Revision 1:
- Title Page: Updated approval signatures.
- Section 10.3: Changed procedure for measuring water samples to reflect our practice.
- Section 10.4: Changed range of initial sample volume to be ± 1 g.
- Section 10.5: Addition of solvent boiling point table.

- Section 10.8: Changed 1:1 sulfuric acid/reagent water to concentrated sulfuric acid.
- All Sections: Added LIMS language.
- Added Appendix B: Standard Preparation Formulas
- Added Appendix C: GPC Column Preparation.

Table 1: Primary Materials Used

Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Appendix A: Terms and Definitions

Acceptance Criteria: specified limits placed on characteristics of an item, process or service defined in requirement documents.

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 which are due to sampling and analytical operations; a data quality indicator.

Analyte: The specific chemicals or components for which a sample is analyzed. (EPA Risk Assessment Guide for Superfund, OSHA Glossary).

Batch: environmental samples that are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria. An analytical batch is composed of prepared environmental samples (extracts, digestates and concentrates), which are analyzed together as a group.

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 the standards.

Calibration Standard: A substance or reference used to calibrate an instrument.

Continuing Calibration Verification (CCV): a single or multi-parameter calibration standard used to verify the stability of the method over time. Usually from the same source as the calibration curve.

Corrective Action: the action taken to eliminate the cause of an existing nonconformity, defect or other undesirable occurrence in order to prevent recurrence.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

Intermediate Standard: a solution made from one or more stock standards at a concentration between the stock and working standard. Intermediate standards may be certified stock standard solutions purchased from a vendor and are also known as secondary standards.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Matrix Spike (MS): a field sample to which a known amount of target analyte(s) is added.

Matrix Spike Duplicate (MSD): a second replicate matrix spike

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Precision: the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Quality Control Sample (QC): a sample used to assess the performance of all or a portion of the measurement system.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample.

Stock Standard: a solution made with one or more neat standards usually with a high concentration. Also known as a primary standard. Stock standards may be certified solutions purchased from a vendor.

Surrogate: a substance with properties that mimic the analyte of interest but that are unlikely to be found in environmental samples.

Appendix B: Standard Preparation Formulas

SOM01.2 PEST/PCB Surrogate Solution

Stock Standard	Vendor	Component	Stock Standard Concentration (ug/mL)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/mL)
2,4,5,6 tetrachloro-m-xylene	Restek #32027	2,4,5,6 tetrachloro-m-xylene	200	1.0	1000	0.2
Decachlorobiphenyl	Ultra# PPS-150	Decachlorobiphenyl	1000	0.4		0.4

Solvent: Acetone

SOM PESTICIDE LCS Spike Solution

Stock Standard	Vendor	Component	Stock Standard Concentration (ug/mL)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/mL)
L/C Pesticide Lab Control Sample	Restek# 32040	gamma-BHC (Lindane)	10	1.0	200	0.05
		Heptachlor epoxide (isomer B)	10			0.05
		gamma-Chlordane	10			0.05
		4,4'-DDE	20			0.1
		Dieldrin	20			0.1
		Endrin	20			0.1
		Endosulfan sulfate	20			0.1

Solvent: Acetone

SOM PESTICIDE MS/MSD Spike Solution

Stock Standard	Vendor	Component	Stock Standard Concentration (ug/mL)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/mL)
Pesticide Matrix Spike Mix	Restek# 32018	gamma-BHC (Lindane)	25	1.0	200	0.5
		Heptachlor	25			0.5
		Aldrin	25			0.5
		Dieldrin	50			1.0
		Endrin	50			1.0
		4,4'-DDT	50			1.0

Solvent: Methanol

GPC Calibration Solution, Restek #54218

The GPC calibration solution is a whole volume standard solution purchased from a commercial vendor. The components of the calibration solution are provided in the following table:

Analyte	Concentration (mg/mL)
Corn Oil	25
Bis (2-ethylhexyl) phthalate	1.0
Methoxychlor	0.10
Perylene	0.02

Sulfur	0.08

SOM FLORISIL CHECK SOLUTION (2,4,5-Trichlorophenol)

Stock Standard	Vendor	Component	Stock Standard Concentration (ug/mL)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/mL)
2,4,5-Trichlorophenol	Ultra# PH-260	2,4,5-Trichlorophenol	100	0.5	500	0.1

Solvent: Acetone

Appendix C: GPC Column Preparation

Weigh 70 g of Bio Beads into a 1-quart amber glass container. Add ~300 mL of methylene chloride to the container and swirl to mix ensuring all beads are wet. Allow the beads to swell for a minimum of 2 hours. Ensure there is sufficient solvent to cover the beads during the entire time period.

With permanent marker, mark a 50cm length, centered on the column. Turn the GPC column upside down and remove the inlet bed support plunger. Position the outlet bed support plunger as close to the outlet end as possible, but no closer than 5 cm from the end of the column. Cap the end of the outlet tube and add a small amount of methylene chloride to the GPC column in order to minimize the formation of air bubbles at the base of the column packing.

After 2 hours is complete, swirl the bead / solvent slurry to achieve a homogenous mixture. Rinse a pre-baked funnel with methylene chloride and place it on top of the GPC column. Slowly pour the bead / solvent slurry into the GPC column, angling the funnel in such a manner that allows the bead slurry to slide down the side of the GPC column filling the column. Carefully remove the cap on the outlet tube and allow the solvent to drain into a solvent waste container.

