165601

ADDENDUM No. 1

To Revision 3 (dated April 15, 2002)

SAUGET AREA 2
RI/FS SUPPORT SAMPLING PLAN
VOL 2A

WASTE, SOIL, STORMWATER, GROUNDWATER & AIR FIELD SAMPLING PLAN

June 17, 2002

JUN 10 2002

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 5
77 WEST JACKSON BOULEVARD
CHICAGO, IL 60604-3590

June 3, 2002

REPLY TO THE ATTENTION OF
(SR-6J)

Mr. Steven D. Smith
Solutia, Inc.
P.O. Box 66760
St. Louis, Missouri 63166-6760

RE: Approval - RI/FS Support Sampling Plan
Sauget Area 2 Site - St. Clair County, Illinois

Dear Mr. Smith:

The United States Environmental Protection Agency (U.S. EPA) has completed the review of the revised pages to the RI/FS Support Sampling Plan (SSP) for the Sauget Area 2 Site submitted by Solutia on May 20th and via fax (pg. 11-13) during the week of May 27. The revised pages have adequately address all of U.S. EPA's May 6th, 2002, comments. Pursuant to Section 2.2 of the November 24, 2000, Administrative Order on Consent, U.S. EPA approves the RI/FS Support Sampling Plan for the Sauget Area 2 Site.

If you have any questions regarding this letter or the enclosure, please feel free to call me at (312) 886-4592.

Sincerely,

Mike Ribordy
Remedial Project Manager
Superfund Division

cc: Thomas Martin, USEPA
Terry Stanuch, USEPA
Sandra Bron, IEPA
Peter Barrett, CH2M HILL
Kevin de la Bruere, USFWS
Michael Henry, IDNR

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JUN 10

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 5
77 WEST JACKSON BOULEVARD
CHICAGO, IL 60604-3590

REPLY TO THE ATTENTION OF:

(SR-6J)

June 4, 2002

Mr. Steven D. Smith
Solutia, Inc.
P.O. Box 66760
St. Louis, Missouri 63166-6760

RE: Approval - Modifications to Support Sampling Plan
Sauget Area 2 Site - St. Clair County, Illinois

Dear Mr. Smith:

The United States Environmental Protection Agency (U.S. EPA) has evaluated your May 23, 2002, proposal (Attachment) to make the following three modifications to the Sauget Area 2 Support Sampling Plan (SSP):

1. To use PROSONIC to install the six bedrock monitoring wells using the sonic drilling method. Temporary sonic override casing will be used during the drilling and installation of these wells in lieu of 5-inch permanent casing. PROSONIC polycarbonate liners will be used to capture and retain sediment samples for subsequent geotechnical analysis.

2. To use PROSONIC to install 27 one-inch piezometers in nine borings, with three piezometers in each boring, set at approximate depths of 20, 80 and 140 feet, respectively.

3. To collect samples for geotechnical analysis using the PROSONIC procedure, from each of the three major hydrologic units during each of the 9 deep piezometer installations. The current workplan calls for the collection of samples for geotechnical analysis at 5-foot intervals in each of the 9 deep piezometers which would result in over 250 geotechnical samples.

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Based on this evaluation and experience at other sites, U.S. EPA is agreeable to these proposed modifications. However, some concern remains regarding the nested piezometers and the ability to provide an adequate seal between sampling intervals within a single borehole. This issue should be more fully addressed in the addendum to the SSP. If it is determined in the field that the screened intervals can not be adequately isolated, separate boreholes will be required for each piezometer.

Pursuant to Section 2.2 of the November 24, 2000, Administrative Order on Consent, U.S. EPA approves the modifications to the RI/FS Support Sampling Plan for the Sauget Area 2 Site contained in your May 23, 2002, letter. Within 14 days, submit an addendum to the SSP documenting these changes.

If you have any questions regarding this letter or the enclosure, please feel free to call me at (312) 886-4592.

Sincerely,

Mike Ribordy
Remedial Project Manager
Superfund Division

Attachment

cc: Sandra Bron, IEPA
Peter Barrett, CH2M HILL

ATTACHMENT

Sauget Area 2 Sites Group

May 23, 2002

Mr. Mike Ribordy
U.S. EPA - Region 5
77 West Jackson Boulevard (SR-6J)
Chicago, Illinois 60604-3590

RE: Sauget Area 2 Sites

Deliver by Electronic and Overnight Mail

Dear Mike:

As we discussed by phone, the SA2SG is requesting the approval of three changes to the SSP work plan. These proposed changes are as follows:

1) Bedrock Monitoring Well Installations:

We propose to use PROSONIC to install the six bedrock monitoring wells using the sonic drilling method. Temporary sonic override casing will be used during the drilling and installation of these wells in lieu of 5-inch permanent casing.

Steps include:

a. Continuously advance four-inch soil core barrel and override casing in ten-foot intervals to anticipated total depth of 140 feet (until bedrock is encountered and visually confirmed by the URS field representative), and then five additional feet into bedrock.
b. Leave 6-inch temporary sonic override casing at the point of being five feet into bedrock. This will serve as the isolation casing to prevent any movement of contaminants into the bedrock formation. When the six-inch casing is sonically resonated, the formation around the casing is energized. When the resonation is stopped, the energized formation seals back around this casing, leaving a tight seal to prevent groundwater migration

downward along the casing wall. A bentonite plug will also be set in the bottom of the casing prior to advancing further into bedrock, adding to the integrity of the seal.

c. The bedrock will be cored using the sonic technique, resulting in a four-inch open rock hole on removal of the core barrel.

d. The two-inch PVC well will then be constructed in the borehole. The six-inch casing will be resonated during removal to form an effective seal against the borehole wall far superior to what could be created in a hole using "mud rotary" methods. Grout will always be maintained up inside of this temporary casing during removal to protect against formation collapse. (The mud rotary hole experiences movement depending on the formation and generally has to be oversized to allow the installation of the casing to the bottom of the hole because the boring is typically not straight or aligned). This effectively precludes the presence of a high-integrity grout seal along the entire length of the casing as the casing will likely be touching the borehole wall in many intervals along the length of the casing. The vibratory action of the sonic method ensures an effective seal, the holes are straight because they are 'cased', and all the mud contamination of the formation and the increased IDW handling and disposal costs are eliminated. This entire process will require only two shifts to install a well, so the time risks of having an open borehole are also minimized with respect to migration of contaminants.

PROSONIC offers the use of polycarbonate liners inside a modified sonic core barrel to capture and retain sediment samples for subsequent analysis. Liners will be used to capture soil samples at the specific formation intervals as required by the SSP. On retrieval from the borehole, these liners will be capped and sealed in the field, and shipped for subsequent geotechnical analysis.

2.) Piezometer Installations in Overburden:

The SA2SG proposes to use PROSONIC to install 27 one-inch piezometers in nine borings, with three piezometers in each boring, set at approximate depths of 20, 80 and 140 feet, respectively. The impetus for the design is to significantly reduce total drill footage as well as the quantity of investigation-derived waste. Borings will be installed by continuously soil coring and temporarily casing to approximately 140 feet using the sonic (or 'rotasonic') drilling method consisting of four-inch diameter core barrel and six-inch diameter override casing.

On reaching total depth with the '4x6' system, the three one-inch nested piezometers will be installed within the six-inch temporary casing and constructed with one-inch PVC screen and filter pack, riser, and bentonite chips or pellets between screened intervals. To ensure a quality installation, seven-inch diameter sonic override casing will be installed to 80 feet, and 8-inch diameter sonic override casing will be installed to 20 feet to provide ample annular space for the nested installations.

All temporary casings will be extracted during well construction while maintaining bentonite levels up inside the casing so no borehole collapse occurs during installation. Specifically, once the first, deep piezometer is set, the six-inch sonic casing will be removed while filter sand and bentonite is emplaced and bentonite is hydrated. Bentonite chips are proposed to ensure the top of each annular seal interval does not interfere with the next higher screened interval. Temporary sonic casings will be removed in the reverse order from which they were installed.

3.) Modification to the number of Geotechnical Samplings During the Piezometer Installation:

The SA2SG requests approval for a modification to the procedure identified in the workplan for the collection of geotechnical samples during the installation of the piezometers. The current workplan calls for the collection of samples for geotechnical analysis at 5-foot intervals in each of the 9 deep piezometers. This would result in over 250 geotechnical samples. Based on a review of the significant amount of geologic data that already exists from previous investigations in this area, it is felt that the geologic conditions are already well understood, and sampling every 5 feet at 9 locations would yield little or no new information. Alternatively, the SA2SG proposes that samples for geotechnical analysis be collected, using the Prosonics procedure outlined above, from each of the three major hydrologic units during each of the 9 deep piezometer installations.

If you have any questions on the above proposals please call.

Sincerely,

Steven D. Smith
Project Coordinator

Cc: SA2SG Technical Committee

SAUGET AREA 2, SAUGET, IL

RI/FS SUPPORT SAMPLING PLAN VOL. 2A

WASTE, SOIL, STORMWATER, GROUNDWATER & AIR FIELD SAMPLING PLAN

Prepared for

Sauget Area 2 Sites Group
c/o Steven Smith 6S
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575 Maryville Centre Drive
St. Louis, Missouri 63141

Submitted by:

URS

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April 15, 2002
Project No. 23-20010024.02

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SECTIONONE Project Background

1.1 INTRODUCTION

In response to the requirements of an Administrative Order on Consent (AOC) the Sauget Area 2 Sites Group (SA2SG) will perform a Remedial Investigation/Feasibility Study (RI/FS) at Sauget Area 2 Sites O, P, Q, R, and S.

A Site Sampling Plan (SSP) has been developed to gather sufficient information from the Sauget Area 2 sites to identify the nature of waste materials at Sites O, P, Q, R, and S and to assess the extent of migration of site-related constituents via the soil, groundwater, surface water, sediment, and air pathways and determination of constituent concentrations in aquatic and terrestrial biota. The main components of the SSP addressed in this Field Sampling Plan (FSP) include:

- Source area sampling (soil gas sampling, waste sampling, buried drum and tank identification)
- Groundwater sampling (upgradient, fill areas, downgradient alluvial aquifer, bedrock slug tests, and grain size analysis)
- Soil sampling (waste areas and background)
- Air sampling
- Treatability test sampling
- Stormwater sampling (exit routes from Sites Q and R).

A complete site description for the Sauget Area 2 Sites is provided in Volume 1, Support Sampling Plan. This discussion addresses sites location and physical setting, a discussion of present and past facility operations and disposal practices for each site, a discussion of the regional and site-specific geology, hydrology and hydrogeology, current and past groundwater uses, surrounding land use and populations, sensitive ecosystems, and meteorology/climatology.

SECTION TWO Project Organization and Responsibilities

URS will perform the field activities, prepare the report, and provide project management for support sampling activities. Analytical services for this FSP will be provided by Severn-Trent Laboratories - Savannah (Savannah Labs) in Savannah, Georgia . AMEC Environmental, Inc. will perform the Ecological Risk Assessment, and ENSR will perform the Human Health Risk Assessment. The responsibilities of key project personnel are described below. The responsibilities of key laboratory personnel are described in section 2.5 of the QAPP.

2.1. PROJECT ORGANIZATION

Sections 2.2 through 2.4 of this FSP present the responsibilities of the key project personnel and the lines of authority for the project personnel are described in each section.

2.2 MANAGEMENT RESPONSIBILITIES

2.2.1 USEPA Region V Remedial Project Manager

Michael Ribordy will serve as the USEPA Region V Remedial Project Manager (USEPA RPM). As such, he will have overall responsibility for all phases of the SSP.

2.2.2 Illinois Environmental Protection Agency (IEPA) Remedial Project Manager

Sandra Bron will serve as the IEPA Remedial Project Manager.

2.2.3 SA2SG Remedial Project Manager

Steven D. Smith of Solutia Inc. will serve as the SA2SG Project Coordinator. As such, he will have the overall responsibility for all phases of the SSP. He will be responsible for implementing the project, and will have the authority to commit the resources necessary to meet project objectives and requirements. His primary function is to verify that technical, financial, and scheduling objectives are achieved successfully. He will provide the major point of contact and control for matters concerning the project. The SA2SG Project Coordinator will:

- Define project objectives and develop a sampling plan schedule
- Establish project policy and procedures to address the specific needs of the project as a whole, as well as the objectives of each task
- Acquire and apply technical and financial resources as needed to verify performance within budget and schedule constraints

- Monitor and direct the field leaders
- Develop and meet ongoing project staffing requirements
- Review the work performed on each task to verify its, quality, responsiveness, and timeliness
- Review and analyze overall task performance with respect to planned requirements and authorizations
- Approve reports before their submission to USEPA Region V
- Ultimately be responsible for the preparation and quality of reports
- Represent the SA2SG at meetings.

2.2.4 URS Project Officer

Robert B. Veenstra will serve as the URS Project Officer. As such, he is responsible for the overall administration and technical execution of the project. He will report directly to the SA2SG Project Coordinator.

2.2.5 URS Project Manager

Steven J. Shroff will serve as the URS Project Manager (PM). As such, he will have overall responsibility for verifying that the project meets the stated objectives and URS's quality standards. He will report directly to the URS Project Officer and is responsible for technical quality control and project oversight.

2.3 Quality Assurance (QA) Responsibilities

2.3.1 URS Data Validator

John Kearns of URS will serve as the lead third party data validator. As such, he will remain independent of direct job involvement and day-to-day operations and have direct access to corporate executive staff as necessary to resolve QA disputes. The data validator will be responsible for auditing the implementation of the QA program in conformance with the

demands of specific investigations, URS's policies, and USEPA requirements. The specific functions that he or a designee perform may include:

- Providing QA audits on various phases of the field operations
- Reviewing and approving the QA plans and procedures
- Reporting on the adequacy, status, and effectiveness of the QA program on a regular basis to the SA2SG Project Coordinator
- Data validation of sample results from the analytical laboratory, as appropriate.

2.3.2 URS QA Officer

Robert B. Billman will serve as the URS QA Officer (QAO). As such, he will report directly to the URS Project Officer and will be responsible for verifying that all URS QA procedures for this project are being followed. In addition, he will be responsible for seeing that internal laboratory audits are conducted as specified in Section 10.

2.3.3 USEPA Region V Quality Assurance Reviewer

Michael Ribordy, the USEPA Region V RPM, or a designee, will serve as the USEPA Region V Quality Assurance Reviewer. As such, he will have the responsibility to review and approve the QAPP. In addition, he will be responsible for conducting external performance and system audits of the laboratory and field activities, and reviewing and evaluating analytical laboratory and field procedures.

2.4 FIELD RESPONSIBILITIES

2.4.1 URS Field Leader

Steven Shroff, or a designee, will serve as the URS Field Leader. He will be responsible for leading, coordinating, and supervising the day-to-day field activities. His responsibilities include:

- Provision of day-to-day coordination with the URS Project Officer on technical issues
- Develop and implement field-related sampling plans and schedule
- Coordinate and manage field staff
- Supervise or act as the field sample custodian
- Implement the QC for technical data, including field measurements

- Adhere to work schedules
- Authorize and approve text and graphics required for field team efforts
- Coordinate and oversee technical efforts of subcontractors assisting the field team
- Identify problems at the field team level, resolve difficulties in consultation with the URS Project Officer, implement and document corrective action procedures, and provide communication between team and upper management
- Prepare the final report.

2.4.2 URS Field Team

The technical staff will be drawn from URS's pool of resources. The technical staff will be utilized to gather and analyze data, and to prepare various task reports and support materials. The technical staff are experienced professionals who possess the degree of specialization and technical competence required to effectively and efficiently perform the required work.

SECTIONTHREE Project Scope and Objectives

The purpose of the FSP is to gather sufficient information from the Sauget Area 2 Sites to identify the nature of waste materials in Sites O, P, Q, R, and S and to assess the extent of constituent migration in soil, groundwater, surface water, sediments, and air at the site.

Collected data will be used by others to prepare a Human Health Risk Assessment (HHRA), an Ecological Risk Assessment (ERA), and an RI/FS. The RI/FS SSP and this FSP include a description of the sample media, sample locations, number of samples, and analytical methods.

The main components of the SSP addressed in this FSP include:

- Sites O, P, Q, R, and S source area sampling (soil gas sampling, waste sampling, buried drum and tank identification)
- Groundwater sampling (upgradient, fill areas, downgradient alluvial aquifer, bedrock, slug tests, and grain size analysis)
- Soil sampling (Sites O, P, Q, R, and S areas and off-site)
- Air sampling
- Treatability test sampling
- Stormwater sampling (exit routes from Sites Q and R).

Site plans showing sampling locations are located in Figures 1 through 12 of this FSP.

3.1 SITE CHARACTERIZATION

The November 24, 2000 Administrative Order on Consent Scope of Work identified the site characterization information needed to define the extent of contamination at Sauget Area 2.

Sections 6 to 10 of the SSP and Section 5 of this FSP address activities designed to provide site characterization data. The sections describe the number, types, and locations of additional samples that will be collected as part of the SSP.

3.1.1 Waste Characterization

The AOC SOW requires inclusion of a program in the SSP for characterizing the waste materials at the Sauget Area 2 Sites including an analysis of current information/data on past disposal practices, test pits/trenches, and deep soil borings to determine waste depths and volume and extent of cover over fill areas, soil gas surveys on and around fill areas, and geophysical delineation of potential drum removal areas. Based on the AOC SOW requirements and a

review of the 1998 Ecology and Environment report, the identified waste characterization data include:

- Past disposal practices
- Waste depths and volumes
- Extent of cover over fill areas
- Soil gas survey on and around fill areas
- Buried drum and tank identification.

Section 6 of the SSP, Waste, Soil, and Stormwater Sampling Plan, describes the work that will be performed to obtain waste characterization data.

3.1.2 Hydrogeology

The AOC SOW requires inclusion of a program in the SSP for performing a hydrogeologic investigation at the Site including assessment of the degree of hazard, regional and local flow direction and quality.

In addition, the SSP was required to develop a strategy for determining horizontal and vertical distribution of contaminants and to include slug tests, grain size analyses and upgradient samples. Based on the AOC SOW requirements and a review of the 1998 Ecology and Environment report, the identified groundwater characterization data include:

- Regional and local flow direction and quality
- Horizontal and vertical distribution of constituents
- Slug tests
- Grain size analyses
- Upgradient samples.

Section 7 of the SSP, Groundwater Sampling Plan, describes the work that will be performed to obtain groundwater characterization data.

3.1.3 Soil

The AOC SOW requires inclusion of a program in the SSP for performing a soil investigation at the Sauget Area 2 Sites to determine the extent of contamination of surface and subsurface soils. Sampling of leachate from the fill areas was also required. Based on the AOC SOW requirements and review of the 1998 Ecology and Environment report, soil characterization data include:

- Extent of contamination of surface and subsurface soils
- Leachate samples from fill areas

Section 6 of the SSP, Waste, Soil and Stormwater Sampling Plan, describes the work that will be performed to obtain soil characterization data.

3.1.4 Air

The AOC SOW requires inclusion of a program in the SSP to determine the extent of atmospheric contamination from the various source areas at the Sauget Area 2 Sites and to address the tendency of substances identified through waste characterization to enter the atmosphere, local wind patterns, and their degree of hazard. Based on the AOC SOW requirements and review of the 1998 Ecology and Environment report, air characterization data include:

- Tendency of constituents to enter the atmosphere
- Tendency of constituents to enter local wind patterns
- Degree of hazard.

Section 9 of the SSP, Air Sampling Plan, describes the work that will be performed to obtain air characterization data.

3.1.5 Pilot Treatability Tests

The AOC SOW requires inclusion of a program in the SSP for any pilot tests necessary to determine the implementability and effectiveness of technologies where sufficient information is not otherwise available. Based on the AOC SOW requirements and a review of the 1998 Ecology and Environment report, pilot treatability tests include:

- Off-site incineration
- Off-site disposal
- On-site thermal desorption
- On-site physical/chemical leachate treatment
- Off-site physical/chemical leachate treatment
- Off-site biological leachate treatment.

Section 10 of the SSP, Treatability Testing Plan, describes the work that will be performed to perform these pilot treatability tests.

3.1.6 Stormwater

In order to characterize stormwater runoff from Sites Q and R, grab samples will be collected during storm events from each disposal area at locations representing the primary drainage route from each site to the Mississippi River. First flush samples will be collected at each site for three storm events using an automated sampling device.

Section 6 of the SSP, Waste, Soil, and Stormwater Sampling Plan, describes the work that will be performed to obtain stormwater characterization data.

3.1.7 Non-Aqueous Phase Liquid

Non-aqueous phase liquid (NAPL) will be evaluated in soil and groundwater samples collected throughout the investigation by several methods. These methods include the use of visual observations, identification of unusual odors, and the screening of samples with direct-reading instruments such as oil/water interface probes, PID and/or FID devices. The presence of NAPL in any samples will be noted in field logs and other documentation as appropriate. If sufficient volume of NAPL is encountered, samples will be collected for the analysis of physical and chemical properties. For groundwater sampling (push point/Geoprobe or bedrock) the presence of NAPL will be screened and samples of NAPL collected before the well is purged. NAPL samples will be collected using a top entry bailer for LNAPL and a bottom entry bailer for DNAPL.

3.2 PROJECT SCHEDULE

The estimated project schedule is presented in Volume 1, Section 15 of the SSP.

SECTIONFOUR Non-Measurement Data Acquisition

4.1 TOPOGRAPHIC MAP AND SAMPLE LOCATION SURVEYING

4.1.1 Topographic Map

Surdex, an aerial photography and mapping subcontractor, flew the study area in late March 1999 and again in early 2001 to obtain current aerial photographs of the study area, prior to the spring emergence of vegetation. These photographs, combined with ground control surveying, will be used to prepare a topographic map of the study area with a 1 inch = 50 foot scale and a topographic contour interval of 1 ft. (This map will meet National Map Standards with a horizontal accuracy of +1- 1.25 ft and a vertical accuracy for contour lines of +1- 0.5 ft.)

4.1.2 Location And Elevation Surveying

Information submitted to USEPA Region V and IEPA describing sampling locations will be identified in the field using a global positioning satellite (GPS) system. It will be capable of producing decimal latitude and longitude readings and it will have a horizontal accuracy of one meter or less. Well elevations will be surveyed to an accuracy of ±0.01 ft. Information submitted to USEPA Region V and IEPA will be in a Microsoft Excel®-compatible electronic spreadsheet and will include columns on:

- Latitude (decimal degrees)
- Longitude (decimal degrees)
- Sample identification
- Sample description (e.g., soil, groundwater)
- Locational method
- Sample depth
- Time and date of sample collection
- Time and date of sample analysis
- Chemical parameter
- Chemical result
- Analysis method
- Detection limit

- Chemical units (ppm, ppb, mg/kg, etc.)
- Result qualifier (non-detect, etc.).

4.2 AERIAL PHOTOGRAPH ACQUISITION AND ANALYSIS

Available historical air photographs not included in the 1988 Ecology and Environment report will be obtained for Sites O, P, Q, R, and S. These photographs, and the results of the E&E evaluation, will be used to define the areal extent of each site. Boundaries of the waste disposal areas will be defined using historical aerial photographs to establish the areal extent of excavation and fill areas over time. For each photo, the boundaries of Sites O, P, Q, R, and S will be traced and input into an AutoCAD file. To define the extent of fill, the AutoCAD files will be overlain for each site and a line will be drawn around the outside boundary of the composite fill areas. If stereoscopic evaluation of historical aerial photographs allows identification of the deepest portion of the fill area, one of the four waste characterization borings, for each site, will be conducted at that location.

Results of the analysis of historical aerial photographs will be used to prepare a map for each site, showing fill area boundaries and the final selected locations of the boundary confirmation trenches and the waste characterization borings. When the map for each fill area is completed, it will be submitted to USEPA Region V for acceptance prior to performance of the boundary confirmation trenching or collection of the waste characterization samples. Boundary confirmation trenches and waste characterization borings will be located in the field by measuring from known points, such as buildings, roads, or other cultural features or by using GPS.

SECTIONFIVE Field Activities by Site

Rationale and field activity discussions have been developed for each of the five sites on a site by site basis. There are however, several types of field activities which are common to all of the sites, such as documentation, QA/QC activities, equipment decontamination, and handling of investigation derived waste. Discussion of these topics are presented below.

DOCUMENTATION

All URS personnel will keep a bound field notebook while performing sampling and oversight activities on-site. The field notebook will contain general information including but not limited to:

- Date, time, weather conditions, equipment, and personnel on site
- Site in which the work was performed
- Specific work activities conducted
- PID, CGM, and RAM readings.

In addition to the general information discussed above, the field notebook will also contain specific information regarding the daily work activities. This information will include but is not limited to:

- Samples collected
- Depth of borings or trenches
- Observations of site conditions
- All changes to the Scope of Work or Health and Safety procedures.

The minimum documentation requirements for the field notebooks are provided in Section 6 of this FSP.

QA/QC

To verify field and laboratory procedures, quality assurance/quality control (QA/QC) samples consisting of duplicate samples, matrix spike/matrix spike duplicate (MS/MSD) samples, field blanks and trip blanks will be collected and submitted to the laboratory. The sampling procedures and frequency will follow QA/QC Standard Operating Procedures (SOP) in Appendix B of this FSP.

All samples (including QA/QC samples) will be tracked using appropriate Chain-of-Custody documentation. The Chain-of-Custody procedures are described in Section 6.1.3 of this FSP. A sample chain-of-custody form is also presented in Appendix F.

Decontamination

In order to reduce the potential for exposure to hazardous materials and limit the possibility of cross contamination of samples, all personnel and equipment will be subject to the decontamination program for this project. All equipment used on-site, from a small handheld PID to a large conventional drilling rig, will be decontaminated prior to beginning work, between sampling locations and/or uses, and prior to demobilizing from the site. Several decontamination stations will be established throughout Area 2. Refer to Section 9 of this report for a discussion of the proper decontamination procedures.

Investigation Derived Waste

All Investigation Derived Waste (IDW) ranging from soil cuttings and purge water to recovered drums, will be placed in containers such as over-pack drums or roll-off containers. The various containers will be stored within a central fenced storage area pending appropriate disposal. The proper procedures for waste disposal are discussed in Section 9 of Volume 2C, The Health and Safety Plan.

The following subsections correspond to the activities to be conducted at the individual Area 2 Sites:

- Section 5.1 Site O
- Section 5.2 Site P
- Section 5.3 Site Q
- Section 5.4 Site R
- Section 5.5 Site S
- Section 5.6 Off-Site Soil and Upgradient Groundwater Locations
- Section 5.7 Area 2 Groundwater Flow Direction and Flow Rate

SECTIONFIVE

Field Activities by Site

5.1 SITE O

5.1.1 Waste Characterization

5.1.1.1 Delineation of Source Area Boundaries – Test Trenches

Rationale

Historical air photos were obtained for this site. These photos were used to define the areal extent of the site over time and to determine the boundaries of the waste disposal area. Boundaries of the site on each photo were observed. To define the maximum extent of fill, the tracings for the site were overlain and a line was drawn around the outside limit of the composite waste disposal area boundary. Results of the historical air photo analysis were used to prepare a map for the site, showing disposal area boundaries. Stereoscopic evaluation of historical air photographs allowed identification of the deepest portion of a waste disposal area, and one of the four waste characterization borings discussed below will be done at that location.

As a result of aerial photo interpretation, three additional areas were identified outside of the previously drawn boundaries for Site O. These included an area adjacent to the northern boundary, which appeared as pits associated with the operation of the P-Chem plant, an area adjacent to the southern boundary, which appeared to be associated with a breach in the dyke of the lagoon, and an area adjacent to the western boundary, which appeared to contain ponded water. Each of these areas will be investigated further through the use of test trenches and soil gas surveys as discussed below.

Test trenches will be used to confirm the boundaries of the waste disposal area identified through air photo analysis. One trench will be installed on each side of the waste disposal area. Thus, there will be a total of four trenches for the site. The four trenches will be positioned to assess the features identified on the air photos. A GPS system will be used to document the locations on aerial site maps. Test trenches will start outside the defined boundary of the disposal area and move toward the defined boundary. When fill materials are encountered, the disposal area boundary will be compared to those identified in the air photo analysis and trenching at that location will then be terminated.

Excavated soil and fill material will be returned to the test trench, with the exception of any intact drums. Intact drums will be removed, provided confined space entry is not needed to retrieve a drum. Trenches will not be entered to recover drums due to the inherent danger in

such activities. Test trench locations will be determined using a GPS system. The trench locations will be recorded for future reference, in the event drum removal is appropriate. The drum removal contractor, in accordance with the requirements of 29 CFR 1910.120(j) will handle drums recovered during trenching activities. Recovered drums will be over-packed and stored pending disposal. Free product and contaminated soil resulting from rupture of drums during removal will be cleaned up by absorbing any liquid materials. The absorbent, solid waste, and contaminated soil will be placed in bulk containers. The over-pack drums and these bulk containers will be temporarily stored at a controlled-access, fenced Investigation Derived Waste (IDW) Storage Area to be constructed at Site R. Recovered drums and wastes will be stored until the capacity of the storage pad is exceeded or the investigation is complete, whichever comes first. Any waste excavated that identifies the source of material present in the fill area will be noted in the field log and photographed.

Trenching locations will be selected in the field with the concurrence of USEPA Region V RPM or his designee.

Field Procedure

All trenching activities will be conducted in a manner to protect existing utilities, structures, surface features, monitoring wells, and the general site environment. Additionally, trenching activities will follow Occupational Safety and Health Administration (OSHA) rules for excavations.

Locations of test trenches for boundary confirmation of Site O are shown on Figure 2. A "competent" person, as defined in 29 CFR 1976.650, will observe the trenching activities and will have authorization to take corrective measures to respond to unsanitary, hazardous, or dangerous conditions to workers. A track-mounted hoe with an extended arm will be used for excavation. A photoionization detector (PID), combustible gas monitor (CGM), and a real-time aerosol monitor (RAM) will be used on a continuous basis to monitor the test trenches for hazardous conditions.

Trenching activities will begin outside the site boundary and move in towards the boundary. The trenching will extend vertically to a maximum depth of 40 ft bgs or to groundwater, whichever is encountered first. No accommodations will be made to dewater test trenches or manage groundwater during excavation activities in order to minimize the generation of investigation-

derived wastes. The trenching will continue until waste material is encountered. Should waste materials be encountered initially, the trenching activities will proceed out and away from the boundary until native soils are encountered. Where native soils are encountered, the excavation will proceed to greater depth up to a maximum of 40 ft below grade, where possible. Should waste materials be encountered again within the test trench, this procedure will be repeated until no waste materials are encountered within the test trench. The location where no additional waste materials are encountered within the test trench will be designated as the extent of the site boundary for that location.

As the trenching proceeds, spoils from the test trenches will be placed on polyethylene plastic, having a minimum thickness of 6 millimeters. Provisions will be made to allow free liquids in the spoils to drain back to the trench. Spoils from each test trench will be segregated and returned to the excavation in reverse order of removal. The gross contamination will be removed from the excavator bucket with a shovel and/or potable water source prior to handling the cover material. Decontamination debris will be placed into the excavation trench prior to placement of cover material. Handling of investigation-derived wastes from these activities is discussed in Section 9.

Backfilling will be conducted in a manner to minimize ponding of water over the trench. A silt fence will be installed around the perimeter of the trench to minimize runoff of surface soils during rain events. A test trench at one location will be backfilled prior to the initiation of a test trench at another location. After completion of site investigation activities, the sites will be revegetated with grass. The silt fence will be maintained until revegetation is completed.

The location of the test trenches will be illustrated on a plan of the site. Digital photographs will be taken of the test trenches, the test trench walls, and any waste materials excavated. The number and location of each photograph will be identified on the field log for each test trench.

5.1.1.2 Soil Gas Surveys

Rationale

A soil gas contractor will perform a soil gas survey at Site O. A shallow soil probe (5 feet) and on-site analysis of collected VOC vapors with a GC will be used in this survey. Soil gas samples will be collected at the center points of a 200 by 200 ft grid, superimposed on the disposal area, as well as along four transects perpendicular to the site boundary. These transects will be

positioned so as to extend into the areas outside of the site boundary as identified in the aerial photos. This will result in approximately 36 sampling locations. The soil gas survey sampling locations for Site O are displayed in Figure 3.

If detectable concentrations of Total VOCs are found in the soil gas samples from the transect locations, the survey will be extended beyond those locations. If need be, soil gas samples will be collected at 100-foot intervals (0, 100, and 200 feet from the outermost transect location) along as many as four 200-foot long transects. Each transect will run perpendicular to the relevant side of the disposal area. If VOCs are detected in soil gas at this site, up to twelve additional soil gas samples may be collected.

If twelve additional samples are not adequate to define the extent of VOC-containing soils in the disposal area, additional soil gas samples will be collected at 100-foot intervals along the appropriate transects until the limits of the impacted fill are determined. If soil gas surveys need to extend into areas for which there are no property access agreements, soil gas sampling will be suspended until access is obtained.

Sampling locations will be selected in the field with the concurrence of USEPA Region V RPM or his designee.

Table 2 is a sample and analysis summary for this activity.

Field Procedure

Direct push technology will be used to advance a retractable point holder to 5.5 feet below existing grade. The rods will then be pulled back to approximately 5 feet below existing grade to disengage the retractable point, therefore, exposing the sampling mechanism. Polyethylene tubing (0.125-inch diameter) will be lowered into the rods. The upper end of the polyethylene tubing will be connected to a 4-inch section of silicone tubing. This will then be attached to a section of polyethylene tubing coming from an active vacuum system and a vacuum will be placed in the tubing. A 60cc sample of soil gas will be withdrawn from the silicone tubing using a 60cc disposable syringe with a stainless steel needle. The sample will then be directly injected into the on-site GC. The GC will provide a report of the total VOC concentrations.

Sample tubing will be removed from the probe and disposed. Probing rods and sampling equipment will be removed from the boring. The probe boring will be filled with bentonite, to

just bgs. The bentonite will be hydrated with potable water and the surface will be restored to its original condition. An SOP for the field GC is contained in Appendix A.

5.1.1.3 Waste Samples

Rationale

Three borings will be advanced at this site to characterize the waste materials present. Continuous samples will be collected from grade to 2 feet below the bottom of the waste material, which is estimated to be a maximum of 40 feet below grade. If wastes are encountered at depths greater than 40 feet bgs (bgs), the boring will continue until the bottom of the waste is encountered. Scaled, color digital photographs will be taken of each waste sample to provide a record of materials present in the disposal area.

One composite waste sample will be collected at each boring location (three total composite waste samples), and analyzed for SVOCs, pesticides, herbicides, PCBs, dioxin, and metals. In addition, a portion of the composite waste sample from above the water table will be extracted using TCLP procedures and analyzed for this same suite of analytes. Visual observations and PID readings will be used to identify whether or not waste is present in a continuous boring sample. If waste is present in a sample, it will be removed, segregated, temporarily stored and used at the completion of the soil boring to prepare a composite waste sample. Since VOC samples cannot be composited without losing volatiles, the waste with the highest PID readings will be used for VOC analysis.

Existing information (e.g., the 1998 Ecology and Environment report and the results of the aerial photograph analysis, and soil gas surveys conducted as part of the SSP) will be used to select boring locations. Approximate waste characterization boring locations for Site O are shown on Figure 2. Additional waste characterization borings may be required by USEPA Region V as a result of variability in waste characteristics observed during the waste characterization boring program.

Table 3 is a sample and analysis summary for waste samples to be collected.

Field Procedure

Borings will be advanced via direct push technology (Geoprobe®). The Geoprobe® will hydraulically drive a stainless steel, acetate-lined MacroCore® sampler (2-inch diameter by 4-

foot length) to the desired subsurface sample depths. Continuous samples will be collected from grade to 2 feet below the bottom of the waste material (estimated to be 40 feet bgs). Between each sample collection, the sampler will be retrieved to the surface and the samples removed from the disposable acetate liner within the sampler.

One composite waste sample will be collected from each boring. Each sample will be visually observed and monitored with PID readings, to determine whether waste is present. If waste is present in a sample, it will be removed, segregated, temporarily stored, and used at the completion of the soil boring to prepare a composite waste sample. The sample exhibiting the highest PID reading at each of the four boring locations within this site will be used for VOC analysis. A 5-gram EnCore® sampler will be used to collect VOC samples.

Refer to Appendix C for detailed soil/waste sampling procedures.

Descriptive logs of each boring will be prepared as described in Appendix E. The three waste borings generated will also be used for surface and subsurface soil sample collection. All borings will be grouted to the surface, following retrieval of both the waste and soil samples.

Logging Unconsolidated Samples

The geologist logging samples will be responsible to interpret the samples following standard and acceptable methods. The geologist implementing this work plan will have training and experience logging boring samples. Soil will be logged according to applicable ASTM standards. As appropriate, ASTM standards will be used to log waste materials. Appendix E presents detailed instructions for logging soil and waste samples.

5.1.1.4 Buried Drum and Tank Identification

Magnetometer Survey

A magnetometer survey is typically conducted to identify anomalies indicative of drum disposal or buried tanks. Magnetometer measurements will not be made at Site O because it was closed under the supervision of Sauget P/Chem Plant personnel in 1980. No drums were present at the time of closure.

Test Trenches

Test trenches will not be installed at Site O because it was closed under the supervision of Sauget P/Chem Plant personnel in 1980. No drums were present at the time of closure.

5.1.1.5 Leachate Samples

Rationale

A 2-inch diameter well, screened at the bottom of the fill material, will be installed in one of the three waste characterization borings completed at this site. The purpose of this well is to characterize leachate at the site. The well will be sampled and analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin, and metals. The analytical methods are presented in Table 1.

Field Procedure

Well Installation

The depth and screened interval for the well will be determined in accordance with the subsurface stratigraphy observed during Geoprobe® waste sampling activities. It is expected that the waste at the site extends to approximately 40 feet bgs. Unless observed conditions indicate otherwise, a screened interval of 10 feet will be used. The well will be seated at the bottom of the waste. A 4-1/4 inch ID hollow-stem auger will be used to advance the boring to the bottom of the waste material. The well will be constructed of two-inch diameter, schedule 40 PVC casing and 0.010-inch slotted schedule 40 PVC well screen. A sand pack, consisting of silica sand, will be installed from the bottom of the well to two feet above the well screen. A bentonite seal with a thickness of between 2 feet and 3 feet will be installed directly above the sand pack. The remaining annular space will be filled with a bentonite and cement grout. The well will be completed with an aboveground well protector and a locking cap.

Following installation of the leachate well, the top of casing and ground surface will be surveyed to establish well and grade elevations and well location. Well installation details will be documented on a test boring log (Appendix D) and in the field notebook. The leachate well will generally be installed according to the typical well construction diagrams and standard procedures presented in Appendix G.

Following completion of monitoring well construction activities, the water level will be allowed to stabilize and will then be gauged to determine groundwater elevation and the total volume of groundwater in the well. After the water level in the well has been determined, the well will be developed to remove the fines from the sand pack. The development will consist of pumping or bailing the well, following the protocol described later in this section.

Sampling locations will be selected in the field with the concurrence of USEPA Region V or its designee. Figure 2 displays the approximate leachate monitoring cell location for Site O.

Well Development

Newly installed wells will require development to clear the well of accumulated sediments. Appendix H presents the standard operating procedure (SOP) for well development.

Well Purging (if necessary)

After installation and development and prior to sampling, the well may be purged to remove the standing water column from the well casing. The SOP for well purging is presented in Appendix H with the procedure for well development.

Water Level Measurements

Prior to initiating groundwater sampling, water elevations will be measured in the well. Refer to Appendix I for well gauging procedures.

Groundwater Pre-Sampling and Well Sampling

Appendix I presents the protocol for groundwater sampling activities.

5.1.2 Hydrogeology

5.1.2.1 Alluvial Aquifer

Horizontal Extent of Contaminant Migration

Rationale

Groundwater samples will be collected in the alluvial aquifer downgradient of this waste disposal area. The purpose of this sampling is to define the extent of migration away from the source area and to provide information for the Human Health Risk Assessment.

Groundwater samples will be collected at three sampling stations located on an east/west transect between the downgradient boundary of Site O and the upgradient boundary of Sites Q and R. Unfiltered groundwater samples will be collected every 10 feet from the water table to the bottom of the aquifer using push sampling technologies such as Geoprobe®, HydroPunch®, Microwell®, Waterloo Profiler® or equivalent low-flow sampling techniques. Aquifer saturated thickness is estimated to be approximately 120 feet with depth to water at 20 feet bgs and bottom of the aquifer at 140 feet bgs. All samples will be analyzed for VOCs and SVOCs. Additionally, unfiltered samples will be collected at 40 foot intervals (i.e., 20, 60, 100, 140 feet bgs) for analysis of pesticides, herbicides, PCBs, metals and several geochemical parameters (presented in Table 1). Dioxin will be analyzed only at the sampling station closest to Site O. For dioxin analysis, unfiltered groundwater samples will be collected at the top, middle, and bottom of the saturated zone (e.g., 20, 80, 140 feet bgs).

Experience at other sites indicates that push-sampling technologies such as Geoprobe® can reach depths of 60 feet. Depth of penetration can be increased at some locations by loosening the soil above the sampling horizon with a small-diameter solid stem auger before pushing the sampling probe to the required sampling depth. When the Geoprobe® sampler or equivalent sampling technology cannot penetrate to the required depth, Microwells® will be used to collect groundwater samples. These small-diameter wells are vibrated into place using a small vibratory hammer. Experience in deep aquifers at other sites indicates that sampling depths of 100 feet can be achieved. If the required sampling depths cannot be reached with either of these two technologies, conventional percussion drilling equipment will be used to drive 1-1/4 inch diameter drive points to the required sampling depths.

Table 1 presents the analytical methods. A detailed sample and analysis summary for the alluvial aquifer groundwater sampling is presented in Table 4.

Sampling locations will be selected in the field with the concurrence of USEPA Region V or its designee. Figure 4 displays approximate groundwater sampling locations for Area 2.

Field Procedure

Establishment of Boreholes

Push Point

Using the hydraulic push system of a Geoprobe®, a 4-foot stainless steel sampler with a wire wrap (slot size of 0.004 inches) will be pushed to the desired sample depth. A bailer or ball and check valve will be sent down to the slotted portion of the sampler to collect the groundwater sample. The groundwater sample will be retrieved to the surface and placed in a sample container. The Geoprobe® will then drive the sampler to the next desired sample depth, by connecting clean sections of push rods to the Geoprobe®, and a second groundwater sample will be collected here. This process will be continued until all samples are collected.

MicroWell®

It is anticipated the above sampling method will be used, as feasible. However based on the location of the site within the Mississippi River flood plain, large gravel or cobbles may be encountered, which will stop the Geoprobe®. Should this occur, MicroWells® will be installed to use as the sample collection point. The MicroWells® will be hydraulically pushed to the appropriate depth, and the sampling procedure described above will be followed. Once the sample is collected, the MicroWell® will be pulled, the screen point decontaminated according to the method described below, and a new well will be advanced further in the same hole. This procedure will be repeated until all samples are collected.

Should MicroWell® installation prove impractical, boreholes will be advanced using conventional hollow stem auger drilling methods. In this instance, the lead auger will have a screened section through which groundwater will flow. Once the sample is collected, the augers will be advanced further for collection at the next sample depth. This procedure will be repeated until all samples are collected within the borehole.

All Geoprobe®, MicroWell®, or Waterloo Profiler® holes will be sealed with grout from the bottom up and the surface will be returned to it's original condition after completion of sampling at each location. A PID, explosimeter, and a RAM will be used on a continuous basis to monitor these activities.

Groundwater Pre-Sampling and Borehole Sampling

Appendix I presents the protocol for groundwater sampling activities.

5.1.2.2 Bedrock Groundwater

Vertical Extent of Contaminant Migration

Rationale

One bedrock well will be installed downgradient of this site. The purpose of the bedrock sampling is to determine the extent of organic and inorganic constituent vertical migration from the site. Steel surface casing will be installed 5 feet into bedrock.

After installing the surface casing 5 feet into bedrock, the bedrock will be cored to a depth of 20 feet below the bottom of the casing. Cores will be digitally photographed in color against a scale and evaluated for porosity by examination and petrographic thin sections. One thin section will be made for each 2 feet of bedrock core. A 2-inch diameter, 5-foot-long screen and casing will be installed in the borehole. The screen will be filter-packed, sealed and grouted from 3 feet above the top of the filter-pack to grade. An unfiltered groundwater sample will be collected from the well following installation and development and will be analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin, and metals.

Table 1 presents the analytical methods. A detailed sample and analysis summary for the bedrock groundwater sampling is presented in Table 5.

Sampling locations will be selected in the field with the concurrence of USEPA Region V or its designee. Figure 4 displays approximate groundwater sampling locations for Site O.

Field Procedure

Mud rotary drilling methods will be used to drill the borehole to set the surface casing and to drill 5 feet into the top of bedrock. Coring will then be accomplished using wireline coring

barrels to generate a 2-inch thick minimum core. Coring will continue for 20 feet into the bedrock. The drilling and sampling procedure will be as follows:

1. A temporary 10-inch ID steel casing will be installed from ground surface to 10 feet bgs. A bentonite/cement grout will be used to fill the annular space.
2. A 8-3/4-inch ID tri-cone bit will then be used to drill down to 145 feet. A 5-inch ID steel casing will be installed from ground surface to 145 feet bgs. A bentonite/cement grout will be used to fill the annular space.
3. Wireline coring barrels (NX rods) will be used to core 20 feet into the bedrock (165 feet bgs). The coring barrels will be retrieved and opened to collect the core sample.
4. Core samples will be photographed and described on test boring logs. Descriptions will follow the procedures outlined below.
5. The borehole will then be reamed to a 4-7/8-inch diameter. A 2-inch PVC casing (schedule 80) will be installed from ground surface to 165 feet bgs (20 feet into bedrock). The PVC casing will have a 5-foot long screen (0.010-inch slots). A bentonite seal with a minimum thickness of two feet will be installed directly above the sand pack. This bentonite seal will be 3 feet in length. The remaining annular space will be filled with a bentonite and cement grout.
6. The temporary 10-inch I.D. steel casing will be removed and the well will be completed with an aboveground well protector and a locking cap.
7. Well development or purging may be necessary before collecting groundwater samples from the cased/screened hole in the bedrock. The procedures for both well development and well purging are presented below.
8. Water level measurements will then be collected, prior to sampling the bedrock groundwater. The procedure for measuring water levels is also presented below.
9. The bedrock groundwater sample collection method is presented after the procedure for water level measurements.

Well Development

Newly installed wells will require development to clear the well of accumulated sediments. Appendix H presents the standard operating procedure (SOP) for well development.

Well Purging (if necessary)

After installation and development and prior to sampling, the well may be purged to remove the standing water column from the well casing. The SOP for well purging is presented in Appendix H with the procedure for well development.

Water Level Measurements

Prior to initiating groundwater sampling, water elevations will be measured in the well. Refer to Appendix I for well gauging procedures.

Groundwater Pre-Sampling and Well Sampling

Appendix I presents the protocol for groundwater sampling activities.

Description of Rock Samples

As mentioned earlier in this section, the rock core will be evaluated via photographs and petrographic thin sections. The geologists and geotechnical engineers will write their description of rock samples with a consistent format. A detailed order and presentation of selection of data are presented in Appendix J.

Groundwater Flow Direction (water levels)

Water levels will be measured quarterly for one year in the bedrock well and used to prepare water-level elevation maps. These will show seasonal changes in groundwater level and flow direction. Water level measurements will be conducted according to the same protocol outlined in Appendix I.

Groundwater Flow Rate (slug tests)

Rationale

Falling and rising head slug tests will be performed on the bedrock well, using a slug of known volume and in-well, short-time interval, automatic water-level recorders. With the falling-head and rising-head slug test data, aquifer hydraulic conductivity will be calculated for the well. Measured groundwater gradients and calculated aquifer hydraulic conductivities will be used to determine groundwater flow rates.

Field Procedure

Appendix K presents the field protocols for the completion of *in situ* hydraulic conductivity (slug) tests.

Slug test data will be downloaded from the data logger each day. The data will be reviewed for errors. If necessary, a slug test will be re-conducted.

5.1.3 Soil

5.1.3.1 Surface Soil Samples

Rationale

Three surface soil samples (0 to 0.5 feet) will be collected at this disposal site. These samples will be collected at the location of each waste sample boring to provide information for the Human Health Risk Assessment and the Ecological Risk Assessment. Scaled, color digital photographs will be taken of each soil sample to provide a record of materials present at this site. Each sample will be analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin and metals.

Table 1 presents the analytical methods. A detailed sample and analysis summary for the surface soil sampling is presented in Table 6.

Figure 2 presents approximate soil sample locations in Site O.

Field Procedure

Surface soil samples will be discrete. A discrete sample represents a single location in the soil column. The soil samples will be collected from the Geoprobe® borings.

Appendix C presents the standard operating procedure for waste and soil sample collection.

5.1.3.2 Subsurface Soil Samples

Rationale

Three subsurface soil samples (0.5 to 6 feet) will be collected at this disposal site. As with the surface soil samples, the subsurface samples will be collected at the location of each waste sample boring to provide information for the Human Health Risk Assessment. Scaled, color

digital photographs will be taken of each soil sample to provide a record of materials present at this site. Each sample will be analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin, and metals.

Table 1 presents the analytical methods. A detailed sample and analysis summary for the subsurface soil sampling is presented in Table 7.

Figure 2 presents approximate soil sample locations for Site O.

Field Procedure

The three soil samples collected at this site will be collected at the location of each waste sample boring. The subsurface soil samples will be collected in the same manner as the waste samples.

Appendix C presents the standard operating procedure for waste and soil sample collection.

5.1.4 Air

5.1.4.1 Rationale

Two upwind and two downwind ambient air samples will be collected to determine the tendency of site constituents to enter the atmosphere and local wind patterns. Air sampling data will be used in the Human Health Risk Assessment and Ecological Risk Assessment. Samples will be analyzed for VOCs, SVOCs, pesticides, PCBs, metals, and dioxin.

Twenty-four hour cumulative duration sorbent tube/PUF/PM2.5 samples will be collected over a 1-day period, using the sampling protocols provided in Appendix L. Two upwind and two downwind samplers will be installed at the site during weather likely to produce emissions (e.g. hot and dry conditions in August). Sampling locations will be selected in the field with the concurrence of USEPA Region V or his designee. Sorbent tube samplers will be used for VOC data collection. Polyurethane foam (PUF) samplers will be used for SVOC, PCB, pesticide, and dioxin data collection. PM2.5 samplers will be used for metal data collection

Ambient air sample collection is required to measure airborne levels of contaminants that may be evolving from the site. A 24-hour sample duration is required to average the air emission differences that may occur from the day time to night time cycle from on-site and off-site conditions and activities. Also, air sample collection locations need to be positioned on the site

to collect up wind and down wind samples for differentiation of constituents originating from the surrounding area and those originating from the site. The sample protocol will collect site samples over a 1-day time period on a warm, dry day.

The level of detection for SVOCs required by USEPA Region V needs to consider sensitivity and selectivity to analyze complex samples. Based on this need, the analytical method of choice is gas chromatography coupled with mass spectrometry (GC/MS) for detection. Based on the GC/MS analytical method and its sensitivity level, the air sample volume needs to exceed 325 standard cubic feet. This enables the collection of a sufficient quantity of SVOCs to meet the level of detection required by USEPA Region V.

The sample method to meet the above requirements for SVOC measurement is USEPA Method TO-13, as identified in the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* (June 1988). This method will use a Graseby/General Metal Works, Inc. high volume air sampling unit or equivalent for sample collection. Sample collection will consist of drawing an ambient air sample at a high volume flow rate through a PUF collection media over a 24-hour time period. The samples will be submitted for analysis of the TO-13 list of SVOCs. Method TO-15 will be used to analyze VOCs. Method TO-4 will be used for pesticides, and PCBs. Method TO-9 will analyze for dioxins.

Table 8 is a sample and analysis summary of this activity.

5.1.4.2 Field Procedure

The following procedure will be used for ambient air samples:

- Place the sorbent tube samplers, PUF samplers, and PM2.5 samplers at upwind and downwind locations.
- Locate sampling positions in an unobstructed area, at least two meters from any obstacle to air flow. Sample locations will be selected in the field with the concurrence of the USEPA Region V, or its designee.
- No local power supply is readily available at the sites. Therefore, gasoline- or diesel-powered generators will be positioned at downwind locations from the sample collection positions. They will supply the electricity for the samplers.
- Record wind direction and velocity readings.

- Follow sample collection protocols identified in Appendix L for sample preparation, calibration, collection, laboratory preparation and shipment, and calculations. Sample data sheets are provided in Appendix L.

Treatability Tests

Rationale

The AOC requires that the SSP present a pilot test program for any treatment technologies lacking sufficient information on implementability and effectiveness. Data gaps exist for off-site incineration, off-site disposal, and on-site thermal desorption for the waste and on-site and off-site physical/chemical treatment, and off-site biological treatment for leachate.

A total of five composite waste samples (one for each site) will be collected for waste treatability testing and sent to appropriate facilities operators for waste profiling, material handling characterization and evaluation of the feasibility of disposing of the waste material by off-site incineration, off-site disposal, and on-site thermal desorption. In addition, five composite leachate samples (one for each site) will be collected for treatability testing to determine if the leachate can be discharged directly to American Bottoms POTW without resulting in pass through and/or interference.

One sample will be collected from each waste disposal area for waste treatability testing. The sample will be made from aliquots collected from the four waste characterization borings installed at each disposal area. One sample will be collected for the leachate treatability testing from each of the five-leachate sampling wells.

Sample Collection

The five composite waste samples that will be collected for treatability testing will be retained from the four-waste/soil borings that will be advanced at each waste disposal area. All of the material recovered from the Geoprobe® samples that are not needed for the other chemical analyses will be composited in 5-gallon buckets. Each bucket will be sealed, labeled and prepared for shipment to the appropriate facilities.

The leachate sample that will be collected for treatability testing will be collected during leachate sampling activities. An equal amount of leachate will be removed, via bailer or pump, from each of the five-leachate monitoring wells and placed in separate 5-gallon buckets. Each bucket will

be sealed, labeled and prepared for shipment to the appropriate facility.

5.2 SITE P

5.2.1 Waste Characterization

5.2.1.1 Delineation of Source Area Boundaries – Test Trenches

Rationale

Historical air photos were obtained for this site. These photos were used to define the areal extent of the site over time and to determine the boundaries of the waste disposal area. Boundaries of the site on each photo were observed. To define the maximum extent of fill, the tracings for the site were overlain and a line was drawn around the outside limit of the composite waste disposal area boundary. Results of the historical air photo analysis were used to prepare a map for the site, showing disposal area boundaries. Stereoscopic evaluation of historical air photographs allowed identification of the deepest portion of a waste disposal area, and one of the four waste characterization borings discussed below will be done at that location.

Test trenches will be used to confirm the boundaries of the waste disposal area identified through air photo analysis. One trench will be installed on each side of the waste disposal area. Thus, there will be a total of four trenches for the site. A GPS system will be used to document the locations on aerial site maps. Test trenches will start outside the defined boundary of the disposal area and move toward the defined boundary. When fill materials are encountered, the disposal area boundary will be compared to those identified in the air photo analysis and trenching at that location will then be terminated.

Excavated soil and fill material will be returned to the test trench, with the exception of any intact drums. Intact drums will be removed, provided confined space entry is not needed to retrieve a drum. Trenches will not be entered to recover drums due to the inherent danger in such activities. Test trench locations will be determined using a GPS system. The trench locations will be recorded for future reference, in the event drum removal is appropriate. The drum removal contractor, in accordance with the requirements of 29 CFR 1910.120(j) will handle drums recovered during trenching activities. Recovered drums will be over-packed and stored pending disposal. Free product and contaminated soil resulting from rupture of drums during removal will be cleaned up by absorbing any liquid materials. The absorbent, solid waste, and contaminated soil will be placed in bulk containers. The over-pack drums and these bulk

containers will be temporarily stored at a controlled-access, fenced Investigation Derived Waste (IDW) Storage Area to be constructed at Site R. Recovered drums and wastes will be stored until the capacity of the storage pad is exceeded or the investigation is complete, whichever comes first. Any waste excavated that identifies the source of material present in the fill area will be noted in the field log and photographed.

Trenching locations will be selected in the field with the concurrence of USEPA Region V RPM or his designee.

Field Procedure

All trenching activities will be conducted in a manner to protect existing utilities, structures, surface features, monitoring wells, and the general site environment. Additionally, trenching activities will follow Occupational Safety and Health Administration (OSHA) rules for excavations.

Locations of test trenches for boundary confirmation of Site P are shown on Figure 5. A "competent" person, as defined in 29 CFR 1976.650, will observe the trenching activities and will have authorization to take corrective measures to respond to unsanitary, hazardous, or dangerous conditions to workers. A track-mounted hoe with an extended arm will be used for excavation. A photoionization detector (PID), combustible gas monitor (CGM), and a real-time aerosol monitor (RAM) will be used on a continuous basis to monitor the test trenches for hazardous conditions.

Trenching activities will begin outside the site boundary and move in towards the boundary. The trenching will extend vertically to a maximum depth of 40 ft bgs or to groundwater, whichever is encountered first. No accommodations will be made to dewater test trenches or manage groundwater during excavation activities in order to minimize the generation of investigation-derived wastes. The trenching will continue until waste material is encountered. Should waste materials be encountered initially, the trenching activities will proceed out and away from the boundary until native soils are encountered. Where native soils are encountered, the excavation will proceed to greater depth up to a maximum of 40 ft below grade, where possible. Should waste materials be encountered again within the test trench, this procedure will be repeated until no waste materials are encountered within the test trench. The location where no additional

waste materials are encountered within the test trench will be designated as the extent of the site boundary for that location.

As the trenching proceeds, spoils from the test trenches will be placed on polyethylene plastic, having a minimum thickness of 6 millimeters. Provisions will be made to allow free liquids in the spoils to drain back to the trench. Spoils from each test trench will be segregated and returned to the excavation in reverse order of removal. The gross contamination will be removed from the excavator bucket with a shovel and/or potable water source prior to handling the cover material. Decontamination debris will be placed into the excavation trench prior to placement of cover material. Handling of investigation-derived wastes from these activities is discussed in Section 9.

Backfilling will be conducted in a manner to minimize ponding of water over the trench. A silt fence will be installed around the perimeter of the trench to minimize runoff of surface soils during rain events. A test trench at one location will be backfilled prior to the initiation of a test trench at another location. After completion of site investigation activities, the sites will be revegetated with grass. The silt fence will be maintained until revegetation is completed.

The location of the test trenches will be illustrated on a plan of the site. Digital photographs will be taken of the test trenches, the test trench walls, and any waste materials excavated. The number and location of each photograph will be identified on the field log for each test trench.

5.2.1.2 Soil Gas Surveys

Rationale

A soil gas contractor will perform a soil gas survey at Site P. A shallow soil probe (5 feet) and on-site analysis of collected VOC vapors with a GC will be used in this survey. Soil gas samples will be collected at the center points of a 200 by 200 ft grid, superimposed on the disposal area, resulting in approximately 25 sampling locations. The soil gas survey sampling grid for Site P is displayed in Figure 6.

If detectable concentrations of Total VOCs are found in the soil gas samples at the disposal area boundary, the survey will be extended beyond that boundary. If extended beyond the site boundary, soil gas samples will be collected at 100-foot intervals (0, 100, and 200 feet from the edge of the disposal area) along as many as four 200-foot long transects. Each transect will run

perpendicular to the relevant sides of the disposal area. If VOCs are detected in soil gas at this site, up to twelve additional soil gas samples may be collected.