Add methylene chloride to the column in an amount sufficient to rewet and compact the gel mixture. Continue to add portions of the slurry and when all of the bead slurry has been added, rinse the beaker with methylene chloride to complete the transfer, add the rinsate to the GPC column. DO NOT ALLOW THE PACKED COLUMN TO GO DRY. Rinse the column walls with methylene chloride. Loosen the seal of the inlet plunger and insert it into the column. Insert the line on the inlet side into a solvent waste container. Tighten the seal so that any beads on the glass surface are pushed forward but not so tight that the plunger cannot be pushed. *Caution: If there are beads between the seal and the glass, do not tighten this seal because doing so will damage the seal causing leaks.*

Push the plunger until it meets the gel, then compress the column bed ~4 cm. Cap the inlet line if it is necessary to prevent channeling and column dryness. Continue to compact the column until the frit on the bed support reaches the previously made 50 cm mark on the inlet side of the column. Quickly cap the inlet and outlet lines. Turn the packed column right side up. Remove the cap from the outlet line and place the line in the solvent waste container. Slowly apply pressure to the plunger and compact the column until the frit reached the 50 cm mark on the outlet side of the column. Quickly cap the outlet line.

Install the packed column on the GPC system following the manufacturer's instructions. Pump methylene chloride through the column for 1-2 hours. Check the column for signs of dryness or channeling. If channeling occurs, remove the gel from the column, re-swell and re-pack the column following the above procedure. If drying occurs, pump a sufficient amount of methylene chloride through the column until the column pressure remains constant and the column appears wet. Label the column with the date made and a unique sequential number. The column is ready for use after it has been calibrated and the calibration meets relevant acceptance criteria. If the GPC system is not in use place the column valves in the bypass position and check the GPC system program to ensure the column is identified as offline.

Title: Sample Preparation and Cleanup Procedures for Aroclors (CLP SOW SOM01.2)

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1.0 Scope and Application

This SOP describes the laboratory procedures used for the extraction of water and soil/sediment samples and the procedures used for extract cleanup in preparation for analysis by Gas Chromatograph / Electron Capture Detector (GC/ECD) to determine the presence and concentration of Aroclors.

This SOP does not include the procedure for the determination of percent solids. These procedures are described in laboratory SOPs BR-WC-006 and BR-EX-016, respectively.

This SOP is applicable to hazardous waste samples for use in the EPA Contract Laboratory Program (CLP). The procedure may be used for other matrices or sample sites if the procedure meets the established data quality and performance objectives for the project.

1.1 Analytes, Matrix(s), and Reporting Limits

This procedure may be used for the following matrices: non-potable water and soil/sediment.

The analyte list and reporting limits are provided in laboratory SOPs for instrument analysis.

2.0 Summary of Method

Water:

1 Liter of sample is spiked with surrogate solution and serially extracted with methylene chloride using a separatory funnel extraction (SFE). The extract is dried with anhydrous sodium sulfate and concentrated to 10 mL in hexane. 2 mL of the 10 mL extract is subjected to sulfuric acid cleanup and sulfur cleanup (as needed). GPC cleanup is optional. If GPC is not performed, the final volume of the extract is 10 mL; if GPG is performed the final volume of the extract is 5 mL.

Soil/Sediment:

30 g of sample is mixed with anhydrous sodium sulfate, spiked with surrogate solution and extracted by sonication with a 1:1 v/v acetone/methylene chloride solvent mixture. The extract is filtered, concentrated to 10 mL in hexane of which 2 mL is subjected to sulfuric acid cleanup and sulfur cleanup (as needed). GPC cleanup is optional. If GPC is not performed, the final volume of the extract is 10 mL; if GPG is performed the final volume of the extract is 5 mL.

This SOP is based on the following reference method:

- SOM1.2 Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration, USEPA Contract Laboratory Program. June 2007.

NOTE: SOM01.2 is defined by the EPA as SOM1.1 SOW combined with the “Modifications Updating SOM01.1 to SOM01.2”.

If the laboratory’s procedure is modified from the reference method, a list of modifications will be provided in Section 16.0

3.0 Definitions

A list of terms and definitions are provided in Appendix A.

4.0 Interferences

- Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing equipment. These contaminants can lead to elevated baselines and discrete artifacts that appear in gas chromatograms. These materials are demonstrated to be free of interferences by the analysis of method blanks. Interferences from phthalate esters can also pose problems for Aroclor analysis. To avoid this type of interference, the use of plastics in the laboratory must be minimized.

- Temperature stability is important to the GPC cleanup process, variations in temperature may cause retention times (RT) to shift and affect the basis of the preset "Dump" and "Collect" times. To prevent RT shift, the temperature of the room should be maintained at a constant temperature.

- Non-target compounds co-extracted from the sample matrix can also cause interference, the extent of which will vary considerably depending on the nature of the samples. The extent of the interference will vary by matrix and are minimized using the various cleanup procedures described in this SOP.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

The use of separatory funnels to extract aqueous samples with methylene chloride creates excessive pressure very rapidly. Initial venting should be done immediately after the sample container has been sealed and inverted. Vent the funnel into the hood away from people and other samples. This is considered a high-risk activity, and a face shield must be worn over safety glasses or goggles when it is performed.

The addition of sulfuric acid to the sample extract has the potential to create an exothermic reaction. Both can cause severe burns, so a face shield must be worn when performing this procedure.

5.2 Primary Materials Used

Table 1 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the SDS. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section.

Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

6.0 Equipment and Supplies

Catalog numbers listed in this SOP are subject to change at the discretion of the vendor. Analysts are cautioned to be sure equipment used meets the specification of this SOP.

6.1 Separatory Funnel Extraction

- Separatory Funnel, 2 Liter with PTFE stopcock and cap. Fisher Scientific or equivalent.
- Separatory Funnel Rotator
- Glass Funnel – 100 mm. Fisher Scientific or equivalent.
- Class A Graduated Cylinder: 1 L capacity. Fisher Scientific or equivalent.
- Fiberglass Wool: 8 um, Fisher Scientific or equivalent.
- pH meter- Denver Instrument or equivalent.

6.2 Ultrasonic Extraction

- Ultrasonic disrupter, Vibra Cell 750-watt Model Dual Output with pulsing capability, 3/4" standard disrupter horn for low level extractions. Sonics and Materials Model Number VC750 or equivalent.
- 400 mL glass beaker. Fisher Scientific
- Sonication box. Sonics and Materials
- Glass Funnels - 100mm. Fisher Scientific.
- Filter paper- No. 54 Whatman 18.5cm, or equivalent
- pH meter- Denver Instruments

6.3 Extract Concentration (KD Apparatus)

- Concentrator tube, 10 mL graduated. ChemGlass Catalog Number CG-1316-11 or equivalent
- Snyder Column, Three ball macro AMK Catalog Number SC2-01 or equivalent
- Snyder Column, Two ball micro AMK Catalog Number SC3-01 or equivalent
- Evaporation Flask, 500 mL attached to concentrator tube with clip. AMK Catalog Number KDF-500 or equivalent
- Boiling Chips, silicon carbide, approximately 10/40 mesh, solvent extracted in methylene chloride. Troemner Catalog Number 133B or equivalent.
- Heating mantle rheostat controlled for water bath capable of temperature control (± 5℃). ChemGlass Catalog Number PL3122 or equivalent.
- Glass Water Bath, AMK Glass
- Solvent Vapor Recovery System, Kontes K-54000-1006, K-547300-000, Ace Glass Catalog Number 6614-30 or equivalent.

6.4 Miscellaneous

- Disposable glass Pasteur pipette and bulb. Fisher Scientific
- Top Loading balance: Capable of measuring to 0.01 gram accuracy. Mettler Model Number PM4800 or equivalent.
- Teflon and Stainless Steel Spatulas. Fisher Scientific
- Adjustable Pipette. Finnpipette or equivalent

- 0.5 mL – 10.0 mL Hamilton Gastight® syringes or equivalent.
- Class "A" Volumetric Flasks: 10 mL to 1000 mL, Fisher Scientific.
- Glass Scintillation Vials: 2, 4, 8, and 16 mL with Teflon lined septa and screw caps, Fisher Scientific.
- Centrifuge: Thermo.
- 50 mL Centrifuge Tubes: Fisher Scientific.
- Vortex mixer- Thermo
- Autovial Filter: Whatman.
- Aluminum Weigh Pans. Fisher Scientific

6.5 Gel Permeation Chromatography

- GPC System: J2 Scientific.
- Chromatographic Column: AMK Glass
- Bio Beads: J2 Scientific
- UV Detector: J2 Scientific.

7.0 Reagents and Standards

7.1 Reagents

- Sodium Sulfate (granular, anhydrous), Na_2SO_4. J.T. Baker or equivalent. Purify by heating at 400°C for at least 4 hours.
- Methylene Chloride (CH_2C_{12}), Pesticide quality, J.T Baker or equivalent.
- Hexane, (C_6H_{14}), Pesticide quality. J.T. Baker or equivalent.
- Acetone, ($(CH_3)_2CO$), Pesticide quality. J.T. Baker or equivalent.
- Reagent Water- RO water filtered through a Nanopure System
- Sodium Hydroxide (NaOH), J.T. Baker- Reagent grade.
- Sulfuric Acid, (H_2SO_4), J.T. Baker-Reagent grade.
- Copper Powder (<10um) Aldrich Chemical or Pre-activated Copper Granules: Restek.

Methylene Chloride/Acetone (1:1): Mix 2 L methylene chloride with 2 L acetone. Transfer to a 4 L amber glass bottle and store in a fume hood.

Sulfuric Acid Solution (1:1 v/v): Slowly add 450 mL of concentrated sulfuric acid to 450 mL of reagent water. Store in a 1L amber glass bottle at ambient temperature.

10N Sodium Hydroxide (10N): Add 40 g of sodium hydroxide to a 100 mL volumetric flask that contains ~ 50 mL reagent water. Adjust to volume with reagent water. Store in a 150 mL amber glass jar.

If pre-activated copper is not available:

Activated Copper Powder: Add 5-8 g of copper powder to a 16 mL clear glass vial. Add 15-20 mL of concentrated hydrochloric acid to the vial. Cap the vial and vortex for 1 minute. Centrifuge for 1 minute. Decant and discard the acid. Repeat the acid wash 2-3 times with fresh portions of acid, discarding the acid each time. Rinse the copper powder two times following the same procedure with reagent water, methanol, methylene chloride and hexane then dry the activated copper with nitrogen. In a separate vial, prepare a saturated sulfur solution by adding 0.5 g of

sulfur to 10 mL of hexane then add ~0.25 g of the activated copper to the sulfur solution. If the copper turns black, the activated copper powder is adequate for use. If the activated copper powder does not turn black, discard the activated copper powder and remake.