If twelve additional samples are not adequate to define the extent of VOC-containing soils in the disposal area, additional soil gas samples will be collected at 100-foot intervals along the appropriate transects until the limits of the impacted fill are determined. If soil gas surveys need to extend into areas for which there are no property access agreements, soil gas sampling will be suspended until access is obtained.

Sampling locations will be selected in the field with the concurrence of USEPA Region V RPM or his designee.

Table 2 is a sample and analysis summary for this activity.

Field Procedure

Direct push technology will be used to advance a retractable point holder to 5.5 feet below existing grade. The rods will then be pulled back to approximately 5 feet below existing grade to disengage the retractable point, therefore, exposing the sampling mechanism. Polyethylene tubing (0.125-inch diameter) will be lowered into the rods. The upper end of the polyethylene tubing will be connected to a 4-inch section of silicone tubing. This will then be attached to a section of polyethylene tubing coming from an active vacuum system and a vacuum will be placed in the tubing. A 60cc sample of soil gas will be withdrawn from the silicone tubing using a 60cc disposable syringe with a stainless steel needle. The sample will then be directly injected into the on-site GC. The GC will provide a report of the total VOC concentrations.

Sample tubing will be removed from the probe and disposed. Probing rods and sampling equipment will be removed from the boring. The probe boring will be filled with bentonite, to just bgs. The bentonite will be hydrated with potable water and the surface will be restored to its original condition. An SOP for the field GC is contained in Appendix A.

5.2.1.3 Waste Samples

Rationale

Four borings will be advanced at this site to characterize the waste materials present. Continuous samples will be collected from grade to two feet below the bottom of the waste material, which is

estimated to be a maximum of 40 feet below grade. If wastes are encountered at depths greater than 40 feet bgs (bgs), the boring will continue until the bottom of the waste is encountered. Scaled, color digital photographs will be taken of each waste sample to provide a record of materials present in the disposal area.

One composite waste sample will be collected at each boring location (4 total composite waste samples), and analyzed for SVOCs, pesticides, herbicides, PCBs, dioxin, and metals. In addition, a portion of the composite waste sample from above the water table will be extracted using TCLP procedures and analyzed for this same suite of analytes. Visual observations and PID readings will be used to identify whether or not waste is present in a continuous boring sample. If waste is present in a sample, it will be removed, segregated, temporarily stored and used at the completion of the boring to prepare a composite waste sample. Since VOC samples cannot be composited without losing volatiles, the waste with the highest PID readings will be used for VOC analysis.

Existing information (e.g., the 1998 Ecology and Environment report and the results of the aerial photograph analysis, soil gas surveys, and magnetometer surveys conducted as part of the SSP) will be used to select boring locations. Approximate waste characterization boring locations for Site P are shown on Figure 5. Additional waste characterization borings may be required by USEPA Region V as a result of variability in waste characteristics observed during the waste characterization boring program.

Table 3 is a sample and analysis summary for waste samples to be collected.

Field Procedure

Borings will be advanced via direct push technology (Geoprobe®). The Geoprobe® will hydraulically drive a stainless steel, acetate-lined MacroCore® sampler (2-inch diameter by 4-foot length) to the desired subsurface sample depths. Continuous samples will be collected from grade to 2 feet below the bottom of the waste material (estimated to be 40 feet bgs). Between each sample collection, the sampler will be retrieved to the surface and the samples removed from the disposable acetate liner within the sampler.

One composite waste sample will be collected from each boring. Each sample will be visually observed and monitored with PID readings, to determine whether waste is present. If waste is present in a sample, it will be removed, segregated, temporarily stored, and used at the

completion of the boring to prepare a composite waste sample. The sample exhibiting the highest PID reading at each of the four boring locations within this site will be used for VOC analysis. A 5-gram EnCore® sampler will be used to collect VOC samples.

Refer to Appendix C for detailed soil/waste sampling procedures.

Descriptive logs of each boring will be prepared as described in Appendix E. The four waste borings generated at each of the five sites will also be used for surface and subsurface soil sample collection. All borings will be grouted to the surface, following retrieval of both the waste and soil samples.

Logging Unconsolidated Samples

The geologist logging samples will be responsible to interpret the samples following standard and acceptable methods. The geologist implementing this work plan will have training and experience logging boring samples. Soil will be logged according to applicable ASTM standards. As appropriate, ASTM standards will be used to log waste materials. Appendix E presents detailed instructions for logging soil and waste samples.

5.2.1.4 Buried Drum and Tank Identification

Magnetometer Survey

Rationale

A magnetometer survey will be conducted at this site to identify anomalies indicative of drum disposal or buried tanks. Magnetometer measurements will be made at locations determined by superimposing a 50-foot by 50-foot grid on the disposal area.

Surface geophysical surveys, which map the distribution of the strength of the earth's magnetic field, have been proven useful in evaluating shallow and deep subsurface conditions at environmental sites. These geophysical surveys have been used to successfully locate buried objects containing magnetically susceptible materials (e.g., iron and nickel metals). The ability of geophysical equipment to locate buried objects is, for the most part, dependent on:

- The strength and orientation of the magnetic anomaly associated with the buried objects
- The strength and natural variation of the earth's magnetic field in response to local geology

- The influence of man-made surface features (such as power lines, buried utilities, vehicles, electric motors, etc.) which may interfere with the collection of data.

By comparing the known surface and geological conditions to a magnetic survey map that includes mapped surface feature interferences, and understanding possible geologic background effects, it is possible to identify the location of suspicious subsurface features which may represent buried tanks or drum disposal areas.

Method

A geophysical survey of the site's magnetic field will be completed utilizing a field magnetometer and electromagnetic induction. The field magnetometer measures the strength of the site's magnetic field regardless of the orientation of the magnetic lines of force. During the performance of the geophysical survey, data for the preparation of a field map will be collected. The final product of this survey will include a description of the site, contour maps, and an explanation of how the survey was conducted.

A correction for diurnal and micropulsation time variations is not necessary because the site and anticipated anomalies are relatively small in area (less than 1 square mile), and subsurface anomalies from buried objects of interest should be relatively large (greater than 100 gammas).

The map showing the distribution of magnetic field strength over the site will be compared with the observed field conditions (including the location of known interfering objects such as vehicles, overhead power lines, and surface debris). By comparison, those magnetic anomalies, which cannot be explained by observed site conditions will be presumed to be a result of, buried subsurface material (e.g., drums, tanks, metal debris, etc.). The depth of detection for suspect objects (such as steel drums) may vary according to orientation, method of manufacture and condition, and numbers present. Steel drums, such as those suspected to be present at this site, may be detected to depths of 40 feet.

Study Area

The area of the properties to be surveyed will be evaluated in the field. Magnetometer surveys will be conducted at a total of four sites (P, Q, R, and S) within Area 2. A general area for Site P survey site has been delineated and provided on Figure 6 (Fill Area Location Map). Overall site

dimensions for the survey sites will be adjusted based upon the findings of the source area boundary delineation activities discussed in Section 5.2.1.1.

Field Procedure

The following field equipment and procedures will be employed during this geophysical investigation.

Equipment

A Geometrics 858 Cesium or a Geometrics 856AX Total Field Magnetometer will be used to collect the field data. Field procedures and operation of the instruments will be in accordance with the recommended manufacturer's field procedure and application manual.

Calibrated field survey equipment consisting of marked survey line, tape rulers, highway danger cones, and marked wooden stakes will be utilized to establish measurement locations.

Measurement Point/Grid Surveying

The established survey lines will be marked in the field using a premarked survey line to maintain straight and precise station locations. Profiles will be completed along a straight line with an unobstructed line of sight. The corners of each of the gridded areas will be marked with temporary corner stakes to permit the relocation of the measurement points within each site.

Data Processing

Following completion of the field phase of investigation, the following data processing will be performed:

- Explanation of where and how the survey was performed
- Description of each of the four sites (P, Q, R, S) in terms of magnetic anomalies detected
- A contour map of these data will be produced showing the location of the measurement points and the corresponding magnetometer reading.

Test Trenches

Rationale

Test trenches will be installed at this site to confirm the presence of buried drums of tanks. One test trench will be installed at this site. The waste disposal areas within Area 2 were used for disposal of municipal and industrial waste as well as construction debris. Magnetic anomalies are likely to be numerous, intense, and widespread. If no location criteria other than the presence of a magnetic anomaly is used to determine whether or not a test trench is appropriate, disturbance of a significant portion of each disposal area is likely to result. Excessive trenching could result in unacceptable risks to the community, on-site workers and the environment.

For this reason, four selection criteria will be used to identify where to install each test trench. Test trenching will be done at the location of the largest magnetic anomaly that coincides with:

1. A soil gas concentration high,
2. Drum or tank disposal locations identified by historical air photo interpretation,
3. An area of high groundwater concentrations (greater than 10,000 ppb) as identified by the 1998 Ecology and Environment Data Report, and
4. Major magnetic anomalies reported in the 1988 Ecology and Environment "Expanded Site Investigation, Dead Creek Project Sites at Cahokia/Sauget, Illinois".

Care will be taken not to place major emphasis on the comparison of historical groundwater concentrations and magnetic anomalies due to the extent of historical industrial groundwater pumping in the area.

Excavated soil and fill material will be returned to the test trench, with the exception of any intact drums. These will be removed, provided confined spaced entry is not needed to retrieve a drum. Trenches will not be entered to recover drums because of the danger inherent in such activities. Test trench locations will be determined using a GPS and recorded for future reference in the event drum removal is appropriate.

Recovered drums will be over-packed and stored pending disposal. Free product and contaminated soil, resulting from rupture of drums during removal, will be cleaned up by absorbing any liquid materials and placing the absorbent, solid waste, and contaminated soil in bulk containers. Over-packed drums and bulk solid and liquid containers will be stored at a

controlled-access, fenced Investigation Derived Waste (IDW) Storage Area to be constructed at Site R. Recovered drums will be stored until the capacity of the storage pad is exceeded or the investigation is complete, whichever comes first. Any waste excavated that identifies the source of material present in the disposal area will be noted in the field log and photographed.

Field Procedure

Anomaly test trench locations will be selected in the field based upon the parameters outlined in the Rationale section, and with the concurrence of the USEPA Region V or its designee.

To complete the anomaly test trench, a track-mounted or wheel-mounted hoe will be utilized. The depth to the top of buried anomalies is not expected to extend past 40 feet below grade; thus, a smaller piece of equipment may be utilized for these anomaly test trenches (in comparison to the trenches completed for delineation of the fill area boundaries). Trenching activities will be conducted in a manner to protect existing utilities, structures, surface features, monitoring wells, and the general site environment. Additionally, trenching will follow OSHA rules for excavations. A PID, CGM, and a RAM will be used on a continuous basis to monitor the anomaly test trenches for hazardous conditions. The hoe operator will have a separate supplied-air system.

Anomaly test trenches will be advanced until evidence as to the source of the anomaly is found or to a maximum depth of 40 feet, where possible. Should groundwater infiltration and/or poor soil stability result in the inability to complete a test trench to 40 feet, the trenching will be terminated at that location. No accommodations will be made to de-water test trenches or manage groundwater during excavation activities, due to the need to minimize the generation of investigation-derived wastes.

As the trenching proceeds, spoils from the test trenches will be placed on polyethylene plastic having a minimum thickness of 6 millimeters. Provisions will be made to allow free liquids in the spoils to drain back to the trench. Spoils from each test trench will be segregated and returned to the excavation in reverse order of removal. Backfilling will be conducted in a manner to minimize ponding of water over the trench. A silt fence will be installed around the perimeter of the trench to minimize runoff of surface soils during rain events.

If intact drums are found during anomaly test trench completion, they will be removed, over-packed, and stored in an area to be designated in accordance with the requirements of 29 CFR

1910.120(j). For planning purposes, it is anticipated that up to ten over-packs will be necessary per site and that one day of anomaly test trenching will occur at each of the four sites. Handling of investigation-derived wastes from these activities is discussed in Section 9.

A test trench at one location will be backfilled prior to the initiation of a test trench at another location. After completion of site investigation activities, the sites will be revegetated with grass. The silt fence will be maintained until revegetation is completed.

5.2.1.5 Leachate Samples

Rationale

A 2-inch diameter well, screened at the bottom of the fill material, will be installed in one of the four waste characterization borings completed at this site. The purpose of this well is to characterize leachate at the site. The well will be sampled and analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin, and metals. The analytical methods are presented in Table 1.

Field Procedure

Well Installation

The depth and screened interval for the well will be determined in accordance with the subsurface stratigraphy observed during Geoprobe® waste sampling activities. It is expected that the waste at the site extends to approximately 40 feet bgs. Unless observed conditions indicate otherwise, a screened interval of 10 feet will be used. The well will be seated at the bottom of the waste. A 4-1/4 inch ID hollow-stem auger will be used to advance the boring to the bottom of the waste material. The well will be constructed of two-inch diameter, schedule 40 PVC casing and 0.010-inch slotted schedule 40 PVC well screen. A sand pack, consisting of silica sand, will be installed from the bottom of the well to two feet above the well screen. A bentonite seal with a thickness of between two feet and three feet will be installed directly above the sand pack. The remaining annular space will be filled with a bentonite and cement grout. The well will be completed with an aboveground well protector and a locking cap.

Following installation of the leachate well, the top of casing and ground surface will be surveyed to establish well and grade elevations and well location. Well installation details will be documented on a test boring log (Appendix D) and in the field notebook. The leachate well will

generally be installed according to the typical well construction diagrams and standard procedures presented in Appendix G.

Following completion of monitoring well construction activities, the water level will be allowed to stabilize and will then be gauged to determine groundwater elevation and the total volume of groundwater in the well. After the water level in the well has been determined, the well will be developed to remove the fines from the sand pack. The development will consist of pumping or bailing the well, following the protocol described later in this section.

Sampling locations will be selected in the field with the concurrence of USEPA Region V or its designee. Figure 5 displays the approximate leachate monitoring well location for Site P.

Well Development

Newly installed wells will require development to clear the well of accumulated sediments. Appendix H presents the standard operating procedure (SOP) for well development.

Well Purging (if necessary)

After installation and development and prior to sampling, the well may be purged to remove the standing water column from the well casing. The SOP for well purging is presented in Appendix H with the procedure for well development.

Water Level Measurements

Prior to initiating groundwater sampling, water elevations will be measured in the well. Refer to Appendix I for well gauging procedures.

Groundwater Pre-Sampling and Well Sampling

Appendix I presents the protocol for groundwater sampling activities.

5.2.2 Hydrogeology

5.2.2.1 Alluvial Aquifer

Horizontal Extent of Contaminant Migration

Rationale

Groundwater samples will be collected in the alluvial aquifer downgradient of this waste disposal area. The purpose of this sampling is to define the extent of migration away from the source area and to provide information for the Human Health Risk Assessment.

Groundwater samples will be collected at three sampling stations located on an east/west transect between the downgradient boundary of Site P and the Mississippi River. Unfiltered groundwater samples will be collected every 10 feet from the water table to the bottom of the aquifer using push sampling technologies such as Geoprobe®, HydroPunch®, Microwell®, Waterloo Profiler® or equivalent low-flow sampling techniques. Aquifer saturated thickness is estimated to be approximately 120 feet with depth to water at 20 feet bgs and bottom of the aquifer at 140 feet bgs. All samples will be analyzed for VOCs and SVOCs. Additionally, unfiltered samples will be collected at 40 foot intervals (i.e., 20, 60, 100, and 140 foot bgs) and will be analyzed for pesticides, herbicides, PCBs, metals, and several geochemical parameters (presented in Table 1). Dioxin will be analyzed only at the sampling station closest to Site P. For dioxin analysis, unfiltered groundwater samples will be collected at the top, middle, and bottom of the saturated zone (e.g., 20, 80, 140 feet bgs).

Experience at other sites indicates that push-sampling technologies such as Geoprobe® can reach depths of 60 feet. Depth of penetration can be increased at some locations by loosening the soil above the sampling horizon with a small-diameter solid stem auger before pushing the sampling probe to the required sampling depth. When the Geoprobe® sampler or equivalent sampling technology cannot penetrate to the required depth, Microwells® will be used to collect groundwater samples. These small-diameter wells are vibrated into place using a small vibratory hammer. Experience in deep aquifers at other sites indicates that sampling depths of 100 feet can be achieved. If the required sampling depths cannot be reached with either of these two technologies, conventional percussion drilling equipment will be used to drive 1-1/4 inch diameter drive points to the required sampling depths.

Table 1 presents the analytical methods. A detailed sample and analysis summary for the alluvial aquifer groundwater sampling is presented in Table 4.

Sampling locations will be selected in the field with the concurrence of USEPA Region V or its designee. Figure 4 displays approximate groundwater sampling locations for Area 2.

Field Procedure

Establishment of Boreholes

Push Point

Using the hydraulic push system of a Geoprobe®, a 4-foot stainless steel sampler with a wire wrap (slot size of 0.004 inches) will be pushed to the desired sample depth. A bailer or ball and check valve will be sent down to the slotted portion of the sampler to collect the groundwater sample. The groundwater sample will be retrieved to the surface and placed in a sample container. The Geoprobe® will then drive the sampler to the next desired sample depth, by connecting clean sections of push rods to the Geoprobe®, and a second groundwater sample will be collected here. This process will be continued until all samples are collected.

MicroWell®

It is anticipated the above sampling method will be used, as feasible. However based on the location of the site within the Mississippi River flood plain, large gravel or cobbles may be encountered, which will stop the Geoprobe®. Should this occur, MicroWells® will be installed to use as the sample collection point. The MicroWells® will be hydraulically pushed to the appropriate depth, and the sampling procedure described above will be followed. Once the sample is collected, the MicroWell® will be pulled, the screen point decontaminated according to the method described below, and a new well will be advanced further in the same hole. This procedure will be repeated until all samples are collected.

Should MicroWell® installation prove impractical, boreholes will be advanced using conventional hollow stem auger drilling methods. In this instance, the lead auger will have a screened section through which groundwater will flow. Once the sample is collected, the augers will be advanced further for collection at the next sample depth. This procedure will be repeated until all samples are collected within the borehole.

All Geoprobe®, MicroWell®, or Waterloo Profiler® holes will be sealed with grout from the bottom up and the surface will be returned to it's original condition after completion of sampling at each location. A PID, explosimeter, and a RAM will be used on a continuous basis to monitor these activities.

Groundwater Pre-Sampling and Borehole Sampling

Appendix I presents the protocol for groundwater sampling activities.

5.2.2.2 Bedrock Groundwater

Vertical Extent of Contaminant Migration

Rationale

One bedrock well will be installed downgradient of this site. The purpose of the bedrock sampling is to determine the extent of organic and inorganic constituent vertical migration from the site. Steel surface casing will be installed 5 feet into bedrock.

After installing the surface casing 5 feet into bedrock, the bedrock will be cored to a depth of 20 feet below the bottom of the casing. Cores will be digitally photographed in color against a scale and evaluated for porosity by examination and petrographic thin sections. One thin section will be made for each 2 feet of bedrock core. A 2-inch diameter, 5-foot-long screen and casing will be installed in the borehole. The screen will be filter-packed, sealed and grouted from 3 feet above the top of the filter-pack to grade. An unfiltered groundwater sample will be collected from the well following installation and development and will be analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin, and metals.

Table 1 presents the analytical methods. A detailed sample and analysis summary for the bedrock groundwater sampling is presented in Table 5.

Sampling locations will be selected in the field with the concurrence of USEPA Region V or its designee. Figure 4 displays approximate groundwater sampling locations for Site P.

Field Procedure

Mud rotary drilling methods will be used to drill the borehole to set the surface casing and to drill 5 feet into the top of bedrock. Coring will then be accomplished using wireline coring

barrels to generate a 2-inch thick minimum core. Coring will continue for 20 feet into the bedrock. The drilling and sampling procedure will be as follows:

1. A temporary 10-inch ID steel casing will be installed from ground surface to 10 feet bgs. A bentonite/cement grout will be used to fill the annular space.
2. A 8-3/4-inch ID tri-cone bit will then be used to drill down to 145 feet. A 5-inch ID steel casing will be installed from ground surface to 145 feet bgs. A bentonite/cement grout will be used to fill the annular space.
3. Wireline coring barrels (NX rods) will be used to core 20 feet into the bedrock (165 feet bgs). The coring barrels will be retrieved and opened to collect the core sample.
4. Core samples will be photographed and described on test boring logs. Descriptions will follow the procedures outlined below.
5. The borehole will then be reamed to a 4-7/8-inch diameter. A 2-inch PVC casing (schedule 80) will be installed from ground surface to 165 feet bgs (20 feet into bedrock). The PVC casing will have a 5-foot long screen (0.010-inch slots). A bentonite seal with a minimum thickness of two feet will be installed directly above the sand pack. This bentonite seal will be 3 feet in length. The remaining annular space will be filled with a bentonite and cement grout.
6. The temporary 10-inch I.D. steel casing will be removed and the well will be completed with an aboveground well protector and a locking cap.
7. Well development or purging may be necessary before collecting groundwater samples from the cased/screened hole in the bedrock. The procedures for both well development and well purging are presented below.
8. Water level measurements will then be collected, prior to sampling the bedrock groundwater. The procedure for measuring water levels is also presented below.
9. The bedrock groundwater sample collection method is presented after the procedure for water level measurements.

Well Development

Newly installed wells will require development to clear the well of accumulated sediments. Appendix H presents the standard operating procedure (SOP) for well development.

Well Purging (if necessary)

After installation and development and prior to sampling, the well may be purged to remove the standing water column from the well casing. The SOP for well purging is presented in Appendix H with the procedure for well development.

Water Level Measurements

Prior to initiating groundwater sampling, water elevations will be measured in the well. Refer to Appendix I for well gauging procedures.

Groundwater Pre-Sampling and Well Sampling

Appendix I presents the protocol for groundwater sampling activities.

Description of Rock Samples

As mentioned earlier in this section, the rock core will be evaluated via photographs and petrographic thin sections. The geologists and geotechnical engineers will write their description of rock samples with a consistent format. A detailed order and presentation of selection of data are presented in Appendix J.

Groundwater Flow Direction (water levels)

Water levels will be measured quarterly for one year in the bedrock well and used to prepare water-level elevation maps. These will show seasonal changes in groundwater level and flow direction. Water level measurements will be conducted according to the same protocol outlined in Appendix I.

Groundwater Flow Rate (slug tests)

Rationale

Falling and rising head slug tests will be performed on the bedrock well, using a slug of known volume and in-well, short-time interval, automatic water-level recorders. With the falling-head and rising-head slug test data, aquifer hydraulic conductivity will be calculated for the well. Measured groundwater gradients and calculated aquifer hydraulic conductivities will be used to determine groundwater flow rates.

Field Procedure

Appendix K presents the field protocols for the completion of *in situ* hydraulic conductivity (slug) tests.

Slug test data will be downloaded from the data logger each day. The data will be reviewed for errors. If necessary, a slug test will be re-conducted.

5.2.3 Soil

5.2.3.1 Surface Soil Samples

Rationale

Four surface soil samples (0 to 0.5 feet) will be collected at this disposal site. These samples will be collected at the location of each waste sample boring to provide information for the Human Health Risk Assessment and the Ecological Risk Assessment. Scaled, color digital photographs will be taken of each soil sample to provide a record of materials present at this site. Each sample will be analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin, and metals.

Table 1 presents the analytical methods. A detailed sample and analysis summary for the surface soil sampling is presented in Table 6.

Figure 5 presents approximate soil sample locations in Site P.

Field Procedure

Surface soil samples will be discrete. A discrete sample represents a single location in the soil column. The soil samples will be collected from the Geoprobe® borings.

Appendix C presents the standard operating procedure for waste and soil sample collection.

5.2.3.2 Subsurface Soil Samples

Rationale

Four subsurface soil samples (0.5 to 6 feet) will be collected at this disposal site. As with the surface soil samples, the subsurface samples will be collected at the location of each waste sample boring to provide information for the Human Health Risk Assessment. Scaled, color digital photographs will be taken of each soil sample to provide a record of materials present at

this site. Each sample will be analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin, and metals.

Table 1 presents the analytical methods. A detailed sample and analysis summary for the subsurface soil sampling is presented in Table 7.

Figure 5 presents approximate soil sample locations for Site P.

Field Procedure

The four soil samples collected at this site will be collected at the location of each waste sample boring. The subsurface soil samples will be collected in the same manner as the waste samples.

Appendix C presents the standard operating procedure for waste and soil sample collection.

5.2.4 Air

5.2.4.1 Rationale

Two upwind and two downwind ambient air samples will be collected to determine the tendency of site constituents to enter the atmosphere and local wind patterns. Air sampling data will be used in the Human Health Risk Assessment and the Ecological Risk Assessment. Samples will be analyzed for VOCs, SVOCs, pesticides, PCBs, metals, and dioxin.

Twenty-four hour cumulative duration sorbent tube/PUF/PM2.5 samples will be collected over a 1-day period, using the sampling protocols provided in Appendix L. Two upwind and two downwind samplers will be installed at the site during weather likely to produce emissions (e.g. hot and dry conditions in August). Sampling locations will be selected in the field with the concurrence of USEPA Region V or his designee. Sorbent tube samplers will be used for VOC data collection. Polyurethane foam (PUF) samplers will be used for SVOC, PCB, pesticide, and dioxin data collection. PM2.5 samplers will be used for metal data collection

Ambient air sample collection is required to measure airborne levels of contaminants that may be evolving from the site. A 24-hour sample duration is required to average the air emission differences that may occur from the day time to night time cycle from on-site and off-site conditions and activities. Also, air sample collection locations need to be positioned on the site to collect up wind and down wind samples for differentiation of constituents originating from the

surrounding area and those originating from the site. The sample protocol will collect site samples over a 1-day time period on a warm, dry day.

The level of detection for SVOCs required by USEPA Region V needs to consider sensitivity and selectivity to analyze complex samples. Based on this need, the analytical method of choice is gas chromatography coupled with mass spectrometry (GC/MS) for detection. Based on the GC/MS analytical method and its sensitivity level, the air sample volume needs to exceed 325 standard cubic feet. This enables the collection of a sufficient quantity of SVOCs to meet the level of detection required by USEPA Region V.

The sample method to meet the above requirements for SVOC measurement is USEPA Method TO-13, as identified in the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* (June 1988). This method will use a Graseby/General Metal Works, Inc. high volume air sampling unit or equivalent for sample collection. Sample collection will consist of drawing an ambient air sample at a high volume flow rate through a PUF collection media over a 24-hour time period. The samples will be submitted for analysis of the TO-4 list of SVOCs. Method TO-15 will be used to analyze VOCs. Method TO-13 will be used for pesticides, and PCBs. Method TO-9 will analyze for dioxins.

Table 8 is a sample and analysis summary of this activity.

5.2.4.2 Field Procedure

The following procedure will be used for ambient air samples:

- Place the sorbent tube samplers, PUF samplers, and PM2.5 samplers at upwind and downwind locations.
- Locate sampling positions in an unobstructed area, at least two meters from any obstacle to air flow. Sample locations will be selected in the field with the concurrence of the USEPA Region V, or its designee.
- No local power supply is readily available at the sites. Therefore, gasoline- or diesel-powered generators will be positioned at downwind locations from the sample collection positions. They will supply the electricity for the samplers.
- Record wind direction and velocity readings.

- Follow sample collection protocols identified in methods Appendix L for sample preparation, calibration, collection, laboratory preparation and shipment, and calculations. Sample data sheets are provided in Appendix L.

Treatability Tests

Rationale

The AOC requires that the SSP present a pilot test program for any treatment technologies lacking sufficient information on implementability and effectiveness. Data gaps exist for off-site incineration, off-site disposal, and on-site thermal desorption for the waste and on-site and off-site physical/chemical treatment, and off-site biological treatment for leachate.

A total of five composite waste samples (one for each site) will be collected for waste treatability testing and sent to appropriate facilities operators for waste profiling, material handling characterization and evaluation of the feasibility of disposing of the waste material by off-site incineration, off-site disposal, and on-site thermal desorption. In addition, five composite leachate samples (one for each site) will be collected for treatability testing to determine if the leachate can be discharged directly to American Bottoms POTW without resulting in pass through and/or interference.

One sample will be collected from each waste disposal area for waste treatability testing. The sample will be made from aliquots collected from the four waste characterization borings installed at each disposal area. One sample will be collected for the leachate treatability testing from each of the five-leachate sampling wells.

Sample Collection

The five composite waste samples that will be collected for treatability testing will be retained from the four-waste/soil borings that will be advanced at each waste disposal area. All of the material recovered from the Geoprobe® samples that are not needed for the other chemical analyses will be composited in 5-gallon buckets. Each bucket will be sealed, labeled and prepared for shipment to the appropriate facilities.

The leachate sample that will be collected for treatability testing will be collected during leachate sampling activities. An equal amount of leachate will be removed, via bailer or pump, from each of the five-leachate monitoring wells and placed in separate 5-gallon buckets. Each bucket will

be sealed, labeled and prepared for shipment to the appropriate facility.

5.3 SITE Q

Because of the larger size and limited extent of previous investigation data for this site, Site Q will be partitioned into three areas and each will be investigated using the investigative programs as discussed below. Generally speaking, the investigative program has been tripled for Site Q as compared to the other four sites. In addition, for these same reasons, a field screening program utilizing on-site analysis of soil samples for VOCs and SVOCs by GC/MS and metals by XRF has been employed at Site Q.

5.3.1 Waste Characterization

5.3.1.1 Delineation of Source Area Boundaries – Test Trenches

Rationale

Historical air photos were obtained for this site. These photos were used to define the areal extent of the site over time and to determine the boundaries of the waste disposal area. Boundaries of the site on each photo were observed. To define the maximum extent of fill, the tracings for the site were overlain and a line was drawn around the outside limit of the composite waste disposal area boundary. Results of the historical air photo analysis were used to prepare a map for the site, showing disposal area boundaries. Stereoscopic evaluation of historical air photographs allows identification of the deepest portion of a waste disposal area, and one or more of the waste characterization borings discussed below will be done at that location.