7.2 Standards

Purchase stock standard solutions from commercial vendors. From these, prepare surrogate and spiking solutions by diluting known volumes of the stock standard solutions in an appropriate solvent using the formulations provided in Appendix B. Record the preparation of the standard in the LIMS. Unless otherwise specified in Appendix B, store the prepared solutions in glass containers at a temperature of 4°C (±2) and assign an expiration date of 6 months from date of preparation unless the parent standard expires sooner in which case use the earliest expiration date.

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection so these procedures are not included in this SOP. Listed below are the recommended minimum sample size needed for analysis and the requirements for preservation and holding times.

Matrix	Sample Container	Minimum Sample Size	Preservation	Holding Time[1]	Reference
Water	Glass	1 L	4°C (±2°C)	5 Days VTSR	CLP SOW
Solid	Glass	80 g	4°C (±2°C)	5 Days VTSR	CLP SOW

[1]Extraction holding time is determined from the date sample were received by the laboratory.

The laboratory routinely retains unused sample volumes in the laboratory for 30 days from date of data submission. For EPA CLP contract work, unused sample volume, partially used sample volume, used sample containers and empty sample containers are retained for 60 days after the date of data submission.

9.0 Quality Control

The laboratory prepares the following quality control samples with each extraction batch:

QC Item	Frequency	Acceptance Criteria
Method Blank (MB)	1 in 20 or fewer samples	See Analytical SOP
Laboratory Control Sample (LCS)	1 in 20 or fewer samples	See Analytical SOP
Matrix Spike(s) MS/MSD	Assigned by client per SDG	See Analytical SOP
Sample Duplicate (SD)	Client Request	See Analytical SOP

10.0 Procedure

10.1 Instrument Calibration and Equipment Preparation

Check and record the calibration of the pH meter and the balance each day of use.

Inspect the tip of the sonicator horn for excessive wear. If the sonicator is not self-tuning, check and record the tuning of the sonicator horn as follows:

To perform the tune check:

1. Attach the converter to the bottom connector.

2. Set the pulsar switch to the off position, the output control to 10 (full power) and the % duty cycle to 50 (energy on 50% of time and off 50% of time).

3. Briefly depress the tune switch and rotate the tuning control clockwise or counterclockwise until a minimum reading of less than 20% is achieved on the power meter.

4. Re-attach the upper converter if using both converters and record the tune calibration in the logbook designated for this purpose.

Wash each piece of glassware and sample preparation equipment using the procedures described in laboratory SOP BR-EX-017. Label the equipment to clearly and unambiguously identify the sample ID during each step of the extraction procedure. Solvent will erase "sharpie" labeling, so caution must be taken to ensure markings are not obliterated during the procedure.

For each water sample: Add a plug of Pyrex glass wool to a 100 mm glass funnel. Add a sufficient amount of purified sodium sulfate to each funnel such that the funnel is approximately ¾ full. Rinse the funnel with ~30 mL of acetone and ~30 mL of methylene chloride, discard the rinsate. Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporation flask. Add 1-2 boiling stones to K-D flask and then place under a drying funnel.

For each soil sample: Add a Whatman No. 54 filter to a 100 mm glass funnel and add a sufficient amount of purified sodium sulfate to each funnel such that the funnel is approximately ¾ full. Rinse the funnel with ~30 mL of acetone and ~30 mL of methylene chloride, discard the rinsate. Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporation flask. Add 1-2 boiling stones to K-D flask and then place under a drying funnel.

10.2 Water Sample Preparation

Measure and record the pH of each sample with wide range pH paper or a pH meter. Adjust the sample pH to between 5 and 9 with 10N sodium hydroxide or 1:1 sulfuric acid, as necessary.

Mark the meniscus of each sample on the sample container. Transfer the sample into a prepared separatory funnel. Rinse each container with 60 mL of methylene chloride and transfer the rinsate into the corresponding separatory funnel to ensure complete transfer of sample.

To prepare the method blank (MB) and LCS, transfer 1 L of reagent water to labeled separatory funnels.

Add an appropriate volume of surrogate and spike solution to field and QC samples. Refer to the Extraction Conditions Workbook to determine the type and volumes of surrogate and spiking solutions to add to each sample. Use the following specification for routine EPA CLP SOW work:

- Add 3.0 mL surrogate solution to each field and QC sample. Add 1.0 mL of matrix spike solution to each MS/MSD and add 1.0 mL of LCS spike solution to the LCS.

Measure and record the sample volume for each field sample by filling each sample container to the meniscus line with water then measure the volume using a Class A graduated cylinder. If the sample volume is less than 900 mL or if the sample has multiple phases notify the PM and wait for further instruction.

Cap each separatory funnel and shake the funnel vigorously for 15-20 seconds with periodic venting into a fume hood to release excess pressure.

***Caution**: Methylene chloride rapidly creates excessive pressure. After sealing the separatory funnel, shake once and immediately vent the sample into a fume hood. Venting must be performed into the fume hood in order to avoid exposure to solvent vapors.*

Place the separatory funnel on the mechanical rotator and rotate for 2 minutes then let the sample sit for 10 minutes to allow the solvent layer to separate. If an emulsion is present and the emulsion interface between layers is more than one-third the size of the solvent layer, drain the solvent into a labeled 50 mL centrifuge tube and centrifuge at full speed (3500 RPM) for ~10 minutes. After centrifugation, transfer the solvent back to the separatory funnel.

After the layers have separated decant the solvent portion into the drying funnel.

Repeat the extraction/decant process two more times using fresh 60 mL portions of methylene chloride each time.

If GPC cleanup is not needed, concentrate the extract to 10 mL in hexane using the techniques provided in section 10.4 then proceed to section 10.6 for sulfuric acid cleanup.

If GPC cleanup is needed, concentrate the extract to 10 mL in methylene chloride then proceed to section 10.5 for GPC cleanup.

10.3 Soil Sample

Mix each sample thoroughly with a spatula and discard any foreign objects such as sticks, leaves, and rocks. If freestanding water remains after mixing, decant the water.

pH Determination:

Add a magnetic stir bar to a clean 400 mL glass beaker. Place the beaker on the balance and tare the balance. Measure ~ 50 g of sample into the beaker and record or upload the sample weight into the LIMS worksheet. Add 50 mL of reagent water to the beaker and place the beaker on a stir plate to mix for 1 hour.

NOTE: If a limited sample mass was received, use a smaller 1:1 ratio of sample to reagent water and record the modification with a nonconformance memo (NCM).

Measure the pH with a pH meter and record the sample pH in the worksheet. If the pH of the sample is greater than 9 or less than 5, notify the Project Manager but do not adjust the pH of the sample.

Discard the portion of sample used for the pH determination.

The percent moisture of samples is determined by the wet chemistry department following the procedure given in laboratory SOP BR-WC-006.

Use the percent moisture determination to determine the amount of sample for extraction. If the percent moisture of the sample is less than 65%, extract 30 g of sample; if the percent moisture is 65% or higher, extract 50 g.

Place a 400 mL glass beaker onto the calibrated top loading balance and tare the balance. Measure the appropriate amount of sample for extraction to within ± 1g into the beaker and upload the sample weight into the LIMS worksheet.

Mix the sample with a sufficient amount of purified anhydrous granulated sodium sulfate to ensure a free-flowing mixture.

Add an appropriate volume of surrogate and spike solution to field and QC samples. Refer to the Extraction Conditions Workbook to determine the type and volumes of surrogate and spiking solutions to add to each sample. Use the following specification for routine EPA CLP SOW work:

- Add 3.0 mL surrogate solution to each field and QC sample. Add 1.0 mL of matrix spike solution to each MS/MSD and add 1.0 mL of LCS spike solution to the LCS.

After spiking, immediately add 100 mL of 1:1 acetone/methylene chloride solvent to each beaker.

Clean the tip of the sonicator horn using a Kimwipe wetted with acetone. Set the control to 10 (full power) and with the mode switch on “Pulse” (pulsing energy rather than continuous energy) and the percent duty cycle switch set to 50% (energy on 50% of time and off 50% of time).

Place a beaker in the sonicator box and place the bottom surface of the tip of the sonicator horn ~1/2 inch below the solvent, but above the sample.

Sonicate the sample for 3 minutes then decant the extract through the drying funnel. Repeat the extraction / decant two more times with fresh 100 mL portions of extraction solvent. Stir each sample with a clean spatula before each extraction to break up any large clumps and to ensure that the sample is free flowing.

After the third extraction, transfer the entire sample into the drying funnel then rinse the beaker with ~30 mL of extraction solvent, transferring the rinsate to the drying funnel. Let the solvent completely drain through the drying funnel into the K-D apparatus. Remove the drying funnel and discard the contents into the solid waste stream.

Concentrate the sample to 10mL in hexane using the techniques described in section 10.4 then proceed to section 10.6 for sulfuric acid cleanup. If GPC is required, concentrate the sample to 1 mL in methylene chloride then adjust the extract volume to 10 mL in methylene chloride and proceed to section 10.5 for GPC cleanup.

10.4 Extract Concentration Techniques

Macro Snyder Column (K-D)

Add one or two clean boiling chips to the K-D evaporation flask and attach a three-ball Snyder column to the flask. Add ~1 mL of methylene chloride to the top of the column then place the K-D

apparatus in a hot water bath (60-70℃) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in hot water vapor.

Attach the solvent vapor recovery glassware to the Snyder column. Adjust the vertical position of the apparatus and check the water bath temperature. The water bath temperature should be between 54.8 – 74.8℃ when methylene chloride is the extraction solvent and 84-89℃ when hexane is the extraction solvent. Higher water bath temperatures may be used so long as the recovery of target analytes is not impacted. The boiling point of each solvent is provided in the following table:

Solvent	Boiling Point	Water Bath Temperature
Hexane	69℃	84 – 89℃
Methylene Chloride	39.8℃	54.8 – 74.8℃

Monitor the concentration and do not let the extract evaporate to dryness. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with solvent.

When the apparent volume of the extract reaches desired amount remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

Micro Snyder Column (K-D)

Add one or two clean boiling chips to the concentrator tube and attach a two ball micro-Snyder column to the tube. Place the concentrator tube into the water bath so that the concentrator tube is partially immersed in hot water. Adjust the vertical position of the concentrator tube and check the temperature of the water bath to ensure the proper temperature for the extract solvent.

Continuously monitor the distillation process to ensure sample extracts do not evaporate to dryness. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with solvent. Remove setup when desired sample volume is reached.

Nitrogen Blowdown

Nitrogen blow down may be used to concentrate extracts as needed.

Place the concentrator tube in a warm water bath maintained at a temperature of 35℃. Apply a steady stream of nitrogen until the desired final extract volume is achieved. Rinse the internal wall of the concentrator tube several times with the appropriate solvent during the evaporation and ensure the solvent level in the concentrator is positioned such to prevent water condensations. Monitor the concentration carefully and do not allow the extract to evaporate to dryness.