The triangular portion of property, which is currently excluded from the site boundaries (adjacent to the river), was also assessed during the historical aerial photography review. This analyses did not indicate potential waste disposal activities have occurred on this piece of property, therefore the soil gas survey and magnetometer survey was not conducted in this area.

Test trenches will be used to confirm the boundaries of the waste disposal area identified through the air photo analysis, magnetometer survey, soil gas survey, and field screening program. One trench will be installed on each side of the waste disposal area for both the northern and southern half. The trenching program for the center area will focus on buried drum identification as discussed elsewhere in this section. Thus, there will be a total of eight trenches utilized for boundary delineation for the site. The eight trenches will be located at the midpoint of the

longest sides of the defined site boundary. A GPS system will be used to document the locations on aerial site maps. Test trenches will start outside the defined boundary of the disposal area and move toward the defined boundary. When fill materials are encountered, the disposal area boundary will be compared to those identified in the air photo analysis and trenching at that location will then be terminated.

Excavated soil and fill material will be returned to the test trench, with the exception of any intact drums. Intact drums will be removed, provided confined space entry is not needed to retrieve a drum. Trenches will not be entered to recover drums due to the inherent danger in such activities. Test trench locations will be determined using a GPS system. The trench locations will be recorded for future reference, in the event drum removal is appropriate. The drum removal contractor, in accordance with the requirements of 29 CFR 1910.120(j) will handle drums recovered during trenching activities. Recovered drums will be over-packed and stored pending disposal. Free product and contaminated soil resulting from rupture of drums during removal will be cleaned up by absorbing any liquid materials. The absorbent, solid waste, and contaminated soil will be placed in bulk containers. The over-packed drums and these bulk containers will be temporarily stored at a controlled-access, fenced Investigation Derived Waste (IDW) Storage Area to be constructed at Site R. Recovered drums and wastes will be stored until the capacity of the storage pad is exceeded or the investigation is complete, whichever comes first. Any waste excavated that identifies the source of material present in the fill area will be noted in the field log and photographed.

Trenching locations will be selected in the field with the concurrence of USEPA Region V RPM or his designee.

Field Procedure

All trenching activities will be conducted in a manner to protect existing utilities, structures, surface features, monitoring wells, and the general site environment. Additionally, trenching activities will follow Occupational Safety and Health Administration (OSHA) rules for excavations.

Locations of test trenches for boundary confirmation of Site Q are shown on Figure 7. A "competent" person, as defined in 29 CFR 1976.650, will observe the trenching activities and will have authorization to take corrective measures to respond to unsanitary, hazardous, or

dangerous conditions to workers. A track-mounted hoe with an extended arm will be used for excavation. A photoionization detector (PID), combustible gas monitor (CGM), and a real-time aerosol monitor (RAM) will be used on a continuous basis to monitor the test trenches for hazardous conditions.

Trenching activities will begin outside the site boundary and move in towards the boundary. The trenching will extend vertically to a maximum depth of 40 ft bgs or to groundwater, whichever is encountered first. No accommodations will be made to dewater test trenches or manage groundwater during excavation activities in order to minimize the generation of investigation-derived wastes. The trenching will continue until waste material is encountered. Should waste materials be encountered initially, the trenching activities will proceed out and away from the boundary until native soils are encountered. Where native soils are encountered, the excavation will proceed to greater depth up to a maximum of 40 ft below grade, where possible. Should waste materials be encountered again within the test trench, this procedure will be repeated until no waste materials are encountered within the test trench. The location where no additional waste materials are encountered within the test trench will be designated as the extent of the site boundary for that location.

As the trenching proceeds, spoils from the test trenches will be placed on polyethylene plastic, having a minimum thickness of 6 millimeters. Provisions will be made to allow free liquids in the spoils to drain back to the trench. Spoils from each test trench will be segregated and returned to the excavation in reverse order of removal. The gross contamination will be removed from the excavator bucket with a shovel and/or potable water source prior to handling the cover material. Decontamination debris will be placed into the excavation trench prior to placement of cover material. Handling of investigation-derived wastes from these activities is discussed in Section 9.

Backfilling will be conducted in a manner to minimize ponding of water over the trench. A silt fence will be installed around the perimeter of the trench to minimize runoff of surface soils during rain events. A test trench at one location will be backfilled prior to the initiation of a test trench at another location. After completion of site investigation activities, the sites will be revegetated with grass. The silt fence will be maintained until revegetation is completed.

The location of the test trenches will be illustrated on a plan of the site. Digital photographs will be taken of the test trenches, the test trench walls, and any waste materials excavated. The number and location of each photograph will be identified on the field log for each test trench.

5.3.1.2 Soil Gas Surveys

Rationale

A soil gas contractor previously performed a soil gas survey at Site Q. A shallow soil probe (5 feet) and on-site analysis of collected VOC vapors with a GC was used in this survey. Soil gas samples werecollected at the center points of a 200 by 200 ft grid, superimposed on the disposal area resulting in 182 locations. The soil gas survey sampling grid for Site Q is displayed in Figure 8.

In several instances, detectable concentrations of Total VOCs were found in the soil gas samples at the disposal area boundary, therefore the survey was extended beyond that boundary. For the survey which was extended beyond the site boundary, soil gas samples were collected at 100-foot intervals (0, 100, and 200 feet from the edge of the disposal area) along one transect at the southern boundary. No VOCs were detected in the soil gas from the off-site samples.

In several locations, the soil gas surveys extended into areas for which there are no property access agreements, therefore soil gas sampling was not conducted in these areas.

Based on the results of the aerial photo review, in which no waste disposal activities were identified in these areas, as well as the significant vegetation growth in these areas, no further soil gas survey work is planned for Site Q..

Table 2 is a sample and analysis summary for this activity.

Field Procedure

Direct push technology was used to advance a retractable point holder to 5.5 feet below existing grade. The rods were then pulled back to approximately 5 feet below existing grade to disengage the retractable point, therefore, exposing the sampling mechanism. Polyethylene tubing (0.125-inch diameter) was lowered into the rods. The upper end of the polyethylene tubing was connected to a 4-inch section of silicone tubing. This was then attached to a section of polyethylene tubing coming from an active vacuum system and a vacuum was placed in the

tubing. A 60cc sample of soil gas was withdrawn from the silicone tubing using a 60cc disposable syringe with a stainless steel needle. The sample was then directly injected into the on-site GC. The GC provided a report of the total VOC concentrations.

Sample tubing was removed from the probe and disposed. Probing rods and sampling equipment was removed from the boring. The probe boring was filled with bentonite, to just bgs. The bentonite will be hydrated with potable water and the surface was restored to its original condition. An SOP for the field GC is contained in Appendix A.

5.3.1.3 Field Screening for Soil Samples

Rationale

A field screening program for soil samples was conducted at Site Q. The objective of this effort was to determine if areas of elevated VOC, SVOC, or metals concentrations exist at this site using a grid-based sampling approach. This data has been used to help identify sampling locations for the soil, waste, and leachate sampling efforts. A mobile laboratory contractor performed a soil screening survey at Site Q. A shallow soil probe and on-site analysis of soil samples for VOCs and SVOCs by GC/MS and metals by XRF was used in this survey. Soil samples were collected at the center points of a 200 by 200 ft grid, superimposed on the disposal area. The soil screening survey sampling grid for Site Q is displayed in Figure 8.

Sampling locations were selected in the field with the concurrence of USEPA Region V RPM or his designee.

Field Procedure

Direct push technology (Geoprobe®) was used to advance a shallow boring to 5.5 feet below exiting grade. The Geoprobe® hydraulically drove a stainless steel, acetate-lined Macrobore® sampler (2-inch diameter by 4-foot length) to the desired sample depths. Between each sample collection, the sampler was retrieved to the surface and samples removed from the disposable acetate liner within the sampler. These samples were properly labeled and transported to the mobile field laboratory for analysis. VOC and SVOC concentrations were determined by GC/MS methodology, and concentrations of the RCRA eight metals were determined by XRF methodology. Upon completion, the probe boring was filled with bentonite to just below ground surface. The bentonite was hydrated with potable water and the surface was restored to its original condition. An SOP for the XRF and field GC/MS is contained in Appendix A.

5.3.1.4 Waste Samples

Rationale

Twelve borings will be advanced at this site to characterize the waste materials present. Continuous samples will be collected from grade to two feet below the bottom of the waste material, which is estimated to be a maximum of 40 feet below grade. If wastes are encountered at depths greater than 40 feet bgs (bgs), the boring will continue until the bottom of the waste is encountered. Scaled, color digital photographs will be taken of each waste sample to provide a record of materials present in the disposal area.

One composite waste sample will be collected at each boring location (twelve total composite waste samples), and analyzed for SVOCs, pesticides, herbicides, PCBs, dioxin, and metals. In addition, a portion of the composite waste sample from above the water table will be extracted using TCLP procedures and analyzed for this same suite of analytes. Visual observations and PID readings will be used to identify whether or not waste is present in a continuous boring sample. If waste is present in a sample, it will be removed, segregated, temporarily stored and used at the completion of the boring to prepare a composite waste sample. Since VOC samples cannot be composited without losing volatiles, the waste with the highest PID readings will be used for VOC analysis.

Existing information (e.g., the 1998 Ecology and Environment report and the results of the aerial photograph analysis, soil gas surveys, field screening of soil samples by GC/MS and XRF methodology and magnetometer surveys conducted as part of the SSP) have been used to select boring locations. Approximate waste characterization boring locations for Site Q are shown on Figure 7. Additional waste characterization borings may be required by USEPA Region V as a result of variability in waste characteristics observed during the waste characterization boring program.

Table 3 is a sample and analysis summary for waste samples to be collected.

Field Procedure

Borings will be advanced via direct push technology (Geoprobe®). The Geoprobe® will hydraulically drive a stainless steel, acetate-lined MacroCore® sampler (2-inch diameter by 4-foot length) to the desired subsurface sample depths. Continuous soil samples will be collected from grade to 2 feet below the bottom of the waste material (estimated to be 40 feet bgs).

Between each sample collection, the sampler will be retrieved to the surface and the samples removed from the disposable acetate liner within the sampler.

One composite waste sample will be collected from each boring. Each sample will be visually observed and monitored with PID readings, to determine whether waste is present. If waste is present in a sample, it will be removed, segregated, temporarily stored, and used at the completion of the boring to prepare a composite waste sample. The sample exhibiting the highest PID reading at each of the four boring locations within this site will be used for VOC analysis. A 5-gram EnCore® sampler will be used to collect VOC samples.

Refer to Appendix C for detailed soil/waste sampling procedures.

Descriptive logs of each boring will be prepared as described in Appendix E. The 12 waste borings generated will also be used for surface and subsurface soil sample collection. All borings will be grouted to the surface, following retrieval of both the waste and soil samples.

Logging Unconsolidated Samples

The geologist logging samples will be responsible to interpret the samples following standard and acceptable methods. The geologist implementing this work plan will have training and experience logging boring samples. Soil will be logged according to applicable ASTM standards. As appropriate, ASTM standards will be used to log waste materials. Appendix E presents detailed instructions for logging soil and waste samples.

5.3.1.5 Buried Drum and Tank Identification

Magnetometer Survey

Rationale

A magnetometer survey was conducted at this site to identify anomalies indicative of drum disposal or buried tanks. Magnetometer measurements were made at locations determined by superimposing a 50-foot by 50-foot grid on the disposal area.

Surface geophysical surveys, which map the distribution of the strength of the earth's magnetic field, have been proven useful in evaluating shallow and deep subsurface conditions at environmental sites. These geophysical surveys have been used to successfully locate buried

objects containing magnetically susceptible materials (e.g., iron and nickel metals). The ability of geophysical equipment to locate buried objects is, for the most part, dependent on:

- The strength and orientation of the magnetic anomaly associated with the buried objects
- The strength and natural variation of the earth's magnetic field in response to local geology
- The influence of man-made surface features (such as power lines, buried utilities, vehicles, electric motors, etc.) which may interfere with the collection of data.

By comparing the known surface and geological conditions to a magnetic survey map that includes mapped surface feature interferences, and understanding possible geologic background effects, it is possible to identify the location of suspicious subsurface features which may represent buried tanks or drum disposal areas.

Method

A geophysical survey of the site's magnetic field was completed utilizing a field magnetometer and electromagnetic induction. The field magnetometer measures the strength of the site's magnetic field regardless of the orientation of the magnetic lines of force. During the performance of the geophysical survey, data for the preparation of a field map was collected. The final product of this survey will include a description of the site, contour maps, and an explanation of how the survey was conducted.

A correction for diurnal and micropulsation time variations is not necessary because the site and anticipated anomalies are relatively small in area (less than 1 square mile), and subsurface anomalies from buried objects of interest should be relatively large (greater than 100 gammas).

The map showing the distribution of magnetic field strength over the site was compared with the observed field conditions (including the location of known interfering objects such as vehicles, overhead power lines, and surface debris). By comparison, those magnetic anomalies, which cannot be explained by observed site conditions are presumed to be a result of buried subsurface material (e.g., drums, tanks, metal debris, etc.). The depth of detection for suspect objects (such as steel drums) may vary according to orientation, method of manufacture and condition, and numbers present. Steel drums, such as those suspected to be present at this site, may be detected to depths of 40 feet.

Study Area

The area of the properties surveyed were evaluated in the field. Magnetometer surveys will be conducted at a total of four sites (P, Q, R, and S) within Area 2. A general area for Site Q survey site has been delineated and provided on Figure 8 (Fill Area Location Map). Overall site dimensions for the survey sites will be adjusted based upon the findings of the source area boundary delineation activities discussed in Section 5.2.1.1.

Field Procedure

The following field equipment and procedures will be employed during this geophysical investigation.

Equipment

Field procedures and operation of the instruments were in accordance with the recommended manufacturer's field procedure and application manual.

Calibrated field survey equipment consisting of marked survey line, tape rulers, highway danger cones, and marked wooden stakes were utilized to establish measurement locations.

Measurement Point/Grid Surveying

The established survey lines were marked in the field using a premarked survey line to maintain straight and precise station locations. Profiles were completed along a straight line with an unobstructed line of sight. The corners of each of the gridded areas were marked with temporary corner stakes to permit the relocation of the measurement points within each site.

Data Processing

Following completion of the field phase of investigation, the following data processing will be performed:

- Explanation of where and how the survey was performed
- Description of each of the four sites (P, Q, R, S) in terms of magnetic anomalies detected
- A contour map of these data will be produced showing the location of the measurement points and the corresponding magnetometer reading.

Test Trenches

Rationale

Test trenches will be installed at this site to confirm the presence of buried drums of tanks. Based on the results of the magnetometer survey, one trench will be located in each of the northern and southern portions of the site, one trench will be located between the southern and center portions, and five trenches will be located in the center portion, for a total of eight trenches.

Excavated soil and fill material will be returned to the test trench, with the exception of any intact drums. These will be removed, provided confined spaced entry is not needed to retrieve a drum. Trenches will not be entered to recover drums because of the danger inherent in such activities. Test trench locations will be determined using a GPS and recorded for future reference in the event drum removal is appropriate.

Recovered drums will be over-packed and stored pending disposal. Free product and contaminated soil, resulting from rupture of drums during removal, will be cleaned up by absorbing any liquid materials and placing the absorbent, solid waste, and contaminated soil in bulk containers. Over-packed drums and bulk solid and liquid containers will be stored at a controlled-access, fenced Investigation Derived Waste (IDW) Storage Area to be constructed at Site R. Recovered drums will be stored until the capacity of the storage pad is exceeded or the investigation is complete, whichever comes first. Any waste excavated that identifies the source of material present in the disposal area will be noted in the field log and photographed.

Field Procedure

Anomaly test trench locations have been selected based upon the parameters outlined in the Rationale section, and with the concurrence of the USEPA Region V or its designee.

To complete the anomaly test trench, a track-mounted or wheel-mounted hoe will be utilized. The depth to the top of buried anomalies is not expected to extend past 40 feet below grade; thus, a smaller piece of equipment may be utilized for these anomaly test trenches (in comparison to the trenches completed for delineation of the fill area boundaries). Trenching activities will be conducted in a manner to protect existing utilities, structures, surface features, monitoring wells, and the general site environment. Additionally, trenching will follow OSHA rules for excavations. A PID, CGM, and a RAM will be used on a continuous basis to monitor the

anomaly test trenches for hazardous conditions. The hoe operator will have a separate supplied-air system.

Anomaly test trenches will be advanced until evidence as to the source of the anomaly is found or to a maximum depth of 40 feet, where possible. Should groundwater infiltration and/or poor soil stability result in the inability to complete a test trench to 40 feet, the trenching will be terminated at that location. No accommodations will be made to de-water test trenches or manage groundwater during excavation activities, due to the need to minimize the generation of investigation-derived wastes.

As the trenching proceeds, spoils from the test trenches will be placed on polyethylene plastic having a minimum thickness of 6 millimeters. Provisions will be made to allow free liquids in the spoils to drain back to the trench. Spoils from each test trench will be segregated and returned to the excavation in reverse order of removal. Backfilling will be conducted in a manner to minimize ponding of water over the trench. A silt fence will be installed around the perimeter of the trench to minimize runoff of surface soils during rain events.

If intact drums are found during anomaly test trench completion, they will be removed, over-packed, and stored in an area to be designated in accordance with the requirements of 29 CFR 1910.120(j). For planning purposes, it is anticipated that up to ten over-packs will be necessary per site and that one day of anomaly test trenching will occur at each of the four sites. Handling of investigation-derived wastes from these activities is discussed in Section 9.

A test trench at one location will be backfilled prior to the initiation of a test trench at another location. After completion of site investigation activities, the sites will be revegetated with grass. The silt fence will be maintained until revegetation is completed.

5.3.1.6 Leachate Samples

Rationale

A 2-inch diameter well, screened at the bottom of the fill material, will be installed in three of the twelve waste characterization borings completed at this site, one each in the north, central, and south portions. The purpose of these wells is to characterize leachate at the site. The wells will be sampled and analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin, and metals. The analytical methods are presented in Table 1.

Field Procedure

Well Installation

The depth and screened interval for the wells will be determined in accordance with the subsurface stratigraphy observed during Geoprobe® waste sampling activities. It is expected that the waste at the site extends to approximately 40 feet bgs. Unless observed conditions indicate otherwise, a screened interval of 10 feet will be used. The wells will be seated at the bottom of the waste. A 4-1/4 inch ID hollow-stem auger will be used to advance the boring to the bottom of the waste material. The wells will be constructed of two-inch diameter, schedule 40 PVC casing and 0.010-inch slotted schedule 40 PVC well screen. A sand pack, consisting of silica sand, will be installed from the bottom of the wells to two feet above the well screen. A bentonite seal with a minimum thickness of two feet will be installed directly above the sand pack. The remaining annular space will be filled with a bentonite and cement grout. The wells will be completed with an aboveground well protector and a locking cap.

Following installation of the leachate wells, the top of casing and ground surface will be surveyed to establish well and grade elevations and well location. Well installation details will be documented on a test boring log (Appendix D) and in the field notebook. The leachate wells will generally be installed according to the typical well construction diagrams and standard procedures presented in Appendix G.

Following completion of monitoring well construction activities, the water level will be allowed to stabilize and will then be gauged to determine groundwater elevation and the total volume of groundwater in the well. After the water level in the well has been determined, the well will be developed to remove the fines from the sand pack. The development will consist of pumping or bailing the well, following the protocol described later in this section.

Sampling locations will be selected in the field with the concurrence of USEPA Region V or its designee. Figure 7 displays approximate leachate monitoring well location for Site Q. At least one of these wells will be located directly adjacent to the east pond.

Well Development

Newly installed wells will require development to clear the well of accumulated sediments. Appendix H presents the standard operating procedure (SOP) for well development.

Well Purging (if necessary)

After installation and development and prior to sampling, the well may be purged to remove the standing water column from the well casing. The SOP for well purging is presented in Appendix H with the procedure for well development.

Water Level Measurements

Prior to initiating groundwater sampling, water elevations will be measured in the well. Refer to Appendix I for well gauging procedures.

Groundwater Pre-Sampling and Well Sampling

Appendix I presents the protocol for groundwater sampling activities.

5.3.2 Hydrogeology

5.3.2.1 Alluvial Aquifer

Horizontal Extent of Contaminant Migration

Rationale

Groundwater samples will be collected in the alluvial aquifer downgradient of this waste disposal area. The purpose of this sampling is to define the extent of migration away from the source area and to provide information for the Human Health Risk Assessment.

Groundwater samples will be collected at eight sampling stations located on the west property boundary of Site Q. Five locations will be parallel to the river where the western boundary of the site is formed by the river, while the three remaining locations will be parallel to the river and the western boundary of the southern portion of the site.

Unfiltered groundwater samples will be collected every 10 feet from the water table to the bottom of the aquifer using push sampling technologies such as Geoprobe®, HydroPunch®, Microwell®, Waterloo Profiler® or equivalent low-flow sampling techniques. Aquifer saturated thickness is estimated to be approximately 120 feet with depth to water at 20 feet bgs and bottom of the aquifer at 140 feet bgs. All samples will be analyzed for VOCs and SVOCs. Additionally, unfiltered samples will be collected at 40 foot intervals (i.e., 20, 60, 100, and 140 foot bgs) and analyzed for pesticides, herbicides, PCBs, metals, and several geochemical parameters (presented in Table 1). Dioxin will be analyzed only at two sampling stations . For

dioxin analysis, unfiltered groundwater samples will be collected at the top, middle, and bottom of the saturated zone (e.g., 20, 80, 140 feet bgs).

Experience at other sites indicates that push-sampling technologies such as Geoprobe® can reach depths of 60 feet. Depth of penetration can be increased at some locations by loosening the soil above the sampling horizon with a small-diameter solid stem auger before pushing the sampling probe to the required sampling depth. When the Geoprobe® sampler or equivalent sampling technology cannot penetrate to the required depth, Microwells® will be used to collect groundwater samples. These small-diameter wells are vibrated into place using a small vibratory hammer. Experience in deep aquifers at other sites indicates that sampling depths of 100 feet can be achieved. If the required sampling depths cannot be reached with either of these two technologies, conventional percussion drilling equipment will be used to drive 1-1/4 inch diameter drive points to the required sampling depths.

Table 1 presents the analytical methods. A detailed sample and analysis summary for the alluvial aquifer groundwater sampling is presented in Table 4.

Sampling locations will be selected in the field with the concurrence of USEPA Region V or its designee. Figure 4 displays approximate groundwater sampling locations for Area 2.

Field Procedure

Establishment of Boreholes

Push Point

Using the hydraulic push system of a Geoprobe®, a 4-foot stainless steel sampler with a wire wrap (slot size of 0.004 inches) will be pushed to the desired sample depth. A bailer or ball and check valve will be sent down to the slotted portion of the sampler to collect the groundwater sample. The groundwater sample will be retrieved to the surface and placed in a sample container. The Geoprobe® will then drive the sampler to the next desired sample depth, by connecting clean sections of push rods to the Geoprobe®, and a second groundwater sample will be collected here. This process will be continued until all samples are collected.

MicroWell®

It is anticipated the above sampling method will be used, as feasible. However based on the location of the site within the Mississippi River flood plain, large gravel or cobbles may be

encountered, which will stop the Geoprobe®. Should this occur, MicroWells® will be installed to use as the sample collection point. The MicroWells® will be hydraulically pushed to the appropriate depth, and the sampling procedure described above will be followed. Once the sample is collected, the MicroWell® will be pulled, the screen point decontaminated according to the method described below, and a new well will be advanced further in the same hole. This procedure will be repeated until all samples are collected.

Should MicroWell® installation prove impractical, boreholes will be advanced using conventional hollow stem auger drilling methods. In this instance, the lead auger will have a screened section through which groundwater will flow. Once the sample is collected, the augers will be advanced further for collection at the next sample depth. This procedure will be repeated until all samples are collected within the borehole.

All Geoprobe®, MicroWell®, or Waterloo Profiler® holes will be sealed with grout from the bottom up and the surface will be returned to it's original condition after completion of sampling at each location. A PID, explosimeter, and a RAM will be used on a continuous basis to monitor these activities.

Groundwater Pre-Sampling and Borehole Sampling

Appendix I presents the protocol for groundwater sampling activities.

5.3.2.2 Bedrock Groundwater

Vertical Extent of Contaminant Migration

Rationale

Two bedrock wells will be installed downgradient of this site. The purpose of the bedrock sampling is to determine the extent of organic and inorganic constituent vertical migration from the site. Steel surface casing will be installed 5 feet into bedrock.

After installing the surface casing 5 feet into bedrock, the bedrock will be cored to a depth of 20 feet below the bottom of the casing. Cores will be digitally photographed in color against a scale and evaluated for porosity by examination and petrographic thin sections. One thin section will be made for each 2 feet of bedrock core. A 2-inch diameter, 5-foot-long screen and casing will be installed in the borehole. The screen will be filter-packed, sealed and grouted from 3 feet above the top of the filter-pack to grade. An unfiltered groundwater sample will be collected

from the well following installation and development and will be analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin, and metals.

Table 1 presents the analytical methods. A detailed sample and analysis summary for the bedrock groundwater sampling is presented in Table 5.

Sampling locations will be selected in the field with the concurrence of USEPA Region V or its designee. Figure 4 displays approximate groundwater sampling locations for Site Q.

Field Procedure

Mud rotary drilling methods will be used to drill the borehole to set the surface casing and to drill 5 feet into the top of bedrock Coring will then be accomplished using wireline coring barrels to generate a 2-inch thick minimum core. Coring will continue for 20 feet into the bedrock. The drilling and sampling procedure will be as follows:

1. A temporary 10-inch ID steel casing will be installed from ground surface to 10 feet bgs. A bentonite/cement grout will be used to fill the annular space.
2. A 8-3/4-inch ID tri-cone bit will then be used to drill down to 145 feet. A 5-inch ID steel casing will be installed from ground surface to 145 feet bgs. A bentonite/cement grout will be used to fill the annular space.
3. Wireline coring barrels (NX rods) will be used to core 20 feet into the bedrock (165 feet bgs). The coring barrels will be retrieved and opened to collect the core sample.
4. Core samples will be photographed and described on test boring logs. Descriptions will follow the procedures outlined below.
5. The borehole will then be reamed to a 4-7/8-inch diameter. A 2-inch PVC casing (schedule 80) will be installed from ground surface to 165 feet bgs (20 feet into bedrock). The PVC casing will have a 5-foot long screen (0.010-inch slots). A bentonite seal with a minimum thickness of two feet will be installed directly above the sand pack. This bentonite seal will be 3 feet in length. The remaining annular space will be filled with a bentonite and cement grout.
6. The temporary 10-inch I.D. steel casing will be removed and the well will be completed with an aboveground well protector and a locking cap.

7. Well development or purging may be necessary before collecting groundwater samples from the cased/screened hole in the bedrock. The procedures for both well development and well purging are presented below.
8. Water level measurements will then be collected, prior to sampling the bedrock groundwater. The procedure for measuring water levels is also presented below.
9. The bedrock groundwater sample collection method is presented after the procedure for water level measurements.

Well Development

Newly installed wells will require development to clear the well of accumulated sediments. Appendix H presents the standard operating procedure (SOP) for well development.

Well Purging (if necessary)

After installation and development and prior to sampling, the well may be purged to remove the standing water column from the well casing. The SOP for well purging is presented in Appendix H with the procedure for well development.

Water Level Measurements

Prior to initiating groundwater sampling, water elevations will be measured in the well. Refer to Appendix I for well gauging procedures.

Groundwater Pre-Sampling and Well Sampling

Appendix I presents the protocol for groundwater sampling activities.

Description of Rock Samples

As mentioned earlier in this section, the rock core will be evaluated via photographs and petrographic thin sections. The geologists and geotechnical engineers will write their description of rock samples with a consistent format. A detailed order and presentation of selection of data are presented in Appendix J.

Groundwater Flow Direction (water levels)

Water levels will be measured quarterly for one year in the bedrock well and used to prepare water-level elevation maps. These will show seasonal changes in groundwater level and flow

direction. Water level measurements will be conducted according to the same protocol outlined in Appendix I.

Groundwater Flow Rate (slug tests)

Rationale

Falling and rising head slug tests will be performed on the bedrock well, using a slug of known volume and in-well, short-time interval, automatic water-level recorders. With the falling-head and rising-head slug test data, aquifer hydraulic conductivity will be calculated for the well. Measured groundwater gradients and calculated aquifer hydraulic conductivities will be used to determine groundwater flow rates.

Field Procedure

Appendix K presents the field protocols for the completion of *in situ* hydraulic conductivity (slug) tests.

Slug test data will be downloaded from the data logger each day. The data will be reviewed for errors. If necessary, a slug test will be re-conducted.

5.3.3 Soil

5.3.3.1 Surface Soil Samples

Rationale

Twelve surface soil samples (0 to 0.5 feet) will be collected at this disposal site. These samples will be collected at the location of each waste sample boring to provide information for the Human Health Risk Assessment and the Ecological Risk Assessment. In addition, one surface soil sample will be collected in the field immediately south of Site Q to determine if chemicals of potential concern have been transported during overland flows. Scaled, color digital photographs will be taken of each soil sample to provide a record of materials present at this site. Each sample will be analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin, and metals.

Table 1 presents the analytical methods. A detailed sample and analysis summary for the surface soil sampling is presented in Table 6.

Figure 7 presents approximate soil sample locations in Site Q.

Field Procedure

Surface soil samples will be discrete. A discrete sample represents a single location in the soil column. The soil samples will be collected from the Geoprobe® borings.

Appendix C presents the standard operating procedure for waste and soil sample collection.