10.5 GPC Cleanup (Optional)

10.5.1 GPC Calibration

Calibrate the GPC system prior to initial use, when the calibration fails to meet acceptance criteria, when the column is changed, when channeling occurs, once every 7 days or when the shift in retention time (RT) is greater than 5% when compared to the RTs in the last calibration UV traces.

Prepare the GPC column following the instructions provided in Appendix B.

Establish the flow rate by pumping methylene chloride through the GPC column for 5 minutes and collecting the eluate in a 25 mL volumetric flask and calculate the flow rate. The flow rate should be between 4.9 and 5.1 mL/minute.

Check the system pressure, the pressure should be less than 30 psi.

Load 10 mL of the stock standard GPC calibration solution onto the GPC system and determine the elution times for phthalate, methoxychlor, and perylene and set the dump and collect cycles on the GPC system.

- Determine a "DUMP" time that will remove > 85% of phthalate. Determine a "COLLECT" time so that > 95% of the methoxychlor is collected. Continue the collect time until just before the elution time of sulfur. Add 2 minutes to the collect time to account for sample volume between the UV detector and the collection vessel. Use a "WASH" time of 15 minutes beginning after the elution of perylene.

After setting the dump and collect times, inject 10 mL of GPC calibration solution onto the system collect the elutriate over the course of 10 minutes into a volumetric flask. Measure and record the volume of eluate collected and calculate the flow rate. The flow rate should be between 4.9 and 5.1 mL per minute. If it is not, adjust the pump speed and repeat the calibration procedure.

The UV trace of the GPC calibration must meet the following criteria:

- Peaks must be observed and the peaks should be symmetrical for each compound in the calibration solution.
- The peaks for corn oil and phthalate should exhibit greater than 85% resolution.
- The peaks for phthalate and methoxychlor should exhibit greater than 85% resolution.
- The peaks for methoxychlor and perylene should exhibit greater than 85% resolution.
- The peaks for perylene and sulfur must not be saturated and should exhibit greater than 90% resolution.
- The solvent flow rate should be between 4.9 and 5.1 mL/min.
- The column pressure should not exceed 30 psi.
- The retention times (RTs) for bis (2-ethylhexyl) phthalate and perylene must not vary more than ±5% between the first and second injections.

If these criteria are not met, identify and correct the problem. Corrective action typically requires preparation of a new GPC column.

After criteria are met, run a GPC blank consisting of 10 mL of methylene chloride through the system to verify it is clean. Concentrate the GPC blank to ~3-5 mL using macro snyder column technique. Exchange the blank into hexane and concentrate the blank to a final volume of 5 mL.

Give the GPC blank to GC for analysis by GC/ECD. There should be no target analytes present in the GPC blank above the CRQL. If contamination is found, pump methylene chloride through the GPC system for 1-2 hours then analyze another GPC blank. Repeat this procedure until the GPC system is proven clean.

10.5.2 Sample Cleanup by GPC

Filter each sample and QC extract through a 0.45 um filter collecting the filtrate in a 16 mL vial and adjust the extract volume to 10 mL. Transfer the extract to an injection vessel.

Extracts with viscosity greater than 1:1 v/v glycerol / water must be diluted prior to GPC cleanup and extracts with more than 40 mg/mL of non-volatile residue must be diluted and processed through the GPC system as multiple fractions that are later recombined.

To determine the dissolved solids in soil extracts: Place an aluminum weigh pan on a calibrated top loading balance and tare the balance. Measure 100 uL of extract into the weigh pan and upload the measurement into the LIMS worksheet. Let the aliquot evaporate to dryness. Reweigh the pan, upload the weight measurement. Dissolved solids are calculated by the LIMS system. If the dissolved solids are greater than 40 mg/mL, split the sample for multiple GPC loops.

Prepare and label a collection vessel for each extract and place the collection vessels in the tray of the GPC system. Place the injection vessels in the autosampler and initiate the cleanup sequence. **NOTE: Place the MB at the end of the GPC sequence.** The GPC system loads 5 mL of each extract through the system using the collect and dump times previously established. After each sample loop, the GPC system rinses the loading port with methylene chloride to minimize cross-contamination.

When the GPC run is finished, concentrate the extract to ~5 mL using the macro snyder column technique. Use hexane as the exchange solvent and concentrate the extract to a final volume of 5 mL.

Perform sulfuric acid cleanup.

10.6 Sulfuric Acid Cleanup (Mandatory)

Working in a fume hood, transfer 2.0 mL of extract to a 16 mL clear vial then carefully add 5 mL of concentrated sulfuric acid to the extract. Tightly cap the vial then vortex the vial for one minute.

Let the phases of the extract to separate then examine the top layer of hexane for color, emulsion or cloudiness. If the hexane layer is colored or if an emulsion is present, remove and dispose the acid layer and repeat the process using a fresh 5 mL portion of concentrated sulfuric acid.

When the extract is clear, carefully transfer the hexane layer from the vial to a clean 10 mL concentrator tube. Take care to ensure that none of the acid layer is transferred because acid can cause damage to the analytical instruments.

To ensure complete transfer, add 1 mL of hexane to the vial. Cap the vial and vortex for one minute, allow the phases to separate then transfer the hexane layer to the concentrator tube.

Concentrate the hexane extract to 2.0 mL using the micro snyder column procedure.

If sulfur cleanup is needed, proceed to the next section, otherwise proceed to Section 11.0.

10.7 Sulfur Cleanup (As Needed)

Add ~0.25 g, up to 2 g of activated copper granules to each 2.0 mL extract and vortex the extract for one minute. If the copper changes color, draw off the extract with a disposable pipette, transfer the extract to a clean 8 mL vial and repeat the procedure. When the copper appears bright, the cleanup step is complete.

Each sample in the extraction batch including the MB is subject to the sulfur cleanup procedure.

NOTE: If all samples in the batch require sulfur cleanup, the MB and LCS in the extraction batch will also receive cleanup. If only a subset of samples in the extraction batch require sulfur cleanup, a sulfur blank is prepared and analyzed with those samples. To prepare the sulfur blank, transfer 1.4 mL of hexane to a clean 8 mL vial, add 0.6 mL of surrogate spike solution to the vial. Subject the sulfur cleanup blank to the same sulfur cleanup and analysis procedure as the field samples.

11.0 Calculations / Data Reduction

11.1 Calculations

The calculation for dissolved solids is performed by the laboratory's LIMS system or the EXCEL worksheet established for this purpose.

11.2 Data Review

Primary Review

Review project documents such as the Project Plan (PP), Project Memo or any other document/process used to communicate project requirements to ensure those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Enter the batch information into LIMS and complete the batch editor and worksheet for each extraction and cleanup performed. Initiate NCMs for any anomalies observed during the preparation process. Set the status of the batch to 1st level review.

Secondary Data Review

Review project documents such as the Project Plan (PP), Project Memo or any other document/process used to communicate project requirements and verify those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Check the batch editor and worksheet to verify the batch is complete and any outages are documented with an NCM along with the results of any corrective actions taken. Set the status of the batch to second level review.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

A Method Detection Limit (MDL) Study must be determined for each test method associated with this extraction procedure during initial method set-up or prior to the analysis of field samples. The MDLs are verified annually or after major instrument maintenance. The procedure for the determination of MDLs is described in laboratory SOP BR-QA-005.

12.2 Demonstration of Capabilities (DOC)

Each analyst must complete an Initial Demonstration of Capability prior to unsupervised performance of this method.

12.3 Training Requirements

Any employee that performs any portion of the procedure described in this SOP must have documentation in their employee training file that they have read this version of this SOP.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to BR-EH-001. The following waste streams are produced when this method is carried out.

- Organic Solvents - Satellite container: 55 gallon covered and vented drum.
- Extracted water samples - Satellite container: 55 gallon covered and vented drum.
- Vials containing extracts - Satellite container: 5 gallon covered bucket in fume hood.
- Methylene Chloride-Waste-Satellite Container: 55 Gallon Waste Drum
- Sulfuric Acid Waste-Satellite Container: 2.5L Waste Bottle Labeled with appropriate acid type (sulfuric).
- Solid Waste-Satellite Container: Solid Waste 5 Gallon Plastic Bucket (inside fume hood)

Transfer the waste stream(s) to the appropriate satellite container(s) located in your work area. Notify authorized personnel when it is time to transfer the contents of the satellite containers to the hazardous waste storage room for future disposal in accordance with Federal, State and Local regulations. The procedures for waste management are further given in laboratory SOP BR-EH-001.

15.0 References / Cross-References

- Exhibits B & D, Analytical Methods for the Analysis of Trace Concentrations of Volatile Organic Compounds, USEPA CLP SOW for Organic Analysis, SOM01.1, May 2005.
- USEPA CLP SOW Clarifications to SOM01.1, November 7, 2005 and September 26, 2006.
- USEPA CLP SOW Modifications Updating SOM01.1 to SOM01.2, October 5, 2006 (Updated 02-12-2007) Amended 04-11-2006.

16.0 Method Modifications

Modification Number	Method Reference	Modification
1	10.3	SOW states to measure sample volume by pouring sample into a graduated Class A cylinder. Our lab practice is to mark the meniscus on the sample's bottle, decant the sample into extraction vessel, fill the bottle back up with water to meniscus mark. After the bottle is filled to the mark it is transferred to a Class A Grad. cylinder to measure the sample volume.
2	10.8	The laboratory uses concentrated sulfuric acid instead of 1:1 sulfuric acid/reagent water solution.

17.0 Attachments

- Table 1: Primary Materials Used
- Appendix A: Terms and Definitions
- Appendix B: Standard Preparation Formulas

18.0 Revision History

BR-EX-013, Revision 1:
- Title Page: Updated approval signatures.
- Updated MSDS to SDS.

BR-EX-013, Revision 1:
- Title Page: Updated approval signatures.
- Section 10.3: Changed procedure for measuring water samples to reflect our practice.
- Section 10.4: Changed range of initial sample volume to be ± 1 g.
- Section 10.5: Addition of solvent boiling point table.
- Section 10.8: Changed 1:1 sulfuric acid/reagent water to concentrated sulfuric acid.
- All Sections: Added LIMS language.
- Added Appendix B: Standard Preparation Formulas
- Added Appendix C: GPC Column Preparation.

Table 1: Primary Materials Used

Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Appendix A: Terms and Definitions

Acceptance Criteria: specified limits placed on characteristics of an item, process or service defined in requirement documents.

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 which are due to sampling and analytical operations; a data quality indicator.

Analyte: The specific chemicals or components for which a sample is analyzed. (EPA Risk Assessment Guide for Superfund, OSHA Glossary).