5.3.3.2 Subsurface Soil Samples

Rationale

Twelve subsurface soil samples (0.5 to 6 feet) will be collected at this disposal site. As with the surface soil samples, the subsurface samples will be collected at the location of each waste sample boring to provide information for the Human Health Risk Assessment. In addition, one subsurface soil sample will be collected in the field immediately south of Site Q to determine if chemicals of potential concern have been transported during overland flows. Scaled, color digital photographs will be taken of each soil sample to provide a record of materials present at this site. Each sample will be analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin, and metals.

Table 1 presents the analytical methods. A detailed sample and analysis summary for the subsurface soil sampling is presented in Table 7.

Figure 7 presents approximate soil sample locations for Site Q.

Field Procedure

The Twelve soil samples collected at this site will be collected at the location of each waste sample boring. The subsurface soil samples will be collected in the same manner as the waste samples.

Appendix C presents the standard operating procedure for waste and soil sample collection.

5.3.4 Air

5.3.4.1 Rationale

Four upwind and four downwind ambient air samples will be collected to determine the tendency of site constituents to enter the atmosphere and local wind patterns. Air sampling data will be used in the Human Health Risk Assessment and Ecological Risk Assessment. Samples will be analyzed for VOCs, SVOCs, pesticides, PCBs, metals, and dioxin.

Twenty-four hour cumulative duration sorbent tube/PUF/PM2.5 samples will be collected over a 1-day period, using the sampling protocols provided in Appendix L. Four upwind and four downwind samplers will be installed at the site during weather likely to produce emissions (e.g. hot and dry conditions in August). Sampling locations will be selected in the field with the concurrence of USEPA Region V or his designee. Sorbent tube samplers will be used for VOC data collection. Polyurethane foam (PUF) samplers will be used for SVOC, PCB, pesticide, and dioxin data collection. PM2.5 samplers will be used for metal data collection

Ambient air sample collection is required to measure airborne levels of contaminants that may be evolving from the site. A 24-hour sample duration is required to average the air emission differences that may occur from the day time to night time cycle from on-site and off-site conditions and activities. Also, air sample collection locations need to be positioned on the site to collect up wind and down wind samples for differentiation of constituents originating from the surrounding area and those originating from the site. The sample protocol will collect site samples over a 1-day time period on a warm, dry day.

The level of detection for SVOCs required by USEPA Region V needs to consider sensitivity and selectivity to analyze complex samples. Based on this need, the analytical method of choice is gas chromatography coupled with mass spectrometry (GC/MS) for detection. Based on the GC/MS analytical method and its sensitivity level, the air sample volume needs to exceed 325 standard cubic feet. This enables the collection of a sufficient quantity of SVOCs to meet the level of detection required by USEPA Region V.

The sample method to meet the above requirements for SVOC measurement is USEPA Method TO-13, as identified in the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* (June 1988). This method will use a Graseby/General Metal Works, Inc. high volume air sampling unit or equivalent for sample collection. Sample collection will

consist of drawing an ambient air sample at a high volume flow rate through a PUF collection media over a 24-hour time period. The samples will be submitted for analysis of the TO-13 list of SVOCs. Method TO-15 will be used to analyze VOCs. Method TO-4 will be used for pesticides, and PCBs. Method TO-9 will analyze for dioxins.

Table 8 is a sample and analysis summary of this activity.

5.3.4.2 Field Procedure

The following procedure will be used for ambient air samples:

- Place the sorbent tube samplers, PUF samplers, and PM2.5 samplers at upwind and downwind locations.
- Locate sampling positions in an unobstructed area, at least two meters from any obstacle to air flow. Sample locations will be selected in the field with the concurrence of the USEPA Region V, or its designee.
- No local power supply is readily available at the sites. Therefore, gasoline- or diesel-powered generators will be positioned at downwind locations from the sample collection positions. They will supply the electricity for the samplers.
- Record wind direction and velocity readings.
- Follow sample collection protocols identified in Appendix L for sample preparation, calibration, collection, laboratory preparation and shipment, and calculations. Sample data sheets are provided in Appendix L.

5.3.5 Stormwater Runoff

5.3.5.1 Rationale

Two stormwater runoff grab samples will be collected at downgradient locations within this site, in an effort to characterize runoff from the site during storm events. Samples will be collected within the primary drainage route, leading from the site to the Mississippi River. This sampling will be conducted at Sites Q and R because they are on the wet side of the floodwall and levee. The other three sites (O, P, and S) are on the dry side of the floodwall and levee and therefore have no drainage route to the Mississippi River. Samples will be collected during three storms to determine variability of constituent concentrations in site runoff. A first flush sample will be collected utilizing an automated sampling device. A first flush sample is one collected at the

very beginning of a storm event (e.g., as the first flow comes through). Collection of a first flush sample insures that any contamination on the ground surface prior to the storm event will be collected before it has the opportunity to wash away. Storm water samples will be analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin, and metals.

The analytical methods are presented in Table 1. Table 9 presents a sample and analysis summary for storm water runoff samples to be collected.

5.3.5.2 Field Procedure

Refer to Appendix M for the standard method of storm water sample collection.

The following method will be used for collection of storm water samples:

1. Identify the primary storm water drainage route, running from the site to the Mississippi River.
2. Collect the sample during a rainfall, which results in a discharge. A storm water sample will be collected during three separate storm events (for a total of three samples per site).
3. Set up appropriate parameters on automated sampler.
4. Remove appropriate sample containers from the transport container, and prepare the sample containers for receiving samples.
5. Fill out a self-adhesive label with the appropriate information and affix it to the appropriate sample container. Place clear polyethylene tape over the completed label to protect it from dirt and water. Sample labels can be prepared prior to sample collection, except for time and date. Labels can be filled in on the date of sample collection and just prior to collecting the sample. Sample containers will be kept cool with their caps on until they are ready to receive samples.
6. Put on a clean pair of disposable gloves.
7. Set sampler to fill sample containers for the VOC sample, prior to filling other sample containers. Verify that there is no air in the sealed sampled container.
8. Transfer sample to appropriate containers for shipment to laboratory.
9. If the sample containers cannot be filled quickly, keep sample containers cool with the cap on until finished. Sample containers will be preserved as described in the QAPP.

10. Return each sample container to its proper transport container. Preserve samples by reducing the temperature within the containers to approximately 4° Celsius, using ice. Samples must not be allowed to freeze.

11. Begin chain-of-custody procedures. A sample chain-of-custody form is included in Appendix F.

12. Record the physical appearance of the storm water observed during sampling in the field notebook.

Treatability Tests

Rationale

The AOC requires that the SSP present a pilot test program for any treatment technologies lacking sufficient information on implementability and effectiveness. Data gaps exist for off-site incineration, off-site disposal, and on-site thermal desorption for the waste and on-site and off-site physical/chemical treatment, and off-site biological treatment for leachate.

A total of five composite waste samples (one for each site) will be collected for waste treatability testing and sent to appropriate facilities operators for waste profiling, material handling characterization and evaluation of the feasibility of disposing of the waste material by off-site incineration, off-site disposal, and on-site thermal desorption. In addition, five composite leachate samples (one from each site) will be collected for treatability testing to determine if the leachate can be discharged directly to American Bottoms POTW without resulting in pass through and/or interference.

One sample will be collected from each waste disposal area for waste treatability testing. The sample will be made from aliquots collected from the four waste characterization borings installed at each disposal area. One sample will be collected for the leachate treatability testing from each of the five-leachate sampling wells.

Sample Collection

The five composite waste samples that will be collected for treatability testing will be retained from the four-waste/soil borings that will be advanced at each waste disposal area. All of the material recovered from the Geoprobe® samples that are not needed for the other chemical analyses will be composited in 5-gallon buckets. Each bucket will be sealed, labeled and

prepared for shipment to the appropriate facilities.

The leachate sample that will be collected for treatability testing will be collected during leachate sampling activities. An equal amount of leachate will be removed, via bailer or pump, from each of the five-leachate monitoring wells and placed in separate 5-gallon buckets. Each bucket will be sealed, labeled and prepared for shipment to the appropriate facility.

5.3.6 Seep Investigation

5.3.6.1 Rationale

A visual reconnaissance survey will be undertaken along the riverbank adjacent to Site Q during the low flow periods to assess the presence of seeps and their impacts, if any, on the Mississippi River. The locations of any seeps observed will be located with a GPS, photographed, and if sufficient quantity is present, sampled for VOC, SVOC, PCBs, dioxin, herbicide, pesticide, and metals. Where appropriate, several smaller seeps in close proximity to each other may be sampled as a single location. If sample volume is limited, sample containers will be prioritized and filled in order of analytical parameters as presented above.

The analytical methods are presented in Table 1.

5.3.6.2 Field Procedure

Refer to Appendix M for the standard method of seep water sample collection.

The following method will be used for collection of seep water samples:

1. Identify the seep location(s) along the riverbank and note location.
2. Remove appropriate sample containers from the transport container, and prepare the sample containers for receiving samples.
3. Fill out a self-adhesive label with the appropriate information and affix it to the appropriate sample container. Place clear polyethylene tape over the completed label to protect it from dirt and water. Sample labels can be prepared prior to sample collection, except for time and date. Labels can be filled in on the date of sample collection and just prior to collecting the sample. Sample containers will be kept cool with their caps on until they are ready to receive samples.

4. Grab sampling procedures and preservation of the collected seep water samples will follow the methods described in the current edition of "Standard Methods for the Examination of Water and Wastewater" (published by the American Public Health Association).
5. Put on a clean pair of disposable gloves.
6. Use a dipping utensil to retrieve a sample.
7. Fill sample containers for the VOC sample, prior to filling other sample containers. Verify that there is no air in the sealed sampled container.
8. Fill remaining sample containers.
9. If the sample containers cannot be filled quickly, keep sample containers cool with the cap on until finished. Sample containers will be preserved as described in the QAPP.
10. Return each sample container to its proper transport container. Preserve samples by reducing the temperature within the containers to approximately 4° Celsius, using ice. Samples must not be allowed to freeze.
11. Begin chain-of-custody procedures. A sample chain-of-custody form is included in Appendix F.
12. Record the physical appearance of the storm water observed during sampling in the field notebook.

5.4 SITE R

5.4.1 Waste Characterization

5.4.1.1 Delineation of Source Area Boundaries – Test Trenches

Rationale

Historical air photos were obtained for this site. These photos were used to define the areal extent of the site over time and to determine the boundaries of the waste disposal area. Boundaries of the site on each photo were observed. To define the maximum extent of fill, the tracings for the site were overlain and a line was drawn around the outside limit of the composite waste disposal area boundary. Results of the historical air photo analysis were used to prepare a map for the site, showing disposal area boundaries. Stereoscopic evaluation of historical air

photographs allowed identification of the deepest portion of a waste disposal area, and one of the four waste characterization borings discussed below will be done at that location.

Test trenches will be used to confirm the boundaries of the waste disposal area identified through air photo analysis. One trench will be installed on each side of the waste disposal area. Thus, there will be a total of four trenches for the site. The four trenches will be located at the midpoint of the four longest sides of the defined site boundary. A GPS system will be used to document the locations on aerial site maps. Test trenches will start outside the defined boundary of the disposal area and move toward the defined boundary. When fill materials are encountered, the disposal area boundary will be compared to those identified in the air photo analysis and trenching at that location will then be terminated.

Excavated soil and fill material will be returned to the test trench, with the exception of any intact drums. Intact drums will be removed, provided confined space entry is not needed to retrieve a drum. Trenches will not be entered to recover drums due to the inherent danger in such activities. Test trench locations will be determined using a GPS system. The trench locations will be recorded for future reference, in the event drum removal is appropriate. The drum removal contractor, in accordance with the requirements of 29 CFR 1910.120(j) will handle drums recovered during trenching activities. Recovered drums will be over-packed and stored pending disposal. Free product and contaminated soil resulting from rupture of drums during removal will be cleaned up by absorbing any liquid materials. The absorbent, solid waste, and contaminated soil will be placed in bulk containers. The over-packed drums and these bulk containers will be temporarily stored at a controlled-access, fenced Investigation Derived Waste (IDW) Storage Area to be constructed at Site R. Recovered drums and wastes will be stored until the capacity of the storage pad is exceeded or the investigation is complete, whichever comes first. Any waste excavated that identifies the source of material present in the fill area will be noted in the field log and photographed.

Trenching locations will be selected in the field with the concurrence of USEPA Region V RPM or his designee.

Field Procedure

All trenching activities will be conducted in a manner to protect existing utilities, structures, surface features, monitoring wells, and the general site environment. Additionally, trenching

activities will follow Occupational Safety and Health Administration (OSHA) rules for excavations.

Locations of test trenches for boundary confirmation of Site R are shown on Figure 9. A "competent" person, as defined in 29 CFR 1976.650, will observe the trenching activities and will have authorization to take corrective measures to respond to unsanitary, hazardous, or dangerous conditions to workers. A track-mounted hoe with an extended arm will be used for excavation. A photoionization detector (PID), combustible gas monitor (CGM), and a real-time aerosol monitor (RAM) will be used on a continuous basis to monitor the test trenches for hazardous conditions.

Trenching activities will begin outside the site boundary and move in towards the boundary. The trenching will extend vertically to a maximum depth of 40 ft bgs or to groundwater, whichever is encountered first. No accommodations will be made to dewater test trenches or manage groundwater during excavation activities in order to minimize the generation of investigation-derived wastes. The trenching will continue until waste material is encountered. Should waste materials be encountered initially, the trenching activities will proceed out and away from the boundary until native soils are encountered. Where native soils are encountered, the excavation will proceed to greater depth up to a maximum of 40 ft below grade, where possible. Should waste materials be encountered again within the test trench, this procedure will be repeated until no waste materials are encountered within the test trench. The location where no additional waste materials are encountered within the test trench will be designated as the extent of the site boundary for that location.

As the trenching proceeds, spoils from the test trenches will be placed on polyethylene plastic, having a minimum thickness of 6 millimeters. Provisions will be made to allow free liquids in the spoils to drain back to the trench. Spoils from each test trench will be segregated and returned to the excavation in reverse order of removal. The gross contamination will be removed from the excavator bucket with a shovel and/or potable water source prior to handling the cover material. Decontamination debris will be placed into the excavation trench prior to placement of cover material. Handling of investigation-derived wastes from these activities is discussed in Section 9.

Backfilling will be conducted in a manner to minimize ponding of water over the trench. A silt fence will be installed around the perimeter of the trench to minimize runoff of surface soils

during rain events. A test trench at one location will be backfilled prior to the initiation of a test trench at another location. After completion of site investigation activities, the sites will be revegetated with grass. The silt fence will be maintained until revegetation is completed.

The location of the test trenches will be illustrated on a plan of the site. Digital photographs will be taken of the test trenches, the test trench walls, and any waste materials excavated. The number and location of each photograph will be identified on the field log for each test trench.

5.4.1.2 Soil Gas Surveys

Rationale

A soil gas contractor will perform a soil gas survey at Site R. A shallow soil probe (5 feet) and on-site analysis of collected VOC vapors with a GC will be used in this survey. Soil gas samples will be collected at the center points of a 200 by 200 ft grid, superimposed on the disposal area, resulting in approximately 30 sampling locations. The soil gas survey sampling grid for Site R is displayed in Figure 10.

If detectable concentrations of Total VOCs are found in the soil gas samples at the disposal area boundary, the survey will be extended beyond that boundary. If extended beyond the boundary, soil gas samples will be collected at 100-foot intervals (0, 100, and 200 feet from the edge of the disposal area) along as many as four 200-foot long transects. Each transect will run perpendicular to the relevant sides of the disposal area. If VOCs are detected in soil gas at this site, up to twelve additional soil gas samples may be collected.

If twelve additional samples are not adequate to define the extent of VOC-containing soils in the disposal area, additional soil gas samples will be collected at 100-foot intervals along the appropriate transects until the limits of the impacted fill are determined. If soil gas surveys need to extend into areas for which there are no property access agreements, soil gas sampling will be suspended until access is obtained.

Sampling locations will be selected in the field with the concurrence of USEPA Region V RPM or his designee.

Table 2 is a sample and analysis summary for this activity.

Field Procedure

Direct push technology will be used to advance a retractable point holder to 5.5 feet below existing grade. The rods will then be pulled back to approximately 5 feet below existing grade to disengage the retractable point, therefore, exposing the sampling mechanism. Polyethylene tubing (0.125-inch diameter) will be lowered into the rods. The upper end of the polyethylene tubing will be connected to a 4-inch section of silicone tubing. This will then be attached to a section of polyethylene tubing coming from an active vacuum system and a vacuum will be placed in the tubing. A 60cc sample of soil gas will be withdrawn from the silicone tubing using a 60cc disposable syringe with a stainless steel needle. The sample will then be directly injected into the on-site GC. The GC will provide a report of the total VOC concentrations.

Sample tubing will be removed from the probe and disposed. Probing rods and sampling equipment will be removed from the boring. The probe boring will be filled with bentonite, to just bgs. The bentonite will be hydrated with potable water and the surface will be restored to its original condition. An SOP for the field GC is contained in Appendix A.

5.4.1.3 Waste Samples

Rationale

Four borings will be advanced at this site to characterize the waste materials present. Continuous samples will be collected from grade to two feet below the bottom of the waste material, which is estimated to be a maximum of 40 feet below grade. If wastes are encountered at depths greater than 40 feet bgs (bgs), the boring will continue until the bottom of the waste is encountered. Scaled, color digital photographs will be taken of each waste sample to provide a record of materials present in the disposal area.

One composite waste sample will be collected at each boring location (4 total composite waste samples), and analyzed for SVOCs, pesticides, herbicides, PCBs, dioxin, and metals. In addition, a portion of the composite waste sample from above the water table will be extracted using TCLP procedures and analyzed for this same suite of analytes. Visual observations and PID readings will be used to identify whether or not waste is present in a continuous boring sample. If waste is present in a sample, it will be removed, segregated, temporarily stored and used at the completion of the soil boring to prepare a composite waste sample. Since VOC

samples cannot be composited without losing volatiles, the waste with the highest PID readings will be used for VOC analysis.

Existing information (e.g., the 1998 Ecology and Environment report and the results of the aerial photograph analysis, soil gas surveys, and magnetometer surveys conducted as part of the SSP) will be used to select boring locations. Approximate waste characterization boring locations for Site R are shown on Figure 9. Additional waste characterization borings may be required by USEPA Region V as a result of variability in waste characteristics observed during the waste characterization boring program.

Table 3 is a sample and analysis summary for waste samples to be collected.

Field Procedure

Borings will be advanced via direct push technology (Geoprobe®). The Geoprobe® will hydraulically drive a stainless steel, acetate-lined MacroCore® sampler (2-inch diameter by 4-foot length) to the desired subsurface sample depths. Continuous samples will be collected from grade to 2 feet below the bottom of the waste material (estimated to be 40 feet bgs). Between each sample collection, the sampler will be retrieved to the surface and the samples removed from the disposable acetate liner within the sampler.

One composite waste sample will be collected from each boring. Each sample will be visually observed and monitored with PID readings, to determine whether waste is present. If waste is present in a sample, it will be removed, segregated, temporarily stored, and used at the completion of the soil boring to prepare a composite waste sample. The sample exhibiting the highest PID reading at each of the four boring locations within this site will be used for VOC analysis. A 5-gram EnCore® sampler will be used to collect VOC samples.

Refer to Appendix C for detailed soil/waste sampling procedures.

Descriptive logs of each boring will be prepared as described in Appendix E. The four waste borings generated at each of the five sites will also be used for surface and subsurface soil sample collection. All borings will be grouted to the surface, following retrieval of both the waste and soil samples.

Logging Unconsolidated Samples

The geologist logging samples will be responsible to interpret the samples following standard and acceptable methods. The geologist implementing this work plan will have training and experience logging boring samples. Soil will be logged according to applicable ASTM standards. As appropriate, ASTM standards will be used to log waste materials. Appendix E presents detailed instructions for logging soil and waste samples.

5.4.1.4 Buried Drum and Tank Identification

Magnetometer Survey

Rationale

A magnetometer survey will be conducted at this site to identify anomalies indicative of drum disposal or buried tanks. Magnetometer measurements will be made at locations determined by superimposing a 50-foot by 50-foot grid on the disposal area.

Surface geophysical surveys, which map the distribution of the strength of the earth's magnetic field, have been proven useful in evaluating shallow and deep subsurface conditions at environmental sites. These geophysical surveys have been used to successfully locate buried objects containing magnetically susceptible materials (e.g., iron and nickel metals). The ability of geophysical equipment to locate buried objects is, for the most part, dependent on:

- The strength and orientation of the magnetic anomaly associated with the buried objects
- The strength and natural variation of the earth's magnetic field in response to local geology
- The influence of man-made surface features (such as power lines, buried utilities, vehicles, electric motors, etc.) which may interfere with the collection of data.

By comparing the known surface and geological conditions to a magnetic survey map that includes mapped surface feature interferences, and understanding possible geologic background effects, it is possible to identify the location of suspicious subsurface features which may represent buried tanks or drum disposal areas.

Method

A geophysical contractor will conduct the magnetometer survey. A geophysical survey of the site's magnetic field will be completed utilizing a field magnetometer and electromagnetic induction. The field magnetometer measures the strength of the site's magnetic field regardless of the orientation of the magnetic lines of force. During the performance of the geophysical survey, data for the preparation of a field map will be collected. The final product of this survey will include a description of the site, contour maps, and an explanation of how the survey was conducted.

A correction for diurnal and micropulsation time variations is not necessary because the site and anticipated anomalies are relatively small in area (less than 1 square mile), and subsurface anomalies from buried objects of interest should be relatively large (greater than 100 gammas).

The map showing the distribution of magnetic field strength over the site will be compared with the observed field conditions (including the location of known interfering objects such as vehicles, overhead power lines, and surface debris). By comparison, those magnetic anomalies, which cannot be explained by, observed site conditions, will be presumed to be a result of buried subsurface material (e.g., drums, tanks, metal debris, etc.). The depth of detection for suspect objects (such as steel drums) may vary according to orientation, method of manufacture and condition, and numbers present. Steel drums, such as those suspected to be present at this site, may be detected to depths of 40 feet.

Study Area

The area of the properties to be surveyed will be evaluated in the field. Magnetometer surveys will be conducted at a total of four sites (P, Q, R, and S) within Area 2. A general area for Site R survey site has been delineated and provided on Figure 10 (Fill Area Location Map). Overall site dimensions for the survey sites will be adjusted based upon the findings of the source area boundary delineation activities discussed in Section 5.2.1.1.

Field Procedure

The following field equipment and procedures will be employed during this geophysical investigation.

Equipment

A Geometrics 858 Cesium or a Geometrics 856AX Total Field Magnetometer will be used to collect the field data. Field procedures and operation of the instruments will be in accordance with the recommended manufacturer's field procedure and application manual.

Calibrated field survey equipment consisting of marked survey line, tape rulers, highway danger cones, and marked wooden stakes will be utilized to establish measurement locations.

Measurement Point/Grid Surveying

The established survey lines will be marked in the field using a premarked survey line to maintain straight and precise station locations. Profiles will be completed along a straight line with an unobstructed line of sight. The corners of each of the gridded areas will be marked with temporary corner stakes to permit the relocation of the measurement points within each site.

Data Processing

Following completion of the field phase of investigation, the following data processing will be performed:

- Explanation of where and how the survey was performed
- Description of each of the four sites (P, Q, R, S) in terms of magnetic anomalies detected
- A contour map of these data will be produced showing the location of the measurement points and the corresponding magnetometer reading.

Test Trenches

Rationale

Test trenches will be installed at this site to confirm the presence of buried drums of tanks. One test trench will be installed at this site. The waste disposal areas within Area 2 were used for disposal of municipal and industrial waste as well as construction debris. Magnetic anomalies are likely to be numerous, intense, and widespread. If no location criteria other than the presence of a magnetic anomaly is used to determine whether or not a test trench is appropriate, disturbance of a significant portion of each disposal area is likely to result. Excessive trenching could result in unacceptable risks to the community, on-site workers and the environment.

For this reason, four selection criteria will be used to identify where to install each test trench. Test trenching will be done at the location of the largest magnetic anomaly that coincides with:

1. A soil gas concentration high,
2. Drum or tank disposal locations identified by historical air photo interpretation,
3. An area of high groundwater concentrations (greater than 10,000 ppb) as identified by the 1998 Ecology and Environment Data Report, and
4. Major magnetic anomalies reported in the 1988 Ecology and Environment "Expanded Site Investigation, Dead Creek Project Sites at Cahokia/Sauget, Illinois".

Care will be taken not to place major emphasis on the comparison of historical groundwater concentrations and magnetic anomalies due to the extent of historical industrial groundwater pumping in the area.

Excavated soil and fill material will be returned to the test trench, with the exception of any intact drums. These will be removed, provided confined spaced entry is not needed to retrieve a drum. Trenches will not be entered to recover drums because of the danger inherent in such activities. Test trench locations will be determined using a GPS and recorded for future reference in the event drum removal is appropriate.

Recovered drums will be over-packed and stored pending disposal. Free product and contaminated soil, resulting from rupture of drums during removal, will be cleaned up by absorbing any liquid materials and placing the absorbent, solid waste, and contaminated soil in bulk containers. Over-packed drums and bulk solid and liquid containers will be stored at a controlled-access, fenced Investigation Derived Waste (IDW) Storage Area to be constructed at Site R. Recovered drums will be stored until the capacity of the storage pad is exceeded or the investigation is complete, whichever comes first. Any waste excavated that identifies the source of material present in the disposal area will be noted in the field log and photographed.

Field Procedure

Anomaly test trench locations will be selected in the field based upon the parameters outlined in the Rationale section, and with the concurrence of the USEPA Region V or its designee.

To complete the anomaly test trench, a track-mounted or wheel-mounted hoe will be utilized. The depth to the top of buried anomalies is not expected to extend past 40 feet below grade; thus, a smaller piece of equipment may be utilized for these anomaly test trenches (in comparison to the trenches completed for delineation of the fill area boundaries). Trenching activities will be conducted in a manner to protect existing utilities, structures, surface features, monitoring wells, and the general site environment. Additionally, trenching will follow OSHA rules for excavations. A PID, CGM, and a RAM will be used on a continuous basis to monitor the anomaly test trenches for hazardous conditions. The hoe operator will have a separate supplied-air system.

Anomaly test trenches will be advanced until evidence as to the source of the anomaly is found or to a maximum depth of 40 feet, where possible. Should groundwater infiltration and/or poor soil stability result in the inability to complete a test trench to 40 feet, the trenching will be terminated at that location. No accommodations will be made to de-water test trenches or manage groundwater during excavation activities, due to the need to minimize the generation of investigation-derived wastes.

As the trenching proceeds, spoils from the test trenches will be placed on polyethylene plastic having a minimum thickness of 6 millimeters. Provisions will be made to allow free liquids in the spoils to drain back to the trench. Spoils from each test trench will be segregated and returned to the excavation in reverse order of removal. Backfilling will be conducted in a manner to minimize ponding of water over the trench. A silt fence will be installed around the perimeter of the trench to minimize runoff of surface soils during rain events.

If intact drums are found during anomaly test trench completion, they will be removed, over-packed, and stored in an area to be designated in accordance with the requirements of 29 CFR 1910.120(j). For planning purposes, it is anticipated that up to ten over-packs will be necessary per site and that one day of anomaly test trenching will occur at each of the four sites. Handling of investigation-derived wastes from these activities is discussed in Section 9.

A test trench at one location will be backfilled prior to the initiation of a test trench at another location. After completion of site investigation activities, the sites will be revegetated with grass. The silt fence will be maintained until revegetation is completed.

5.4.1.5 Leachate Samples

Rationale

A 2-inch diameter well, screened at the bottom of the fill material, will be installed in one of the four waste characterization borings completed at this site. The purpose of this well is to characterize leachate at the site. The well will be sampled and analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, metals, and dioxin. The analytical methods are presented in Table 1.

Field Procedure

Well Installation

The depth and screened interval for the well will be determined in accordance with the subsurface stratigraphy observed during Geoprobe® waste sampling activities. It is expected that the waste at the site extends to approximately 40 feet bgs. Unless observed conditions indicate otherwise, a screened interval of 10 feet will be used. The well will be seated at the bottom of the waste. A 4-1/4 inch ID hollow-stem auger will be used to advance the boring to the bottom of the waste material. The well will be constructed of two-inch diameter, schedule 40 PVC casing and 0.010-inch slotted schedule 40 PVC well screen. A sand pack, consisting of silica sand, will be installed from the bottom of the well to two feet above the well screen. A bentonite seal with a thickness of between two feet and three feet will be installed directly above the sand pack. The remaining annular space will be filled with a bentonite and cement grout. The well will be completed with an aboveground well protector and a locking cap.

Following installation of the leachate well, the top of casing and ground surface will be surveyed to establish well and grade elevations and well location. Well installation details will be documented on a test boring log (Appendix D) and in the field notebook. The leachate well will generally be installed according to the typical well construction diagrams and standard procedures presented in Appendix G.

Following completion of monitoring well construction activities, the water level will be allowed to stabilize and will then be gauged to determine groundwater elevation and the total volume of groundwater in the well. After the water level in the well has been determined, the well will be developed to remove the fines from the sand pack. The development will consist of pumping or bailing the well, following the protocol described later in this section.

Sampling locations will be selected in the field with the concurrence of USEPA Region V or its designee. Figure 9 displays the approximate leachate monitoring well location for Site R.

Well Development

Newly installed wells will require development to clear the well of accumulated sediments. Appendix H presents the standard operating procedure (SOP) for well development.

Well Purging (if necessary)

After installation and development and prior to sampling, the well may be purged to remove the standing water column from the well casing. The SOP for well purging is presented in Appendix H with the procedure for well development.

Water Level Measurements

Prior to initiating groundwater sampling, water elevations will be measured in the well. Refer to Appendix I for well gauging procedures.

Groundwater Pre-Sampling and Well Sampling

Appendix I presents the protocol for groundwater sampling activities.

5.4.2 Hydrogeology

5.4.2.1 Alluvial Aquifer

Horizontal Extent of Contaminant Migration

Rationale

Groundwater samples will be collected in the alluvial aquifer downgradient of this waste disposal area. The purpose of this sampling is to define the extent of migration away from the source area and to provide information for the Human Health Risk Assessment.