Batch: environmental samples that are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria. An analytical batch is composed of prepared environmental samples (extracts, digestates and concentrates), which are analyzed together as a group.

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 the standards.

Calibration Standard: A substance or reference used to calibrate an instrument.

Continuing Calibration Verification (CCV): a single or multi-parameter calibration standard used to verify the stability of the method over time. Usually from the same source as the calibration curve.

Corrective Action: the action taken to eliminate the cause of an existing nonconformity, defect or other undesirable occurrence in order to prevent recurrence.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

Intermediate Standard: a solution made from one or more stock standards at a concentration between the stock and working standard. Intermediate standards may be certified stock standard solutions purchased from a vendor and are also known as secondary standards.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Matrix Spike (MS): a field sample to which a known amount of target analyte(s) is added.

Matrix Spike Duplicate (MSD): a second replicate matrix spike

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Precision: the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Quality Control Sample (QC): a sample used to assess the performance of all or a portion of the measurement system.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample.

Stock Standard: a solution made with one or more neat standards usually with a high concentration. Also known as a primary standard. Stock standards may be certified solutions purchased from a vendor.

Surrogate: a substance with properties that mimic the analyte of interest but that are unlikely to be found in environmental samples.

Appendix B: Standard Preparation Formulas

SOM01.2 PEST/PCB Surrogate Solution

Stock Standard	Vendor	Component	Stock Standard Concentration (ug/mL)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/mL)
2,4,5,6 tetrachloro-m-xylene	Restek #32027	2,4,5,6 tetrachloro-m-xylene	200	1.0	1000	0.2
Decachlorobiphenyl	Restek #32029	Decachlorobiphenyl	200	2.0		0.4

Solvent: Acetone

LCS AROCLOR 1660 Spike Solution

Stock Standard	Vendor	Component	Stock Standard Concentration (ug/mL)	Volume Added (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Aroclor 1016/1260	Restek #32039	Aroclor 1016 Aroclor 1260	1000	100	100	1.0

Solvent: Acetone

MS/MD AROCLOR 1660 Spike Solution

Stock Standard	Vendor	Component	Stock Standard Concentration (ug/mL)	Volume Added (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Aroclor 1016/1260	Restek #32039	Aroclor 1016 Aroclor 1260	1000	400	100	4.0

Solvent: Acetone

GPC Calibration Solution, Restek #54218

The GPC calibration solution is a whole volume standard solution purchased from a commercial vendor. The components of the calibration solution are provided in the following table:

Analyte	Concentration (mg/mL)
Corn Oil	25
Bis (2-ethylhexyl) phthalate	1.0
Methoxychlor	0.10
Perylene	0.02
Sulfur	0.08

Appendix C: GPC Column Preparation

Weigh 70 g of Bio Beads into a 1-quart amber glass container. Add ~300 mL of methylene chloride to the container and swirl to mix ensuring all beads are wet. Allow the beads to swell for a minimum of 2 hours. Ensure there is sufficient solvent to cover the beads during the entire time period.

With permanent marker, mark a 50cm length, centered on the column. Turn the GPC column upside down and remove the inlet bed support plunger. Position the outlet bed support plunger as close to the outlet end as possible, but no closer than 5 cm from the end of the column. Cap the end of the outlet tube and add a small amount of methylene chloride to the GPC column in order to minimize the formation of air bubbles at the base of the column packing.

After 2 hours is complete, swirl the bead / solvent slurry to achieve a homogenous mixture. Rinse a pre-baked funnel with methylene chloride and place it on top of the GPC column. Slowly pour the bead / solvent slurry into the GPC column, angling the funnel in such a manner that allows the bead slurry to slide down the side of the GPC column filling the column. Carefully remove the cap on the outlet tube and allow the solvent to drain into a solvent waste container.

Add methylene chloride to the column in an amount sufficient to rewet and compact the gel mixture. Continue to add portions of the slurry and when all of the bead slurry has been added, rinse the beaker with methylene chloride to complete the transfer, add the rinsate to the GPC column. DO NOT ALLOW THE PACKED COLUMN TO GO DRY. Rinse the column walls with methylene chloride. Loosen the seal of the inlet plunger and insert it into the column. Insert the line on the inlet side into a solvent waste container. Tighten the seal so that any beads on the glass surface are pushed forward but not so tight that the plunger cannot be pushed. *Caution: If there are beads between the seal and the glass, do not tighten this seal because doing so will damage the seal causing leaks.*

Push the plunger until it meets the gel, then compress the column bed ~4 cm. Cap the inlet line if it is necessary to prevent channeling and column dryness. Continue to compact the column until the frit on the bed support reaches the previously made 50 cm mark on the inlet side of the column. Quickly cap the inlet and outlet lines. Turn the packed column right side up. Remove the cap from the outlet line and place the line in the solvent waste container. Slowly apply pressure to the plunger and compact the column until the frit reached the 50 cm mark on the outlet side of the column. Quickly cap the outlet line.

Install the packed column on the GPC system following the manufacturer's instructions. Pump methylene chloride through the column for 1-2 hours. Check the column for signs of dryness or channeling. If channeling occurs, remove the gel from the column, re-swell and re-pack the column following the above procedure. If drying occurs, pump a sufficient amount of methylene chloride through the column until the column pressure remains constant and the column appears wet. Label the column with the date made and a unique sequential number. The column is ready for use after it has been calibrated and the calibration meets relevant acceptance criteria. If the GPC system is not in use place the column valves in the bypass position and check the GPC system program to ensure the column is identified as offline.