Groundwater samples will be collected at one sampling station located on the west property boundary of Site R. Unfiltered groundwater samples will be collected every 10 feet from the water table to the bottom of the aquifer using push sampling technologies such as Geoprobe®, HydroPunch®, Microwell®, Waterloo Profiler® or equivalent low-flow sampling techniques. Aquifer saturated thickness is estimated to be approximately 120 feet with depth to water at 20 feet bgs and bottom of the aquifer at 140 feet bgs. All samples will be analyzed for VOCs and

SVOCs. Additionally, unfiltered samples will be collected at 40 foot intervals (20, 60, 100, and 140 foot bgs) and analyzed for pesticides, herbicides, PCBs, metals, and several geochemical parameters (presented in Table 1 For dioxin analysis, unfiltered groundwater samples will be collected at the top, middle, and bottom of the saturated zone (e.g., 20, 80, 140 feet bgs).

Experience at other sites indicates that push-sampling technologies such as Geoprobe® can reach depths of 60 feet. Depth of penetration can be increased at some locations by loosening the soil above the sampling horizon with a small-diameter solid stem auger before pushing the sampling probe to the required sampling depth. When the Geoprobe® sampler or equivalent sampling technology cannot penetrate to the required depth, Microwells® will be used to collect groundwater samples. These small-diameter wells are vibrated into place using a small vibratory hammer. Experience in deep aquifers at other sites indicates that sampling depths of 100 feet can be achieved. If the required sampling depths cannot be reached with either of these two technologies, conventional percussion drilling equipment will be used to drive 1-1/4 inch diameter drive points to the required sampling depths.

Table 1 presents the analytical methods. A detailed sample and analysis summary for the alluvial aquifer groundwater sampling is presented in Table 4.

Sampling locations will be selected in the field with the concurrence of USEPA Region V or its designee. Figure 4 displays approximate groundwater sampling locations for Area 2.

Field Procedure

Establishment of Boreholes

Push Point

Using the hydraulic push system of a Geoprobe®, a 4-foot stainless steel sampler with a wire wrap (slot size of 0.004 inches) will be pushed to the desired sample depth. A bailer or ball and check valve will be sent down to the slotted portion of the sampler to collect the groundwater sample. The groundwater sample will be retrieved to the surface and placed in a sample container. The Geoprobe® will then drive the sampler to the next desired sample depth, by connecting clean sections of push rods to the Geoprobe®, and a second groundwater sample will be collected here. This process will be continued until all samples are collected.

MicroWell®

It is anticipated the above sampling method will be used, as feasible. However based on the location of the site within the Mississippi River flood plain, large gravel or cobbles may be encountered, which will stop the Geoprobe®. Should this occur, MicroWells® will be installed to use as the sample collection point. The MicroWells® will be hydraulically pushed to the appropriate depth, and the sampling procedure described above will be followed. Once the sample is collected, the MicroWell® will be pulled, the screen point decontaminated according to the method described below, and a new well will be advanced further in the same hole. This procedure will be repeated until all samples are collected.

Should MicroWell® installation prove impractical, boreholes will be advanced using conventional hollow stem auger drilling methods. In this instance, the lead auger will have a screened section through which groundwater will flow. Once the sample is collected, the augers will be advanced further for collection at the next sample depth. This procedure will be repeated until all samples are collected within the borehole.

All Geoprobe®, MicroWell®, or Waterloo Profiler® holes will be sealed with grout from the bottom up and the surface will be returned to it's original condition after completion of sampling at each location. A PID, explosimeter, and a RAM will be used on a continuous basis to monitor these activities.

Groundwater Pre-Sampling and Borehole Sampling

Appendix I presents the protocol for groundwater sampling activities.

5.4.2.2 Bedrock Groundwater

Vertical Extent of Contaminant Migration

Rationale

One bedrock well will be installed downgradient of this site. The purpose of the bedrock sampling is to determine the extent of organic and inorganic constituent vertical migration from the site. Steel surface casing will be installed 5 feet into bedrock.

After installing the surface casing 5 feet into bedrock, the bedrock will be cored to a depth of 20 feet below the bottom of the casing. Cores will be digitally photographed in color against a scale

and evaluated for porosity by examination and petrographic thin sections. One thin section will be made for each 2 feet of bedrock core. A 2-inch diameter, 5-foot-long screen and casing will be installed in the borehole. The screen will be filter-packed, sealed and grouted from 3 feet above the top of the filter-pack to grade. An unfiltered groundwater sample will be collected from the well following installation and development and will be analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin, and metals.

Table 1 presents the analytical methods. A detailed sample and analysis summary for the bedrock groundwater sampling is presented in Table 5.

Sampling locations will be selected in the field with the concurrence of USEPA Region V or its designee. Figure 4 displays approximate groundwater sampling locations for Site R.

Field Procedure

Mud rotary drilling methods will be used to drill the borehole to set the surface casing and to drill 5 feet into the top of bedrock. Coring will then be accomplished using wireline coring barrels to generate a 2-inch thick minimum core. Coring will continue for 20 feet into the bedrock. The drilling and sampling procedure will be as follows:

1. A temporary 10-inch ID steel casing will be installed from ground surface to 10 feet bgs. A bentonite/cement grout will be used to fill the annular space.
2. A 8-3/4-inch ID tri-cone bit will then be used to drill down to 145 feet. A 5-inch ID steel casing will be installed from ground surface to 145 feet bgs. A bentonite/cement grout will be used to fill the annular space.
3. Wireline coring barrels (NX rods) will be used to core 20 feet into the bedrock (165 feet bgs). The coring barrels will be retrieved and opened to collect the core sample.
4. Core samples will be photographed and described on test boring logs. Descriptions will follow the procedures outlined below.
5. The borehole will then be reamed to a 4-7/8-inch diameter. A 2-inch PVC casing (schedule 80) will be installed from ground surface to 165 feet bgs (20 feet into bedrock). The PVC casing will have a 5-foot long screen (0.010-inch slots). A bentonite seal with a minimum thickness of two feet will be installed directly above the sand pack. This

bentonite seal will be 3 feet in length. The remaining annular space will be filled with a bentonite and cement grout.

6. The temporary 10-inch I.D. steel casing will be removed and the well will be completed with an aboveground well protector and a locking cap.
7. Well development or purging may be necessary before collecting groundwater samples from the cased/screened hole in the bedrock. The procedures for both well development and well purging are presented below.
8. Water level measurements will then be collected, prior to sampling the bedrock groundwater. The procedure for measuring water levels is also presented below.
9. The bedrock groundwater sample collection method is presented after the procedure for water level measurements.

Well Development

Newly installed wells will require development to clear the well of accumulated sediments. Appendix H presents the standard operating procedure (SOP) for well development.

Well Purging (if necessary)

After installation and development and prior to sampling, the well may be purged to remove the standing water column from the well casing. The SOP for well purging is presented in Appendix H with the procedure for well development.

Water Level Measurements

Prior to initiating groundwater sampling, water elevations will be measured in the well. Refer to Appendix I for well gauging procedures.

Groundwater Pre-Sampling and Well Sampling

Appendix I presents the protocol for groundwater sampling activities.

Description of Rock Samples

As mentioned earlier in this section, the rock core will be evaluated via photographs and petrographic thin sections. The geologists and geotechnical engineers will write their description

of rock samples with a consistent format. A detailed order and presentation of selection of data are presented in Appendix J.

Groundwater Flow Direction (water levels)

Water levels will be measured quarterly for one year in the bedrock well and used to prepare water-level elevation maps. These will show seasonal changes in groundwater level and flow direction. Water level measurements will be conducted according to the same protocol outlined in Appendix I.

Groundwater Flow Rate (slug tests)

Rationale

Falling and rising head slug tests will be performed on the bedrock well, using a slug of known volume and in-well, short-time interval, automatic water-level recorders. With the falling-head and rising-head slug test data, aquifer hydraulic conductivity will be calculated for the well. Measured groundwater gradients and calculated aquifer hydraulic conductivities will be used to determine groundwater flow rates.

Field Procedure

Appendix K presents the field protocols for the completion of *in situ* hydraulic conductivity (slug) tests.

Slug test data will be downloaded from the data logger each day. The data will be reviewed for errors. If necessary, a slug test will be re-conducted.

5.4.3 Soil

5.4.3.1 Surface Soil Samples

Rationale

Four surface soil samples (0 to 0.5 feet) will be collected at this disposal site. These samples will be collected at the location of each waste sample boring to provide information for the Human Health Risk Assessment and Ecological Risk Assessment. Scaled, color digital photographs will be taken of each soil sample to provide a record of materials present at this site. Each sample will be analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin, and metals.

Table 1 presents the analytical methods. A detailed sample and analysis summary for the surface soil sampling is presented in Table 6.

Figure 9 presents approximate soil sample locations in Site R.

Field Procedure

Surface soil samples will be discrete. A discrete sample represents a single location in the soil column. The soil samples will be collected from the Geoprobe® borings.

Appendix C presents the standard operating procedure for waste and soil sample collection.

5.4.3.2 Subsurface Soil Samples

Rationale

Four subsurface soil samples (0.5 to 6 feet) will be collected at this disposal site. As with the surface soil samples, the subsurface samples will be collected at the location of each waste sample boring to provide information for the Human Health Risk Assessment. Scaled, color digital photographs will be taken of each soil sample to provide a record of materials present at this site. Each sample will be analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin, and metals.

Table 1 presents the analytical methods. A detailed sample and analysis summary for the subsurface soil sampling is presented in Table 7.

Figure 9 presents approximate soil sample locations for Site R.

Field Procedure

The four soil samples collected at this site will be collected at the location of each waste sample boring. The subsurface soil samples will be collected in the same manner as the waste samples.

Appendix C presents the standard operating procedure for waste and soil sample collection.

5.4.4 Air

5.4.4.1 Rationale

Two upwind and two downwind ambient air samples will be collected to determine the tendency of site constituents to enter the atmosphere and local wind patterns. Air sampling data will be used in the Human Health Risk Assessment and Ecological Risk Assessment. Samples will be analyzed for VOCs, SVOCs, pesticides, PCBs, metals, and dioxin.

Twenty-four hour cumulative duration sorbent tube/PUF/PM2.5 samples will be collected over a 1-day period, using the sampling protocols provided in Appendix L. Two upwind and two downwind samplers will be installed at the site during weather likely to produce emissions (e.g. hot and dry conditions in August). Sampling locations will be selected in the field with the concurrence of USEPA Region V or his designee. Sorbent tube samplers will be used for VOC data collection. Polyurethane foam (PUF) samplers will be used for SVOC, PCB, pesticide, and dioxin data collection. PM2.5 samplers will be used for metal data collection

Ambient air sample collection is required to measure airborne levels of contaminants that may be evolving from the site. A 24-hour sample duration is required to average the air emission differences that may occur from the day time to night time cycle from on-site and off-site conditions and activities. Also, air sample collection locations need to be positioned on the site to collect up wind and down wind samples for differentiation of constituents originating from the surrounding area and those originating from the site. The sample protocol will collect site samples over a 1-day time period on a warm, dry day.

The level of detection for SVOCs required by USEPA Region V needs to consider sensitivity and selectivity to analyze complex samples. Based on this need, the analytical method of choice is gas chromatography coupled with mass spectrometry (GC/MS) for detection. Based on the GC/MS analytical method and its sensitivity level, the air sample volume needs to exceed 325 standard cubic feet. This enables the collection of a sufficient quantity of SVOCs to meet the level of detection required by USEPA Region V.

The sample method to meet the above requirements for SVOC measurement is USEPA Method TO-13, as identified in the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* (June 1988). This method will use a Graseby/General Metal Works, Inc. high volume air sampling unit or equivalent for sample collection. Sample collection will

consist of drawing an ambient air sample at a high volume flow rate through a PUF collection media over a 24-hour time period. The samples will be submitted for analysis of the TO-13 list of SVOCs. Method TO-15 will be used to analyze VOCs. Method TO-4 will be used for pesticides, and PCBs. Method TO-9 will analyze for dioxins.

Table 8 is a sample and analysis summary of this activity.

5.4.4.2 Field Procedure

The following procedure will be used for ambient air samples:

- Place the sorbent tube samplers, PUF samplers, and PM2.5 samplers at upwind and downwind locations.
- Locate sampling positions in an unobstructed area, at least two meters from any obstacle to air flow. Sample locations will be selected in the field with the concurrence of the USEPA Region V, or its designee.
- No local power supply is readily available at the sites. Therefore, gasoline- or diesel-powered generators will be positioned at downwind locations from the sample collection positions. They will supply the electricity for the samplers.
- Record wind direction and velocity readings.
- Follow sample collection protocols identified in Appendix L for sample preparation, calibration, collection, laboratory preparation and shipment, and calculations. Sample data sheets are provided in Appendix L.

5.4.5 Stormwater Runoff

5.4.5.1 Rationale

One stormwater runoff grab sample will be collected at a downgradient location within this site, in an effort to characterize runoff from the site during storm events. Samples will be collected within the primary drainage route, leading from the site to the Mississippi River. This sampling will be conducted at Sites Q and R because they are on the wet side of the floodwall and levee. The other three sites (O, P, and S) are on the dry side of the floodwall and levee and therefore have no drainage route to the Mississippi River. Samples will be collected during three storms to determine variability of constituent concentrations in site runoff. A first flush sample will be collected utilizing an automated sampling device. A first flush sample is one collected at the

very beginning of a storm event (e.g., as the first flow comes through). Collection of a first flush sample insures that any contamination on the ground surface prior to the storm event will be collected before it has the opportunity to wash away. Storm water samples will be analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin, and metals.

The analytical methods are presented in Table 1. Table 9 presents a sample and analysis summary for storm water runoff samples to be collected.

5.4.5.2 Field Procedure

Refer to Appendix M for the standard method of storm water sample collection.

The following method will be used for collection of storm water samples:

1. Identify the primary storm water drainage route, running from the site to the Mississippi River
2. Collect the sample during a rainfall, which results in a discharge. A storm water sample will be collected during three separate storm events (for a total of three samples per site).
3. Set up appropriate parameters on automated sampler.
4. Remove appropriate sample containers from the transport container, and prepare the sample containers for receiving samples.
5. Fill out a self-adhesive label with the appropriate information and affix it to the appropriate sample container. Place clear polyethylene tape over the completed label to protect it from dirt and water. Sample labels can be prepared prior to sample collection, except for time and date. Labels can be filled in on the date of sample collection and just prior to collecting the sample. Sample containers will be kept cool with their caps on until they are ready to receive samples.
6. Put on a clean pair of disposable gloves.
7. Set sampler to sample containers for the VOC sample, prior to filling other sample containers. Verify that there is no air in the sealed sampled container.
8. Transfer sample to appropriate containers for shipment to laboratory.
9. If the sample containers cannot be filled quickly, keep sample containers cool with the cap on until finished. Sample containers will be preserved as described in the QAPP.

10. Return each sample container to its proper transport container. Preserve samples by reducing the temperature within the containers to approximately 4° Celsius, using ice. Samples must not be allowed to freeze.

11. Begin chain-of-custody procedures. A sample chain-of-custody form is included in Appendix F.

12. Record the physical appearance of the storm water observed during sampling in the field notebook.

Treatability Tests

Rationale

The AOC requires that the SSP present a pilot test program for any treatment technologies lacking sufficient information on implementability and effectiveness. Data gaps exist for off-site incineration, off-site disposal, and on-site thermal desorption for the waste and on-site and off-site physical/chemical treatment, and off-site biological treatment for leachate.

A total of five composite waste samples (one for each site) will be collected for waste treatability testing and sent to appropriate facilities operators for waste profiling, material handling characterization and evaluation of the feasibility of disposing of the waste material by off-site incineration, off-site disposal, and on-site thermal desorption. In addition, five composite leachate samples (one for each site) will be collected for treatability testing to determine if the leachate can be discharged directly to American Bottoms POTW without resulting in pass through and/or interference.

One sample will be collected from each waste disposal area for waste treatability testing. The sample will be made from aliquots collected from the four waste characterization borings installed at each disposal area. One sample will be collected for the leachate treatability testing from each of the five-leachate sampling wells.

Sample Collection

The five composite waste samples that will be collected for treatability testing will be retained from the four-waste/soil borings that will be advanced at each waste disposal area. All of the material recovered from the Geoprobe® samples that are not needed for the other chemical analyses will be composited in 5-gallon buckets. Each bucket will be sealed, labeled and

prepared for shipment to the appropriate facilities.

The leachate sample that will be collected for treatability testing will be collected during leachate sampling activities. An equal amount of leachate will be removed, via bailer or pump, from each of the five-leachate monitoring wells and placed in separate 5-gallon buckets. Each bucket will be sealed, labeled and prepared for shipment to the appropriate facility.

5.4.6 Seep Investigation

5.4.6.1 Rationale

A visual reconnaissance survey will be undertaken along the riverbank adjacent to Site R to assess the presence of seeps and their impacts, if any, on the Mississippi River. The locations of any seeps observed will be located with a GPS, photographed, and if sufficient quantity is present, sampled for VOC, SVOC, PCBs, dioxin, herbicide, pesticide, and metals. Where appropriate, several smaller seeps in close proximity to each other may be sampled as a single location. If sample volume is limited, sample containers will be prioritized and filled in order of analytical parameters as presented above.

The analytical methods are presented in Table 1.

5.4.6.2 Field Procedure

Refer to Appendix M for the standard method of seep water sample collection.

The following method will be used for collection of seep water samples:

1. Identify the seep location(s) along the riverbank and note location.
2. Remove appropriate sample containers from the transport container, and prepare the sample containers for receiving samples.
3. Fill out a self-adhesive label with the appropriate information and affix it to the appropriate sample container. Place clear polyethylene tape over the completed label to protect it from dirt and water. Sample labels can be prepared prior to sample collection, except for time and date. Labels can be filled in on the date of sample collection and just prior to collecting the sample. Sample containers will be kept cool with their caps on until they are ready to receive samples.

4. Grab sampling procedures and preservation of the collected seep water samples will follow the methods described in the current edition of "Standard Methods for the Examination of Water and Wastewater" (published by the American Public Health Association).
5. Put on a clean pair of disposable gloves.
6. Use a dipping utensil to retrieve a sample.
7. Fill sample containers for the VOC sample, prior to filling other sample containers. Verify that there is no air in the sealed sampled container.
8. Fill remaining sample containers.
9. If the sample containers cannot be filled quickly, keep sample containers cool with the cap on until finished. Sample containers will be preserved as described in the QAPP.
10. Return each sample container to its proper transport container. Preserve samples by reducing the temperature within the containers to approximately 4° Celsius, using ice. Samples must not be allowed to freeze.
11. Begin chain-of-custody procedures. A sample chain-of-custody form is included in Appendix F.
12. Record the physical appearance of the storm water observed during sampling in the field notebook.

5.5 SITE S

5.5.1 Waste Characterization

5.5.1.1 Delineation of Source Area Boundaries – Test Trenches

Rationale

Historical air photos were obtained for this site. These photos were used to define the areal extent of the site over time and to determine the boundaries of the waste disposal area. Boundaries of the site on each photo were observed. To define the maximum extent of fill, the tracings for the site were overlain and a line was drawn around the outside limit of the composite waste disposal area boundary. Results of the historical air photo analysis were used to prepare a map for the site, showing disposal area boundaries. Stereoscopic evaluation of historical air

photographs allowed identification of the deepest portion of a waste disposal area, and one of the four waste characterization borings discussed below will be done at that location.

Test trenches will be used to confirm the boundaries of the waste disposal area identified through air photo analysis. One trench will be installed on each side of the waste disposal area. Thus, there will be a total of four trenches for the site. The four trenches will be located at the midpoint of the four longest sides of the defined site boundary. A GPS system will be used to document the locations on aerial site maps. Test trenches will start outside the defined boundary of the disposal area and move toward the defined boundary. When fill materials are encountered, the disposal area boundary will be compared to those identified in the air photo analysis and trenching at that location will then be terminated.

Excavated soil and fill material will be returned to the test trench, with the exception of any intact drums. Intact drums will be removed, provided confined space entry is not needed to retrieve a drum. Trenches will not be entered to recover drums due to the inherent danger in such activities. Test trench locations will be determined using a GPS system. The trench locations will be recorded for future reference, in the event drum removal is appropriate. The drum removal contractor, in accordance with the requirements of 29 CFR 1910.120(j) will handle drums recovered during trenching activities. Recovered drums will be over-packed and stored pending disposal. Free product and contaminated soil resulting from rupture of drums during removal will be cleaned up by absorbing any liquid materials. The absorbent, solid waste, and contaminated soil will be placed in bulk containers. The over-packed drums and these bulk containers will be temporarily stored at a controlled-access, fenced Investigation Derived Waste (IDW) Storage Area to be constructed at Site R. Recovered drums and wastes will be stored until the capacity of the storage pad is exceeded or the investigation is complete, whichever comes first. Any waste excavated that identifies the source of material present in the fill area will be noted in the field log and photographed.

Trenching locations will be selected in the field with the concurrence of USEPA Region V RPM or his designee.

Field Procedure

All trenching activities will be conducted in a manner to protect existing utilities, structures, surface features, monitoring wells, and the general site environment. Additionally, trenching

activities will follow Occupational Safety and Health Administration (OSHA) rules for excavations.

Locations of test trenches for boundary confirmation of Site S are shown on Figure 11. A "competent" person, as defined in 29 CFR 1976.650, will observe the trenching activities and will have authorization to take corrective measures to respond to unsanitary, hazardous, or dangerous conditions to workers. A track-mounted hoe with an extended arm will be used for excavation. A photoionization detector (PID), combustible gas monitor (CGM), and a real-time aerosol monitor (RAM) will be used on a continuous basis to monitor the test trenches for hazardous conditions.

Trenching activities will begin outside the site boundary and move in towards the boundary. The trenching will extend vertically to a maximum depth of 40 ft bgs or to groundwater, whichever is encountered first. No accommodations will be made to dewater test trenches or manage groundwater during excavation activities in order to minimize the generation of investigation-derived wastes. The trenching will continue until waste material is encountered. Should waste materials be encountered initially, the trenching activities will proceed out and away from the boundary until native soils are encountered. Where native soils are encountered, the excavation will proceed to greater depth up to a maximum of 40 ft below grade, where possible. Should waste materials be encountered again within the test trench, this procedure will be repeated until no waste materials are encountered within the test trench. The location where no additional waste materials are encountered within the test trench will be designated as the extent of the site boundary for that location.

As the trenching proceeds, spoils from the test trenches will be placed on polyethylene plastic, having a minimum thickness of 6 millimeters. Provisions will be made to allow free liquids in the spoils to drain back to the trench. Spoils from each test trench will be segregated and returned to the excavation in reverse order of removal. The gross contamination will be removed from the excavator bucket with a shovel and/or potable water source prior to handling the cover material. Decontamination debris will be placed into the excavation trench prior to placement of cover material. Handling of investigation-derived wastes from these activities is discussed in Section 9.

Backfilling will be conducted in a manner to minimize ponding of water over the trench. A silt fence will be installed around the perimeter of the trench to minimize runoff of surface soils

during rain events. A test trench at one location will be backfilled prior to the initiation of a test trench at another location. After completion of site investigation activities, the sites will be revegetated with grass. The silt fence will be maintained until revegetation is completed.

The location of the test trenches will be illustrated on a plan of the site. Digital photographs will be taken of the test trenches, the test trench walls, and any waste materials excavated. The number and location of each photograph will be identified on the field log for each test trench.

5.5.1.2 Soil Gas Surveys

Rationale

A soil gas contractor will perform a soil gas survey at Site S. A shallow soil probe (5 feet) and on-site analysis of collected VOC vapors with a GC will be used in this survey. Soil gas samples will be collected at the center of the site and along each side, resulting in five sampling locations. The soil gas survey sampling points for Site S are displayed in Figure 12.

If detectable concentrations of Total VOCs are found in the soil gas samples at the disposal area boundary, the survey will be extended beyond that boundary. If extended beyond the boundary, soil gas samples will be collected at 100-foot intervals (0, 100, and 200 feet from the edge of the disposal area) along as many as four 200-foot long transects. Each transect will run perpendicular to the relevant sides of the disposal area. If VOCs are detected in soil gas at this site, up to twelve additional soil gas samples may be collected.

If twelve additional samples are not adequate to define the extent of VOC-containing soils in the disposal area, additional soil gas samples will be collected at 100-foot intervals along the appropriate transects until the limits of the impacted fill are determined. If soil gas surveys need to extend into areas for which there are no property access agreements, soil gas sampling will be suspended until access is obtained.

Sampling locations will be selected in the field with the concurrence of USEPA Region V RPM or his designee.

Table 2 is a sample and analysis summary for this activity.

Field Procedure

Direct push technology will be used to advance a retractable point holder to 5.5 feet below

existing grade. The rods will then be pulled back to approximately 5 feet below existing grade to disengage the retractable point, therefore, exposing the sampling mechanism. Polyethylene tubing (0.125-inch diameter) will be lowered into the rods. The upper end of the polyethylene tubing will be connected to a 4-inch section of silicone tubing. This will then be attached to a section of polyethylene tubing coming from an active vacuum system and a vacuum will be placed in the tubing using a 60cc sample of soil gas will be withdrawn. From the silicone tubing using a 60cc disposable syringe with a stainless steel needle. The sample will then be directly injected into the on-site GC. The GC will provide a report of the total VOC concentrations.

Sample tubing will be removed from the probe and disposed. Probing rods and sampling

equipment will be removed from the boring. The probe boring will be filled with bentonite, to just bgs. The bentonite will be hydrated with potable water and the surface will be restored to its original condition. An SOP for the field GC is contained in Appendix A.

5.5.1.3 Waste Samples

Rationale

Two borings will be advanced at this site to characterize the waste materials present. Continuous samples will be collected from grade to two feet below the bottom of the waste material, which is estimated to be a maximum of 40 feet below grade. If wastes are encountered at depths greater than 40 feet bgs (bgs), the boring will continue until the bottom of the waste is encountered. Scaled, color digital photographs will be taken of each waste sample to provide a record of materials present in the disposal area.

One composite waste sample will be collected at each boring location (2 total composite waste samples), and analyzed for SVOCs, pesticides, herbicides, PCBs, dioxin, and metals. In addition, a portion of the composite waste sample from above the water table will be extracted using TCLP procedures and analyzed for this same suite of analytes. Visual observations and PID readings will be used to identify whether or not waste is present in a continuous boring sample. If waste is present in a sample, it will be removed, segregated, temporarily stored and used at the completion of the soil boring to prepare a composite waste sample. Since VOC samples cannot be composited without losing volatiles, the waste with the highest PID readings will be used for VOC analysis.

Existing information (e.g., the 1998 Ecology and Environment report and the results of the aerial photograph analysis, soil gas surveys, and magnetometer surveys conducted as part of the SSP) will be used to select boring locations. Approximate waste characterization boring locations for Site S are shown on Figure 11. Additional waste characterization borings may be required by USEPA Region V as a result of variability in waste characteristics observed during the waste characterization boring program.

Table 3 is a sample and analysis summary for waste samples to be collected.

Field Procedure

Borings will be advanced via direct push technology (Geoprobe®). The Geoprobe® will hydraulically drive a stainless steel, acetate-lined MacroCore® sampler (2-inch diameter by 4-foot length) to the desired subsurface sample depths. Continuous samples will be collected from grade to 2 feet below the bottom of the waste material (estimated to be 40 feet bgs). Between each sample collection, the sampler will be retrieved to the surface and the samples removed from the disposable acetate liner within the sampler.

One composite waste sample will be collected from each boring. Each sample will be visually observed and monitored with PID readings, to determine whether waste is present. If waste is present in a sample, it will be removed, segregated, temporarily stored, and used at the completion of the soil boring to prepare a composite waste sample. The soil sample exhibiting the highest PID reading at each of the four boring locations within this site will be used for VOC analysis. A 5-gram EnCore® sampler will be used to collect VOC samples.

Refer to Appendix C for detailed soil/waste sampling procedures.

Descriptive logs of each boring will be prepared as described in Appendix E. The two waste borings generated will also be used for surface and subsurface soil sample collection. All borings will be grouted to the surface, following retrieval of both the waste and soil samples.

Logging Unconsolidated Samples

The geologist logging samples will be responsible to interpret the samples following standard and acceptable methods. The geologist implementing this work plan will have training and experience logging boring samples. Soil will be logged according to applicable ASTM

standards. As appropriate, ASTM standards will be used to log waste materials. Appendix E presents detailed instructions for logging soil and waste samples.

5.5.1.4 Buried Drum and Tank Identification

Magnetometer Survey

Rationale

A magnetometer survey will be conducted at this site to identify anomalies indicative of drum disposal or buried tanks. Magnetometer measurements will be made at locations determined by superimposing a 50-foot by 50-foot grid on the disposal area.

Surface geophysical surveys, which map the distribution of the strength of the earth's magnetic field, have been proven useful in evaluating shallow and deep subsurface conditions at environmental sites. These geophysical surveys have been used to successfully locate buried objects containing magnetically susceptible materials (e.g., iron and nickel metals). The ability of geophysical equipment to locate buried objects is, for the most part, dependent on:

- The strength and orientation of the magnetic anomaly associated with the buried objects
- The strength and natural variation of the earth's magnetic field in response to local geology
- The influence of man-made surface features (such as power lines, buried utilities, vehicles, electric motors, etc.) which may interfere with the collection of data.

By comparing the known surface and geological conditions to a magnetic survey map that includes mapped surface feature interferences, and understanding possible geologic background effects, it is possible to identify the location of suspicious subsurface features which may represent buried tanks or drum disposal areas.

Method

A geophysical contractor will conduct the magnetometer survey. A geophysical survey of the site's magnetic field will be completed utilizing a field magnetometer and electromagnetic induction. The field magnetometer measures the strength of the site's magnetic field regardless of the orientation of the magnetic lines of force. During the performance of the geophysical survey, data for the preparation of a field map will be collected. The final product of this survey

will include a description of the site, contour maps, and an explanation of how the survey was conducted.

A correction for diurnal and micropulsation time variations is not necessary because the site and anticipated anomalies are relatively small in area (less than 1 square mile), and subsurface anomalies from buried objects of interest should be relatively large (greater than 100 gammas).

The map showing the distribution of magnetic field strength over the site will be compared with the observed field conditions (including the location of known interfering objects such as vehicles, overhead power lines, and surface debris). By comparison, those magnetic anomalies, which cannot be explained by, observed site conditions, will be presumed to be a result of buried subsurface material (e.g., drums, tanks, metal debris, etc.). The depth of detection for suspect objects (such as steel drums) may vary according to orientation, method of manufacture and condition, and numbers present. Steel drums, such as those suspected to be present at this site, may be detected to depths of 40 feet.

Study Area

The area of the properties to be surveyed will be evaluated in the field. Magnetometer surveys will be conducted at a total of four sites (P, Q, R, and S) within Area 2. A general area for Site S survey site has been delineated and provided on Figure 12 (Fill Area Location Map). Overall site dimensions for the survey sites will be adjusted based upon the findings of the source area boundary delineation activities discussed in Section 5.2.1.1.

Field Procedure

The following field equipment and procedures will be employed during this geophysical investigation.

Equipment

A Geometrics 858 Cesium or a Geometrics 856AX Total Field Magnetometer will be used to collect the field data. Field procedures and operation of the instruments will be in accordance with the recommended manufacturer's field procedure and application manual.

Calibrated field survey equipment consisting of marked survey line, tape rulers, highway danger cones, and marked wooden stakes will be utilized to establish measurement locations.

Measurement Point/Grid Surveying

The established survey lines will be marked in the field using a premarked survey line to maintain straight and precise station locations. Profiles will be completed along a straight line with an unobstructed line of sight. The corners of each of the gridded areas will be marked with temporary corner stakes to permit the relocation of the measurement points within each site.

Data Processing

Following completion of the field phase of investigation, the following data processing will be performed:

- Explanation of where and how the survey was performed
- Description of each of the four sites (P, Q, R, S) in terms of magnetic anomalies detected
- A contour map of these data will be produced showing the location of the measurement points and the corresponding magnetometer reading.

Test Trenches

Rationale

Test trenches will be installed at this site to confirm the presence of buried drums of tanks. One test trench will be installed at this site. The waste disposal areas within Area 2 were used for disposal of municipal and industrial waste as well as construction debris. Magnetic anomalies are likely to be numerous, intense, and widespread. If no location criteria other than the presence of a magnetic anomaly is used to determine whether or not a test trench is appropriate, disturbance of a significant portion of each disposal area is likely to result. Excessive trenching could result in unacceptable risks to the community, on-site workers and the environment.

For this reason, four selection criteria will be used to identify where to install each test trench. Test trenching will be done at the location of the largest magnetic anomaly that coincides with:

1. A soil gas concentration high,
2. Drum or tank disposal locations identified by historical air photo interpretation,
3. An area of high groundwater concentrations (greater than 10,000 ppb) as identified by the 1998 Ecology and Environment Data Report, and

4. Major magnetic anomalies reported in the 1988 Ecology and Environment "Expanded Site Investigation, Dead Creek Project Sites at Cahokia/Sauget, Illinois".

Care will be taken not to place major emphasis on the comparison of historical groundwater concentrations and magnetic anomalies due to the extent of historical industrial groundwater pumping in the area.

Excavated soil and fill material will be returned to the test trench, with the exception of any intact drums. These will be removed, provided confined spaced entry is not needed to retrieve a drum. Trenches will not be entered to recover drums because of the danger inherent in such activities. Test trench locations will be determined using a GPS and recorded for future reference in the event drum removal is appropriate.

Recovered drums will be over-packed and stored pending disposal. Free product and contaminated soil, resulting from rupture of drums during removal, will be cleaned up by absorbing any liquid materials and placing the absorbent, solid waste, and contaminated soil in bulk containers. Over-packed drums and bulk solid and liquid containers will be stored at a controlled-access, fenced Investigation Derived Waste (IDW) Storage Area to be constructed at Site R. Recovered drums will be stored until the capacity of the storage pad is exceeded or the investigation is complete, whichever comes first. Any waste excavated that identifies the source of material present in the disposal area will be noted in the field log and photographed.

Field Procedure

Anomaly test trench locations will be selected in the field based upon the parameters outlined in the Rationale section, and with the concurrence of the USEPA Region V or its designee.

To complete the anomaly test trench, a track-mounted or wheel-mounted hoe will be utilized. The depth to the top of buried anomalies is not expected to extend past 40 feet below grade; thus, a smaller piece of equipment may be utilized for these anomaly test trenches (in comparison to the trenches completed for delineation of the fill area boundaries). Trenching activities will be conducted in a manner to protect existing utilities, structures, surface features, monitoring wells, and the general site environment. Additionally, trenching will follow OSHA rules for excavations. A PID, CGM, and a RAM will be used on a continuous basis to monitor the anomaly test trenches for hazardous conditions. The hoe operator will have a separate supplied-air system.

Anomaly test trenches will be advanced until evidence as to the source of the anomaly is found or to a maximum depth of 40 feet, where possible. Should groundwater infiltration and/or poor soil stability result in the inability to complete a test trench to 40 feet, the trenching will be terminated at that location. No accommodations will be made to de-water test trenches or manage groundwater during excavation activities, due to the need to minimize the generation of investigation-derived wastes.

As the trenching proceeds, spoils from the test trenches will be placed on polyethylene plastic having a minimum thickness of 6 millimeters. Provisions will be made to allow free liquids in the spoils to drain back to the trench. Spoils from each test trench will be segregated and returned to the excavation in reverse order of removal. Backfilling will be conducted in a manner to minimize ponding of water over the trench. A silt fence will be installed around the perimeter of the trench to minimize runoff of surface soils during rain events.

If intact drums are found during anomaly test trench completion, they will be removed, over-packed, and stored in an area to be designated in accordance with the requirements of 29 CFR 1910.120(j). For planning purposes, it is anticipated that up to ten over-packs will be necessary per site and that one day of anomaly test trenching will occur at each of the four sites. Handling of investigation-derived wastes from these activities is discussed in Section 9.

A test trench at one location will be backfilled prior to the initiation of a test trench at another location. After completion of site investigation activities, the sites will be revegetated with grass. The silt fence will be maintained until revegetation is completed.

5.5.1.5 Leachate Samples

Rationale

A 2-inch diameter well, screened at the bottom of the fill material, will be installed in one of the two waste characterization borings completed at this site. The purpose of this well is to characterize leachate at the site. The well will be sampled and analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin, and metals. The analytical methods are presented in Table 1.

Field Procedure

Well Installation

The depth and screened interval for the well will be determined in accordance with the subsurface stratigraphy observed during Geoprobe® waste sampling activities. It is expected that the waste at the site extends to approximately 40 feet bgs. Unless observed conditions indicate otherwise, a screened interval of 10 feet will be used. The well will be seated at the bottom of the waste. A 4-1/4 inch ID hollow-stem auger will be used to advance the boring to the bottom of the waste material. The well will be constructed of two-inch diameter, schedule 40 PVC casing and 0.010-inch slotted schedule 40 PVC well screen. A sand pack, consisting of silica sand, will be installed from the bottom of the well to two feet above the well screen. A bentonite seal with a thickness of between two feet and three feet will be installed directly above the sand pack. The remaining annular space will be filled with a bentonite and cement grout. The well will be completed with an aboveground well protector and a locking cap.

Following installation of the leachate well, the top of casing and ground surface will be surveyed to establish well and grade elevations and well location. Well installation details will be documented on a test boring log (Appendix D) and in the field notebook. The leachate well will generally be installed according to the typical well construction diagrams and standard procedures presented in Appendix G.

Following completion of monitoring well construction activities, the water level will be allowed to stabilize and will then be gauged to determine groundwater elevation and the total volume of groundwater in the well. After the water level in the well has been determined, the well will be developed to remove the fines from the sand pack. The development will consist of pumping or bailing the well, following the protocol described later in this section.

Sampling locations will be selected in the field with the concurrence of USEPA Region V or its designee. Figure 11 displays the approximate leachate monitoring well location for Site S.

Well Development

Newly installed wells will require development to clear the well of accumulated sediments. Appendix H presents the standard operating procedure (SOP) for well development.

Well Purging (if necessary)

After installation and development and prior to sampling, the well may be purged to remove the standing water column from the well casing. The SOP for well purging is presented in Appendix H with the procedure for well development.

Water Level Measurements

Prior to initiating groundwater sampling, water elevations will be measured in the well. Refer to Appendix I for well gauging procedures.

Groundwater Pre-Sampling and Well Sampling

Appendix I presents the protocol for groundwater sampling activities.

5.5.2 Hydrogeology

5.5.2.1 Alluvial Aquifer

Horizontal Extent of Contaminant Migration

Rationale

Groundwater samples will be collected in the alluvial aquifer downgradient of this waste disposal area. The purpose of this sampling is to define the extent of migration away from the source area and to provide information for the Human Health Risk Assessment.

Groundwater samples will be collected at three sampling stations located on an east/west transect between the downgradient boundary of Site S and the upgradient boundary of Sites Q and R. Unfiltered groundwater samples will be collected every 10 feet from the water table to the bottom of the aquifer using push sampling technologies such as Geoprobe®, HydroPunch®, Microwell®, Waterloo Profiler® or equivalent low-flow sampling techniques. Aquifer saturated thickness is estimated to be approximately 120 feet with depth to water at 20 feet bgs and bottom of the aquifer at 140 feet bgs. All samples will be analyzed for VOCs and SVOCs. Additionally, unfiltered samples will be collected at 40 foot intervals (i.e., 20, 60, 100, and 140 foot bgs) and analyzed for pesticides, herbicides, PCBs, metals, and several geochemical parameters (presented in Table 1). Dioxin will be analyzed only at the sampling station closest to Site S. For dioxin analysis, unfiltered groundwater samples will be collected at the top, middle, and bottom of the saturated zone (e.g., 20, 80, 140 feet bgs).

Experience at other sites indicates that push-sampling technologies such as Geoprobe® can reach depths of 60 feet. Depth of penetration can be increased at some locations by loosening the soil above the sampling horizon with a small-diameter solid stem auger before pushing the sampling probe to the required sampling depth. When the Geoprobe® sampler or equivalent sampling technology cannot penetrate to the required depth, Microwells® will be used to collect groundwater samples. These small-diameter wells are vibrated into place using a small vibratory hammer. Experience in deep aquifers at other sites indicates that sampling depths of 100 feet can be achieved. If the required sampling depths cannot be reached with either of these two technologies, conventional percussion drilling equipment will be used to drive 1-1/4 inch diameter drive points to the required sampling depths.

Table 1 presents the analytical methods. A detailed sample and analysis summary for the alluvial aquifer groundwater sampling is presented in Table 4.

Sampling locations will be selected in the field with the concurrence of USEPA Region V or its designee. Figure 4 displays approximate groundwater sampling locations for Area 2.

Field Procedure

Establishment of Boreholes

Push Point

Using the hydraulic push system of a Geoprobe®, a 4-foot stainless steel sampler with a wire wrap (slot size of 0.004 inches) will be pushed to the desired sample depth. A bailer or ball and check valve will be sent down to the slotted portion of the sampler to collect the groundwater sample. The groundwater sample will be retrieved to the surface and placed in a sample container. The Geoprobe® will then drive the sampler to the next desired sample depth, by connecting clean sections of push rods to the Geoprobe®, and a second groundwater sample will be collected here. This process will be continued until all samples are collected.

MicroWell®

It is anticipated the above sampling method will be used, as feasible. However based on the location of the site within the Mississippi River flood plain, large gravel or cobbles may be encountered, which will stop the Geoprobe®. Should this occur, MicroWells® will be installed to use as the sample collection point. The MicroWells® will be hydraulically pushed to the

appropriate depth, and the sampling procedure described above will be followed. Once the sample is collected, the MicroWell® will be pulled, the screen point decontaminated according to the method described below, and a new well will be advanced further in the same hole. This procedure will be repeated until all samples are collected.

Should MicroWell® installation prove impractical, boreholes will be advanced using conventional hollow stem auger drilling methods. In this instance, the lead auger will have a screened section through which groundwater will flow. Once the sample is collected, the augers will be advanced further for collection at the next sample depth. This procedure will be repeated until all samples are collected within the borehole.

All Geoprobe®, MicroWell®, or Waterloo Profiler® holes will be sealed with grout from the bottom up and the surface will be returned to it's original condition after completion of sampling at each location. A PID, explosimeter, and a RAM will be used on a continuous basis to monitor these activities.

Groundwater Pre-Sampling and Borehole Sampling

Appendix I presents the protocol for groundwater sampling activities.

5.5.2.2 Bedrock Groundwater

Vertical Extent of Contaminant Migration

Rationale

One bedrock well will be installed downgradient of this site. The purpose of the bedrock sampling is to determine the extent of organic and inorganic constituent vertical migration from the site. Steel surface casing will be installed 5 feet into bedrock.

After installing the telescoping surface casing 5 feet into bedrock, the bedrock will be cored to a depth of 20 feet below the bottom of the casing. Cores will be digitally photographed in color against a scale and evaluated for porosity by examination and petrographic thin sections. One thin section will be made for each 2 feet of bedrock core. A 2-inch diameter, 5-foot-long screen and casing will be installed in the borehole. The screen will be filter-packed, sealed and grouted from 3 feet above the top of the filter-pack to grade. An unfiltered groundwater sample will be

collected from the well following installation and development and will be analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin, and metals.

Table 1 presents the analytical methods. A detailed sample and analysis summary for the bedrock groundwater sampling is presented in Table 5.

Sampling locations will be selected in the field with the concurrence of USEPA Region V or its designee. Figure 4 displays approximate groundwater sampling locations for Site S.

Field Procedure

Mud rotary drilling methods will be used to drill the borehole to set the surface casing and to drill 5 feet into the top of bedrock. Coring will then be accomplished using wireline coring barrels to generate a 2-inch thick minimum core. Coring will continue for 20 feet into the bedrock. The drilling and sampling procedure will be as follows:

1. A temporary 10-inch ID steel casing will be installed from ground surface to 10 feet bgs. A bentonite/cement grout will be used to fill the annular space.
2. A 8-3/4-inch ID tri-cone bit will then be used to drill down to 145 feet. A 5-inch ID steel casing will be installed from ground surface to 145 feet bgs. A bentonite/cement grout will be used to fill the annular space.
3. Wireline coring barrels (NX rods) will be used to core 20 feet into the bedrock (165 feet bgs). The coring barrels will be retrieved and opened to collect the core sample.
4. Core samples will be photographed and described on test boring logs. Descriptions will follow the procedures outlined below.
5. The borehole will then be reamed to a 4-7/8-inch diameter. A 2-inch PVC casing (schedule 80) will be installed from ground surface to 165 feet bgs (20 feet into bedrock). The PVC casing will have a 5-foot long screen (0.010-inch slots). A bentonite seal with a minimum thickness of two feet will be installed directly above the sand pack. This bentonite seal will be 3 feet in length. The remaining annular space will be filled with a bentonite and cement grout.
6. The temporary 10-inch I.D. steel casing will be removed and the well will be completed with an aboveground well protector and a locking cap.

7. Well development or purging may be necessary before collecting groundwater samples from the cased/screened hole in the bedrock. The procedures for both well development and well purging are presented below.
8. Water level measurements will then be collected, prior to sampling the bedrock groundwater. The procedure for measuring water levels is also presented below.
9. The bedrock groundwater sample collection method is presented after the procedure for water level measurements.

Well Development

Newly installed wells will require development to clear the well of accumulated sediments. Appendix H presents the standard operating procedure (SOP) for well development.

Well Purging (if necessary)

After installation and development and prior to sampling, the well may be purged to remove the standing water column from the well casing. The SOP for well purging is presented in Appendix H with the procedure for well development.

Water Level Measurements

Prior to initiating groundwater sampling, water elevations will be measured in the well. Refer to Appendix I for well gauging procedures.

Groundwater Pre-Sampling and Well Sampling

Appendix I presents the protocol for groundwater sampling activities.

Description of Rock Samples

As mentioned earlier in this section, the rock core will be evaluated via photographs and petrographic thin sections. The geologists and geotechnical engineers will write their description of rock samples with a consistent format. A detailed order and presentation of selection of data are presented in Appendix J.

Groundwater Flow Direction (water levels)

Water levels will be measured quarterly for one year in the bedrock well and used to prepare water-level elevation maps. These will show seasonal changes in groundwater level and flow

direction. Water level measurements will be conducted according to the same protocol outlined in Appendix I.

Groundwater Flow Rate (slug tests)

Rationale

Falling and rising head slug tests will be performed on the bedrock well, using a slug of known volume and in-well, short-time interval, automatic water-level recorders. With the falling-head and rising-head slug test data, aquifer hydraulic conductivity will be calculated for the well. Measured groundwater gradients and calculated aquifer hydraulic conductivities will be used to determine groundwater flow rates.

Field Procedure

Appendix K presents the field protocols for the completion of *in situ* hydraulic conductivity (slug) tests.

Slug test data will be downloaded from the data logger each day. The data will be reviewed for errors. If necessary, a slug test will be re-conducted.

5.5.3 Soil

5.5.3.1 Surface Soil Samples

Rationale

Two surface soil samples (0 to 0.5 feet) will be collected at this disposal site. These samples will be collected at the location of each waste sample boring to provide information for the Human Health Risk Assessment and Ecological Risk Assessment. Scaled, color digital photographs will be taken of each soil sample to provide a record of materials present at this site. Each sample will be analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin, and metals.

Table 1 presents the analytical methods. A detailed sample and analysis summary for the surface soil sampling is presented in Table 6.

Figure 11 presents appropriate soil sample locations in Site S.

Field Procedure

Surface soil samples will be discrete. A discrete sample represents a single location in the soil column. The soil samples will be collected from the Geoprobe® borings.

Appendix C presents the standard operating procedure for waste and soil sample collection.

5.5.3.2 Subsurface Soil Samples

Rationale

Two subsurface soil samples (0.5 to 6 feet) will be collected at each disposal site. As with the surface soil samples, the subsurface samples will be collected at the location of each waste sample boring to provide information for the Human Health Risk Assessment. Scaled, color digital photographs will be taken of each soil sample to provide a record of materials present at this site. Each sample will be analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin, and metals.

Table 1 presents the analytical methods. A detailed sample and analysis summary for the subsurface soil sampling is presented in Table 7.

Figure 11 presents appropriate soil sample locations for Site S.

Field Procedure

The two soil samples collected at this site will be collected at the location of each waste sample boring. The subsurface soil samples will be collected in the same manner as the waste samples.

Appendix C presents the standard operating procedure for waste and soil sample collection.

5.5.4 Air

5.5.4.1 Rationale

Two upwind and two downwind ambient air samples will be collected to determine the tendency of site constituents to enter the atmosphere and local wind patterns. Air sampling data will be used in the Human Health Risk Assessment and Ecological Risk Assessment. Samples will be analyzed for VOCs, SVOCs, pesticides, PCBs, metals, and dioxin.

Twenty-four hour cumulative duration sorbent tube/PUF/PM2.5 samples will be collected over a 1-day period, using the sampling protocols provided in Appendix L. Two upwind and two downwind samplers will be installed at the site during weather likely to produce emissions (e.g. hot and dry conditions in August). Sampling locations will be selected in the field with the concurrence of USEPA Region V or his designee. Sorbent tube samplers will be used for VOC data collection. Polyurethane foam (PUF) samplers will be used for SVOC, PCB, pesticide, and dioxin data collection. PM2.5 samplers will be used for metal data collection

Ambient air sample collection is required to measure airborne levels of contaminants that may be evolving from the site. A 24-hour sample duration is required to average the air emission differences that may occur from the day time to night time cycle from on-site and off-site conditions and activities. Also, air sample collection locations need to be positioned on the site to collect up wind and down wind samples for differentiation of constituents originating from the surrounding area and those originating from the site. The sample protocol will collect site samples over a 1-day time period on a warm, dry day.

The level of detection for SVOCs required by USEPA Region V needs to consider sensitivity and selectivity to analyze complex samples. Based on this need, the analytical method of choice is gas chromatography coupled with mass spectrometry (GC/MS) for detection. Based on the GC/MS analytical method and its sensitivity level, the air sample volume needs to exceed 325 standard cubic feet. This enables the collection of a sufficient quantity of SVOCs to meet the level of detection required by USEPA Region V.

The sample method to meet the above requirements for SVOC measurement is USEPA Method TO-13, as identified in the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* (June 1988). This method will use a Graseby/General Metal Works, Inc. high volume air sampling unit or equivalent for sample collection. Sample collection will consist of drawing an ambient air sample at a high volume flow rate through a PUF collection media over a 24-hour time period. The samples will be submitted for analysis of the TO-13 list of SVOCs. Method TO-15 will be used to analyze VOCs. Method TO-4 will be used for pesticides, and PCBs. Method TO-9 will analyze for dioxins.

Table 8 is a sample and analysis summary of this activity.

5.5.4.2 Field Procedure

The following procedure will be used for ambient air samples:

- Place the sorbent tube samplers, PUF samplers, and PM2.5 samplers at upwind and downwind locations.
- Locate sampling positions in an unobstructed area, at least two meters from any obstacle to air flow. Sample locations will be selected in the field with the concurrence of the USEPA Region V, or its designee.
- No local power supply is readily available at the sites. Therefore, gasoline- or diesel-powered generators will be positioned at downwind locations from the sample collection positions. They will supply the electricity for the samplers.
- Record wind direction and velocity readings.
- Follow sample collection protocols identified Appendix L for sample preparation, calibration, collection, laboratory preparation and shipment, and calculations. Sample data sheets are provided in Appendix L.

Treatability Tests

Rationale

The AOC requires that the SSP present a pilot test program for any treatment technologies lacking sufficient information on implementability and effectiveness. Data gaps exist for off-site incineration, off-site disposal, and on-site thermal desorption for the waste and on-site and off-site physical/chemical treatment, and off-site biological treatment for leachate.

A total of five composite waste samples (one for each site) will be collected for waste treatability testing and sent to appropriate facilities operators for waste profiling, material handling characterization and evaluation of the feasibility of disposing of the waste material by off-site incineration, off-site disposal, and on-site thermal desorption. In addition, five composite leachate samples (one for each site) will be collected for treatability testing to determine if the leachate can be discharged directly to American Bottoms POTW without resulting in pass through and/or interference.

One sample will be collected from each waste disposal area for waste treatability testing. The sample will be made from aliquots collected from the four waste characterization borings

installed at each disposal area. One sample will be collected for the leachate treatability testing from each of the five-leachate sampling wells.

Sample Collection

The five composite waste samples that will be collected for treatability testing will be retained from the four-waste/soil borings that will be advanced at each waste disposal area. All of the material recovered from the Geoprobe® samples that are not needed for the other chemical analyses will be composited in 5-gallon buckets. Each bucket will be sealed, labeled and prepared for shipment to the appropriate facilities.

The leachate sample that will be collected for treatability testing will be collected during leachate sampling activities. An equal amount of leachate will be removed, via bailer or pump, from each of the five-leachate monitoring wells and placed in separate 5-gallon buckets. Each bucket will be sealed, labeled and prepared for shipment to the appropriate facility.

5.6 UPGRADIENT GROUNDWATER AND OFF-SITE SOILS LOCATIONS

5.6.1 Hydrogeology

5.6.1.1 Alluvial Aquifer

Rationale

Groundwater samples will be collected at four sampling stations located east of the Sauget Area 2 Sites. One sampling station will be located upgradient and east of Site P, two sampling stations will be located upgradient and east of Sites O, S, R, and the northern portion of Q. The fourth sampling station will be located upgradient and east of the southern portion of Site Q.

Unfiltered groundwater samples will be collected every 10 feet from the water table to the bottom of the aquifer. Push sampling technologies, such as Geoprobe®, HydroPunch®, Microwell®, Waterloo Profiler®, or equivalent, and low-flow sampling techniques will be used. Aquifer saturated thickness is estimated to be approximately 120 feet with depth to water at 20 feet bgs and bottom of the aquifer at 140 feet bgs. All samples will be analyzed for VOCs and SVOCs. Additionally, unfiltered samples will be collected at 40 foot intervals (i.e., 20, 60, and 100 foot bgs) and analyzed for pesticides, herbicides, PCBs, metals, and several geochemical parameters (Table 1).

Unfiltered groundwater samples will be collected at the top, middle, and bottom of the saturated zone (i.e. 20, 80, and 140 feet bgs) at the two upgradient sampling locations east of Site O. These six samples will be analyzed for dioxin.

Experience at other sites indicates that push-sampling technologies such as Geoprobe® can reach depths of 60 feet. Depth of penetration can be increased at some locations by loosening the soil above the sampling horizon with a small-diameter solid stem auger before pushing the sampling probe to the required sampling depth. When the Geoprobe® sampler or equivalent sampling technology cannot penetrate to the required depth, Microwells® will be used to collect groundwater samples. These small-diameter wells are vibrated into place using a small vibratory hammer. Experience in deep aquifers at other sites indicates that sampling depths of 100 feet can be achieved. If the required sampling depths cannot be reached with either of these two technologies, conventional percussion drilling equipment will be used to drive 1-1/4 inch diameter drive points to the required sampling depths.

Table 1 presents the analytical methods. A sample and analysis summary for the upgradient groundwater sampling is presented in Table 10.

Figure 4 displays approximate groundwater sampling locations for Area 2. Sampling locations will be selected in the field with the concurrence of USEPA Region V or its designee.

Field Procedure

Establishment of Boreholes

Push Point

Using the hydraulic push system of a Geoprobe®, a 4-foot stainless steel sampler with a wire wrap (slot size of 0.004 inches) will be pushed to the desired sample depth. A bailer or ball and check valve will be sent down to the slotted portion of the sampler to collect the groundwater sample. The groundwater sample will be retrieved to the surface and placed in a sample container. The Geoprobe® will then drive the sampler to the next desired sample depth, by connecting clean sections of push rods to the Geoprobe®, and a second groundwater sample will be collected here. This process will be continued until all samples are collected.

MicroWell®

It is anticipated the above sampling method will be used, as feasible. However, based on the location of the site within the Mississippi River flood plain, large gravel or cobbles may be encountered, which will stop the Geoprobe®. Should this occur, MicroWells® will be installed to use as the sample collection point. The MicroWells® will be hydraulically pushed to the appropriate depth, and the sampling procedure described above will be followed. Once the sample is collected, the MicroWell® will be pulled, the screen point decontaminated according to the method described below, and a new well will be advanced further in the same hole. This procedure will be repeated until all samples are collected.

Should MicroWell® installation prove impractical, boreholes will be advanced using conventional hollow stem auger drilling methods. In this instance, the lead auger will have a screened section through which groundwater will flow. Once the sample is collected, the augers will be advanced further for collection at the next sample depth. This procedure will be repeated until all samples are collected within the borehole.

All Geoprobe®, MicroWell®, or Waterloo Profiler® holes will be sealed with grout from the bottom up after completion of sampling at each location. A PID, explosimeter, and a RAM will be used on a continuous basis to monitor these activities.

Groundwater Pre-Sampling and Borehole Sampling

Appendix I presents the protocol for groundwater sampling activities.

5.6.2 Soil

5.6.2.1 Surface Soil Samples

Rationale

Off-site soil samples will be collected at four locations east of the study area as generally shown in Figure 4. Samples will be collected from a depth of 0 to 0.5 feet bgs. All four surface soil samples will be analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin, and metals.

Figure 4 displays the approximate off-site surface soil sample locations for Area 2. Sample locations will be selected in the field with concurrence of USEPA Region V or its designee.

Table 1 presents the analytical methods. A sample and analysis summary for the off-site soil sampling is presented in Table 11.

Field Procedure

Surface soil samples will be discrete. A discrete sample represents a single location in the soil column. Hand augers, disposable scoops, hand trowels, or shovels are used to collect these samples.

Refer to Appendix C for standard waste and soil sampling methods.

5.6.2.2 Subsurface Soil Samples

Rationale

Subsurface off-site soil samples will be collected at the same four locations used for the surface soils as discussed in Section 5.6.2.1. Samples will be collected from a depth of 0.5 to 6 feet. The subsurface soil samples will be analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin, and metals.

Table 1 presents the analytical methods. A sample and analysis summary for the off-site soil sampling in presented in Table 11a and Table 11b.

Field Procedure

The subsurface off-site soil samples will be collected in the same manner as the fill area subsurface soil and waste samples.

Refer to Appendix C for the appropriate subsurface soil sampling procedure.

5.7 AREA 2 GROUNDWATER FLOW DIRECTION AND FLOW RATE

5.7.1 Alluvial Aquifer – Piezometer Clusters

5.7.1.1 Water Levels

Nine piezometer clusters will be installed in the study area to define groundwater flow direction. Three piezometer clusters will be installed at the upgradient portion of the study area, adjacent to Mississippi Avenue (Route 3). Three piezometer clusters will be installed midway between the Mississippi River and Route 3. The third group of three piezometer clusters will be installed at the downgradient end of the study area adjacent to the Mississippi River. Each piezometer

cluster will consist of three small-diameter (1-inch) wells. In each cluster, one piezometer will be completed in the shallow portion of the aquifer, one piezometer will be completed in the intermediate portion of the aquifer, and one piezometer will be completed in the deep portion of the aquifer.

Figure 4 shows the approximate piezometer locations for Area 2. Piezometer locations will be selected in the field with concurrence of USEPA Region V or its designee.

Water levels will be measured quarterly for one year in each piezometer. They will be used to prepare water-level elevation maps, which show seasonal changes in groundwater level and flow direction.

Piezometer Installation

1. Borings will be advanced via direct push technology (Geoprobe®). The Geoprobe® will hydraulically drive 2-1/4-inch probe rods down to the desired depth (e.g., shallow, intermediate, or deep portion of the aquifer).
2. Soil samples will be collected in the nine piezometers installed in the deep portion of the aquifer. Samples are to be collected every 5 feet and at every change in formation. These samples will be continuously collected during advancement of the boring.
3. For installation of the nine deep borings, the Geoprobe® will hydraulically drive a stainless steel, acetate-lined MacroCore® sampler (2-inch diameter by 4-foot length) to the desired subsurface sample depth. Continuous soil samples will be collected. Between each sample collection, the sampler will be retrieved to the surface and the soil samples removed from the disposable acetate liner within the sampler.
4. The piezometers will be constructed of 1-inch diameter PVC (schedule 40) riser pipe and screen. A sand filter pack will not be installed in any of the piezometers.
5. The nine piezometers to be completed in the shallow portion of the aquifer will be constructed such that the water table intersects the screen. Thus, a screen length of approximately 10 feet will be required for these nine piezometers. The screens of the intermediate and deep piezometers will be completely submerged; therefore, it is not necessary that they have a length of 10 feet.
6. The piezometer installation will be completed with either bentonite or concrete.

7. The top of the well risers and the ground surface will be surveyed for elevation and horizontal control.
8. Piezometer installation details will be documented on a test boring log (Appendix D) and in the field notebook.

The piezometers will generally be installed according to the typical construction diagrams in Appendix G. They will also be constructed according to the standard procedures described in Appendix G, with the exception of the following:

- The screen will be installed such that its midpoint approximately intersects the groundwater table in the shallow piezometers.
- The piezometers will not have a filter pack, bentonite seal, or bentonite/cement grout.
- They will not have protective casings.
- The surface installation will be completed with either bentonite or cement.

Water Level Measurements

Prior to initiating groundwater sampling, water elevations will be measured in the well. Refer to Appendix I for well gauging procedures. . .

5.7.1.2 Geotechnical Samples

Geotechnical samples will be collected in the nine, deep piezometer borings. These samples will be collected every 5 feet and at every change in formation. The geotechnical samples will be tested for:

- Grain size
- Particle size distribution
- Porosity
- Bulk density
- Specific gravity
- Moisture content

- pH
- Total organic carbon.

As described earlier in this section (with piezometer installation) a large bore (MacroCore®) soil sampler, using clear acetate liners, will be hydraulically pushed to collect soil samples at the specified depths. Each collected sample will be placed into a labeled, plastic, wide-mouth container and sealed. The MacroCore® sampler will collect approximately 1300 mL of material, which is sufficient for grain size analysis. Should larger (large gravel to cobble) size materials be encountered, additional core samples will be obtained and placed into additional containers. Collected samples will be placed into plastic coolers or corrugated boxes for shipment. Chain-of-custody procedures will be followed in order to track samples.

Table 12 presents a sample and analysis summary for grain size analysis.

5.7.1.3 Slug Tests

Rationale

Falling and rising head slug tests will be performed on each of the 27 piezometers installed in Area 2. A slug of known volume and in-well, short-time interval, automatic water-level recorders will be used. Aquifer hydraulic conductivity will be calculated for each piezometer using the falling head and rising head slug test data. Groundwater flow rates will be determined by using measured groundwater gradients and calculated aquifer hydraulic conductivities.

QA/QC Procedures

QA/QC procedures will consist of equipment test checks.

Field Procedure

Appendix K presents the field protocols for the completion of in situ hydraulic conductivity tests

SECTIONSIX Field Operations Documentation

The field sampling team will maintain a set of field logbooks. Forms that will be used include: chain-of-custody, test boring log, and groundwater sampling log, slug test, field log, and air sampling data sheets. The appendices contain copies of these forms.

The field logbooks will contain tabulated results of field measurements and documentation of field instrument calibration activities. The field logbooks will also record the following:

- Personnel conducting the site activities, their arrival and departure times and their destination at the site
- Incidents and unusual activities that occur on the site such as, but not limited to, accidents, breaches of security, injuries, equipment failures, or weather related problems
- Changes to the FSP and the HASP
- Daily information such as:
  - Work accomplished and the current site status
  - Equipment calibrations, repairs and results
  - Site work zones.

In the field sampler's individual bound field logbook, samplers will note, with permanent ink, meteorological data, equipment employed for sample collection, calculations, information regarding collection of QA/QC samples, and any observations. All entries will be signed and dated, and any entry, which is to be deleted will have a single cross out which is signed and dated. The following sampling-related information will be recorded in the field logbook by the field sampling team:

- Sample number
- Project identification
- Sampling location
- Required analysis
- Date and time of sample collection
- Type and matrix of sample
- Sampling technique

- Preservative used, if applicable
- Sampling conditions
- Observations
- Initials of the sampler.

Field data documentation procedures will be minimal in scope. Only direct reading instrumentation will be employed in the field. The use of pH, conductivity, turbidity meters, a photoionization detector (PID); a real time aerosol monitor (RAM), and thermometers will generate some measurements directly read from the meters, following calibration by the respective manufacturer's recommendations. Such data will be written into field logbooks immediately after measurements are taken. If errors are made, results will be legibly crossed out, initialed, and dated by the field member. Errors will be corrected in a space adjacent to the original entry. Later, when the results forms are filled out, the URS Field Leader will proofread the forms to assess whether transcription errors have been made.

Photographic records will be developed through the use of digital photographs, showing pre-sampling and post-sampling conditions at each site.

6.1 SAMPLE DOCUMENTATION

6.1.1 Sample Identification System

The sample identification system will involve the following:

- Soil gas survey data will be labeled SG-P-1 where "SG" denotes soil gas survey, "P" is the site designations, and "1" denotes a sequential sample number.
- Field soil screening by GC/MS will be labeled GCMS-Q-1 where "GCMS" denotes a field screening sample by GC/MS, "Q" is the site designation and "1" denotes a sequential sample number.
- Field soil screening data by XRF will be labeled XRF-Q-1 where "XRF" denotes a field screening sample by XRF, "Q" is the site designation and "1" denotes a sequential sample number.

- Waste samples will be labeled WASTE-P-__FT where "WASTE" denotes a waste sample, "P" is the site designation, and "__FT" indicates sample depth, which is filled in by the sampler.
- Leachate samples will be labeled LEACH-P-1 where "LEACH" denotes a leachate sample, "P" is the site designation, and "1" denotes a subsequent sample number.
- Alluvial aquifer samples will be labeled AA-P-S1-__FT where "AA" denotes an alluvial aquifer sample, "P" is the site designation, "S1" is the sequentially numbered sampling station, and "__FT" indicates sample depth, which is filled in by the sampler.
- Bedrock groundwater samples will be labeled BR-1 and BR-2 where "BR" denotes a bedrock groundwater sample and "1" and "2" denote sequential numbers that correspond to the monitoring well ID.
- Upgradient groundwater samples will be labeled UAA-S1-__FT where "UAA" denotes a upgradient alluvial aquifer sample, "S1" is the sequentially number sampling station, and "__FT" indicates sample depth.
- Piezometer soil samples will be labeled PIEZ-S1-__FT where "PIEZ" denotes a piezometer soil sample, S1 is the sequentially number sampling station, and "__FT" indicates sample depth.
- Soil samples will be labeled SOIL-P-S1-__FT where "SOIL" denotes a soil sample, "P" is the site designation, "S1" is the sequentially numbered sampling station, and "__FT" indicates sample depth.
- Off-site soil samples will be labeled OS-S1-__FT where "OS" denotes an off-site soil sample, "S1" is the sequentially numbered sampling station, and "__FT" indicated sample depth, which is filled in by the sampler.
- Air samples will be labeled AIR-P-V-l, AIR-P-S-l, or AIR-P-M-1 where "AIR" denotes an air sample, "P" is the site designation, "V", "S", "P", "H", "C", "D", or "M" designate a VOC, SVOC, pesticide, herbicide, PCB, dioxin, or metals sample, respectively, and "1" denotes a sequential sample number.
- "MS/MSD" or "DUP" at the end of a sample identification will indicate a matrix spike/matrix spike duplicate/spike duplicate or a duplicate sample, respectively.

- Stormwater samples will be labeled STORM-P-1 where "STORM" denotes stormwater, "P" is the site designation, and "1" denotes a sequential sample number.
- Seep samples will be labeled SEEP-Q-1 where "SEEP" denotes a seep sample, "Q" is the site designation, and "1" denotes a sequential sample number.
- Off-site incineration pilot test samples will be labeled WI-P-1 where "WI" denotes a waste sample for off-site incineration testing, "P" is the site designation, and "1" denotes a sequential sample number.
- Off-site disposal pilot test samples will be labeled DISPOSE-P-1 where "DISPOSE" denotes a waste number sample for off-site disposal testing, "P" is the site designation, and "1" denotes a sequential sample number
- On-site thermal desorption pilot test samples will be labeled TD-P-1 where "TD" denotes a waste sample for on-site thermal desorption testing, "P" is the site designation, and "1" denotes a sequential sample number.
- On-site physical/chemical leachate treatment pilot test samples will be labeled PCHEM-P-1 where "PCHEM" denotes a leachate sample for on-site physical/chemical testing, "P" is the site designation, and "1" denotes a sequential sample number.
- Off-site biological leachate pilot test samples will be labeled BIO-P-1 where "BIO" denotes a leachate sample for off-site biological testing, "P" is the site designation, and "1" denotes a sequential sample number.

6.1.2 Sample Labels

For proper identification in the field and proper tracking by the analytical laboratory, samples will be labeled in a clear and consistent fashion. Sample labels will be waterproof, or sample containers will be sealed in plastic bags. Field personnel will maintain a sampling log sheet containing information sufficient to allow reconstruction of the sample collection and handling procedures at a later time.

A completed sample label will be attached to each investigative or QC sample. The following will be recorded with permanent ink on sample labels by the field sampling team:

- Project name and number
- Sample number identification

- Initials of sampler
- Sampling location (if not already encoded in the sample number)
- Required analysis
- Date and time of sample collection
- Space for laboratory sample number (only on the sample tag)
- Preservative used, if applicable.

6.1.3 Chain-of-Custody Records

Chain-of-custody procedures will be instituted and followed throughout the sampling activities Samples are physical evidence and will be handled according to strict chain-of-custody protocols. The field sampler is personally responsible for the care and custody of the sample until transferred. For proper identification in the field and proper tracking by the analytical laboratory, samples will be labeled in a clear and consistent fashion.

The following information will be recorded with permanent ink on the chain-of-custody by the field sampling team:

- Project identification and number
- Sample description/location
- Required analysis
- Date and time of sample collection
- Type and matrix of sample
- Number of sample containers
- Analysis requested/comments
- Sampler signature/date/time
- Air bill number.

The laboratory will assign a number for each sample upon receipt. That sample number will be placed on the sample label. The label will be attached to the sample container. A chain-of-custody document providing all information, signatures, dates, and other information, as required

on the example chain-of-custody form in Appendix C will be completed by the field sampler and provided for each sample cooler. When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the chain-of-custody. The field sampler will sign the chain-of-custody form when relinquishing custody, make a copy to keep with the field logbook, and include the original form in an air-tight plastic bag in the sample cooler with the associated samples.

6.2 FIELD ANALYTICAL RECORDS

Field analytical records will consist of gas chromatograms from the field gas chromatograph used in the soil gas survey, and the field GC/MS screening of soil samples, XRF readings from the field screening of soil samples, and field logbook entries for field instruments. Chromatograms will be taped into an analytical notebook. In addition to information printed on the chromatograms, field notes will be added as appropriate information detailed on each chromatogram will include:

- Sample number identification
- Initials of sampler
- Sampling location (if not already encoded in the sample number)
- Required analysis
- Date and time of sample collection
- Date and time of analysis
- Instrument name
- Column and detector type
- Carrier gas and flowrate
- Backflush time
- Injection volume
- Gain setting.

Only direct reading instrumentation will be employed in the field. The use of pH, conductivity; and turbidity meters, a photoionization detector (PID), a real time aerosol monitor (RAM), and

thermometers will generate some measurements directly read from the meters following calibration by the respective manufacturer's recommendations. Such data will be written into field logbooks immediately after measurements are taken. Calibration records will also be recorded in the logbooks.

6.3 DATA MANAGEMENT AND RETENTION

The field data and documentation, as described in this section, will become a part of the final evidence file. The final evidence file will be the central repository for all documents which constitute evidence relevant to sampling and analysis activities as described in this FSP and the QAPP. URS is the custodian of the evidence file and maintains the contents of evidence files for the site, including all relevant records, logs, field logbooks, pictures, subcontractor reports, data reviews, and the database management system.

Upon completion of the analyses, the URS QAO will begin assimilating the field and laboratory notes. In this way, the file for the samples will be generated. The final file for the samples will be stored at URS and will consist of the following:

- Laboratory data packages, including summary and raw data from the analysis of environmental and QC samples, chromatograms, mass spectra, calibration data, work sheets, and sample preparation notebooks
- Chain-of-custody records
- Data validation reports.

The following documentation will supplement the chain-of-custody records:

- Field logbooks and data
- Field collection report
- Photographs and drawings
- Progress and QA reports
- Contractor and subcontractor reports
- Correspondence.

The evidence file must be maintained in a secured, limited access area until all submittals for the project have been reviewed and approved, and for a minimum of six years-past the submittal date of the final report.

SECTIONSEVEN Personal Protective Equipment

Personal protective equipment (PPE) requirements for each level of protection for URS personnel are described in the HASP prepared for these field activities.

7.1. PROTECTIVE EQUIPMENT SELECTION

Initial levels of PPE will be as shown in the following table.

Activity	Level B	Level C	Modified Level D	Level D
Trenching		Observation		
Soil Gas Sampling		Initial		
Magnetometer Survey			Initial	
Installation of Soil Borings and collection of cuttings		Initial		
Installation and sampling of groundwater wells		Initial		
Surface and subsurface soil sampling		Initial		
Air sampling			Initial	

SECTIONEIGHT Sample Packaging and Shipping

A completed sample label will be attached to each investigative or QC sample and the sample placed in a shipping container. Information to be recorded on sample labels is described in Section 6.1.2. Information to be recorded on chain-of-custody forms is described in Section 6.1.3. The sample identification system used in the field is described in Section 6.1.1.

Sampling containers will be packed in such a way as to help prevent breakage and cross-contamination. Samples will be shipped in coolers, each containing a chain-of-custody form and ice and ice packs to maintain inside temperature at approximately 4°C. Sample coolers will then be sealed between the lid and sides of the cooler with a custody seal prior to shipment. The custody seal will be an adhesive-backed tape that easily rips if it is disturbed. Samples will be shipped to Savannah Laboratory by common overnight carrier.

Samples will not be sent to another laboratory without the permission of USEPA Region V. Sample transportation will comply with U.S. Department of Transportation and IICAO/IATA (1999) regulations. Special sampling packing provisions will be made for samples requiring additional protection.

Samples will remain in the custody of the sampler until transfer of custody is completed. Transfer consists of:

- Delivery of samples to the laboratory sample custodian
- Signature of the laboratory sample custodian on the chain-of-custody document as receiving the samples, and signature of sampler, as relinquishing the samples.

If a carrier is used to take samples between the sampler and the laboratory, a copy of the air bill must be attached to the chain-of-custody to maintain proof of custody.

SECTIONNINE Investigation-Derived Wastes

Sampling activities will occur in widely-separated locations. Therefore, personnel and equipment decontamination will be accomplished at each sampling area using temporary facilities. Section 9 of the HASP describes personnel and monitoring equipment decontamination procedures and supplies. PPE, disposable sampling equipment, cuttings, purge waters, and field decontamination wastes will be collected at the point of generation and stored in temporary containers. PPE, solids, and liquids will be consolidated in separate bulk containers at a central area. The sampling procedures have been developed to minimize the quantity of waste generated. Additional activity-specific information on disposal of investigation-derived wastes is contained in Section 5 of this FSP.

The performance audit is an independent check to evaluate the quality of data being generated. The system audit is an on-site review and evaluation of the quality control practices, sampling procedures, and documentation procedures.

At the discretion of the URS PM, performance and system audits of field activities will be conducted to verify that sampling and analyses are performed in accordance with the procedures established in this FSP and the QAPP. The audits of field activities include two independent parts: internal and external audits.

The internal audits will be performed by the URS QAO. The external audits will be performed by USEPA Region V.

10.1 FIELD PERFORMANCE AND SYSTEM AUDITS

10.1.1 Internal Field Audits

Internal field audit responsibilities. Internal audits of field activities, including sampling and field measurements will be conducted by the URS QAO or his designee.

Internal field audit frequency. These audits will verify that all established procedures are being followed. Internal field audits will be conducted at least once at the beginning of the site sample collection activities and annually thereafter.

Internal field audit procedures. The audits will include examination of field sampling records, field instrumentation operating records, sample collection, handling and packaging in compliance with the established procedures, maintenance of QA procedures, chain-of-custody, and other elements of the field program. Follow up audits will be conducted to correct deficiencies and to verify that QA procedures are maintained throughout the project. The audits will involve review of field measurement records, instrumentation calibration records, and sample documentation. The areas of concern in a field audit include:

- Sampling procedures
- Decontamination of sampling equipment, if applicable
- Chain-of-custody procedures
- Standard operating procedures

- Proper documentation in field notebooks
- Subcontractor procedures.

10.1.2 External Field Audits

External field audit responsibilities. External field audits may be conducted by USEPA Region V.

External field audit frequency. External field audits may be conducted at any time during the field operations. These audits may or may not be announced and are at the discretion of USEPA Region V.

Overview of the external field audit process. External field audits will be conducted according to the field activity information presented in this FSP and the QAPP.

SECTIONELEVEN Corrective Action

Corrective action is the process of identifying, recommending, approving, and implementing measures to counter unacceptable procedures or out-of-control performance which can affect data quality. Corrective action can occur during field activities, laboratory analyses, data validation, and data assessment. Corrective action proposed and implemented will be documented in the regular quality assurance reports to management. Corrective action should only be implemented after approval by the URS PM or the URS Field Leader. If immediate corrective action is required, approvals secured by telephone from the Project Manager should be documented in an additional memorandum.

For noncompliance problems, a formal corrective action program will be developed and implemented at the time the problem is identified. The person who identifies the problem will be responsible for notifying the URS PM, who in turn will notify the URS PO. Implementation of corrective action will be confirmed in writing through the same channels. Nonconformance with the established quality control procedures in the QAPP or FSP will be identified and corrected in accordance with the QAPP.

11.1 FIELD CORRECTIVE ACTION

Corrective action in the field can be needed when the sample network is changed (i.e., more or less samples, sampling location changes, and related modifications) or sampling procedures and/or field analytical procedures require modification due to unexpected conditions. Technical staff and project personnel will be responsible for reporting all suspected technical or QA nonconformances or suspected deficiencies of any activity or issued document by reporting the situation to the URS Field Leader. The URS Field Leader will be responsible for assessing the suspected problems in consultation with the URS PM and assessing the potential for the situation to impact the quality of the data. If the situation warrants reportable nonconformance requiring corrective action, a nonconformance report will be initiated by the URS PM.

The URS PM will be responsible for seeing that corrective actions for nonconformance are initiated by:

- Evaluating reported nonconformances
- Controlling additional work on nonconforming items
- Establishing disposition or action to be taken

- Maintaining a log of nonconformances
- Reviewing nonconformance reports and corrective actions taken
- Verifying nonconformance reports are included in the final site documentation in project files.

If appropriate, the URS Field Leader will verify that no additional work dependent on the nonconforming activity is performed until the corrective actions are completed. Corrective action for field measurements may include:

- Repeat the measurement to check the error
- Check for proper adjustments for ambient conditions, such as temperature
- Check the batteries
- Recalibration
- Check the calibration
- Replace the instrument or measurement devices
- Stop work (if necessary).

The URS Field Leader is responsible for site activities. In this role, the URS Field Leader, at times, is required to adjust the site programs to accommodate site-specific needs. When it becomes necessary to modify a program, the responsible person notifies the URS Field Leader of the anticipated change and implements the necessary changes after obtaining the approval of the URS Field Leader. The change in the program will be documented on the field change request (FCR) that will be signed by the initiators and the URS Field Leader. The FCR for each document will be numbered serially as required. The FCR will be attached to the file copy of the affected document. The URS Field Leader must approve the change in writing or verbally prior to field implementation, if feasible. If unacceptable, the action taken during the period of deviation will be evaluated to determine the significance of any departure from established program practices.

The URS Field Leader is responsible for controlling, tracking, and implementing identified changes. Reports on changes will be distributed to affected parties, which includes USEPA Region V.

SECTIONELEVEN Corrective Action

Corrective action resulting from internal field audits will be implemented immediately if data may be adversely affected due to unapproved or improper use of approved methods. The URS QAO will identify deficiencies and recommend corrective action to the URS PM. Implementation of corrective actions will be performed by the URS Field Leader and the field team. Corrective action will be documented in the quality assurance report to the project management.

Corrective actions will be implemented and documented in the field notebook. No staff member will initiate corrective action without prior communication of findings through the proper channels. If corrective actions are insufficient, work may be stopped by USEPA Region V.

The URS QAO and Laboratory QAO may identify the need for corrective action during either the data validation or data assessment. Potential types of corrective action may include resampling by the field team or reinjection or reanalysis of samples by the laboratory. These actions are dependent upon the ability to mobilize the field team or, whether the data to be collected is necessary to meet the required quality assurance objectives. When the URS QAO or Laboratory QAO identifies a corrective action situation, it is the URS PM who will be responsible for approving the implementation of corrective action, including resampling, during data assessment. Corrective-actions of this type will be documented by the URS QAO and the Laboratory QAO.

SECTIONTWELVE References

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URS Corporation, 2001. *Health and Safety Plan, Sauget Area II Support Sampling Project, Sauget and Cahokia, Illinois. Volume 2C.*

URS Corporation, 2001. *Quality Assurance Project Plan, Sauget Area II Support Sampling Project, Sauget and Cahokia, Illinois, Volume 2B.*

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U.S. Environmental Protection Agency (USEPA). 1988. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air,* EPA/600/4-89/017, June 1988, Research Triangle Park, NC.

U.S. Environmental Protection Agency (USEPA). 1999. *Final Administrative Order by Consent, Sauget Area II Site, Sauget and Cahokia, Illinois.*

Tables

Table 1
Analytical Methods Used for Fill Area Samples
Sauget Area 2 Support Sampling Plan, Volume 2A

Area 2 Analyses

Analyte	Method
VOCs	8260B
SVOCs	8270C
Pesticides	8081A
Herbicides	8151A
PCBs	680
Metals	6010B
Dioxin	8280 (water) / 8290 (solids)

Geochemical Parameters

Oxidation Reduction Potential (ORP)
Dissolved Oxygen (DO)
Ferrous Iron
Manganese
Nitrate
Sulfate
Alkalinity
Methane
Carbon Dioxide

Table 2
Fill Areas Soil Gas Survey - Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Matrix	Parameters	Number of Environmental Samples per Site	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time
O	Soil Gas	VOC-Field GC 3810[1]	50	N/A	N/A	N/A	N/A	N/A	N/A	N/A
P	Soil Gas	VOC-Field GC 3810[1]	25	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Q	Soil Gas	VOC-Field GC 3810[1]	182	N/A	N/A	N/A	N/A	N/A	N/A	N/A
R	Soil Gas	VOC-Field GC 3810[1]	30	N/A	N/A	N/A	N/A	N/A	N/A	N/A
S	Soil Gas	VOC-Field GC 3810[1]	5	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Total Number of Samples			278							

[1] Static headspace analysis, closely parallels USEPA Method 3810

Table 3
Fill Areas Waste and Leachate Sampling – Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Parameters	Number of Environmental Samples per Site (waste, leachate)	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
O	VOCs	6,1	One per 10, or fraction of 10, samples collected (5, 1)	One per 10, or fraction of 10, samples (5, 1)	One per 20, or fraction of 20, samples collected (3, 1)	One per sample cooler containing VOC analysis (3, 1)	3-Encore™ samplers (or in accordance with USEPA Method 5035)	4°C	Transferred to soil container or analyzed 48 hours from collection; For TCLP VOCs, 14 days from collection to TCLP extract generation, 14 days from TCLP extraction to analysis
P	VOCs	8,1							
Q	VOCs	24,3							
R	VOCs	8,1							
S	VOCs	4,1							
O	SVOCs	6,1	One per 10, or fraction of 10, samples collected (5, 1)	One per 10, or fraction of 10, samples (5, 1)	One per 20, or fraction of 20, samples collected (3, 1)	NA	250 mL wide mouth glass container with Teflon™-lined lid	4°C	14 days from collection to extraction; 40 days from extraction to analysis; For TCLP-SVOCs, 14 days from collection to TCLP extract generation, 7 days from TCLP extract generation to extraction, 40 days from extraction to analysis
P	SVOCs	8,1							
Q	SVOCs	24,3							
R	SVOCs	8,1							
S	SVOCs	4,1							

Table 3
Fill Areas Waste and Leachate Sampling – Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Parameters	Number of Environmental Samples per Site (waste, leachate)	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
O	Pesticides	6,1	One per 10, or fraction of 10, samples collected (5, 1)	One per 10, or fraction of 10, samples (5, 1)	One per 20, or fraction of 20, samples collected (3, 1)	NA	250 mL wide mouth glass container with Teflon™-lined lid	4°C	14 days from collection to extraction; 40 days from extraction to analysis; For TCLP, 14 days from collection to TCLP extract generation, 14 days from TCLP extract generation to extraction, 40 days from extraction to analysis
P	Pesticides	8,1							
Q	Pesticides	24,3							
R	Pesticides	8,1							
S	Pesticides	4,1							
O	Herbicides	6,1	One per 10, or fraction of 10, samples collected (5, 1)	One per 10, or fraction of 10, samples (5, 1)	One per 20, or fraction of 20, samples collected (3, 1)	NA	250 mL wide mouth glass container with Teflon™-lined lid	4°C	14 days from collection to extraction; 40 days from extraction to analysis; For TCLP, 14 days from collection to TCLP extract generation, 14 days from TCLP extract generation to extraction, 40 days from extraction to analysis
P	Herbicides	8,1							
Q	Herbicides	24,3							
R	Herbicides	8,1							
S	Herbicides	4,1							

Table 3
Fill Areas Waste and Leachate Sampling – Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Parameters	Number of Environmental Samples per Site (waste, leachate)	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
O	PCBs	6,1	One per 10, or fraction of 10, samples collected (5, 1)	One per 10, or fraction of 10, samples (5, 1)	One per 20, or fraction of 20, samples collected (3, 1)	NA	500 mL wide mouth glass container	4oC	14 days from collection to extraction; 40 days from extraction to analysis
P	PCBs	8,1							
Q	PCBs	24,3							
R	PCBs	8,1							
S	PCBs	4,1							
O	Metals	6,1	One per 10, or fraction of 10, samples collected (5, 1)	One per 10, or fraction of 10, samples (5, 1)	One per 20, or fraction of 20, samples collected (3, 1)	NA	4 ounce wide mouth polyethylene or fluorocarbon (TFE or PFA) container	4°C	180 days from collection; For TCLP, 180 days from collection to TCLP extract generation, 180 days from extraction to analysis
P	Metals	8,1							
Q	Metals	24,3							
R	Metals	8,1							
S	Metals	4,1							
O	Dioxin	6,1	One per 10, or fraction of 10, samples collected (5, 1)	One per 10, or fraction of 10, samples (5, 1)	One per 20, or fraction of 20, samples collected (3, 1)	NA	100 grams in 4 oz. Amber glass jar with Teflon™-lined lid	4°C	30 days from collection to extraction, 45 days from extraction to analysis
P	Dioxin	8,1							
Q	Dioxin	24,3							
R	Dioxin	8,1							
S	Dioxin	4,1							
Total Number of Samples		350	(35, 7)	(35, 7)	(21, 7)	(3)			

* (x) Estimated number, criteria presented shall be used ot determine actual numbers.

Table 4
Fill Areas Alluvial Groundwater Sampling – Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Parameters	Number of Environmental Samples per Site	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike/Matrix Spike Duplicates or Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
O,P,S	VOCs	39	One per 10, or fraction of 10, samples collected (24)	One per 10, or fraction of 10, samples (24)	One per 20, or fraction of 20, samples collected (12)	One per sample cooler containing VOC analysis (12)	3-40 mL glass vials with Teflon™-lined septum caps	4°C HCl to pH<2 FC	14 days from collection
R	VOCs	13							
Q	VOCs	104							
O,P,S	SVOCs	39	One per 10, or fraction of 10, samples collected (24)	One per 10, or fraction of 10, samples (24)	One per 20, or fraction of 20, samples collected (12)	NA	2-one liter amber glass containers with Teflon™ lined screw caps	4°C FC	7 days from collection to extraction, 40 days from extraction to analysis
R	SVOCs	13							
Q	SVOCs	104							
O,P,S	Pesticides	12	One per 10, or fraction of 10, samples collected (8)	One per 10, or fraction of 10, samples (8)	One per 20, or fraction of 20, samples collected (4)	NA	4-one liter amber glass containers with Teflon™ lined screw caps	4°C	7 days from collection to extraction, 40 days from extraction to analysis
R	Pesticides	4							
Q	Pesticides	32							
O,P,S	Herbicides	12	One per 10, or fraction of 10, samples collected (8)	One per 10, or fraction of 10, samples (8)	One per 20, or fraction of 20, samples collected (4)	NA	1-250 or 500 mL polyethylene or fluorocarbon (TFE or PFA) container	4°C HNO_3 to pH<2	180 days from collection
R	Herbicides	4							
Q	Herbicides	32							
O,P,S	PCBs	12	One per 10, or fraction of 10, samples collected (8)	One per 10, or fraction of 10, samples (8)	One per 20, or fraction of 20, samples collected (4)	NA	2-one liter amber glass containers with Teflon™ lined screw caps	4°C	7 days from collection to extraction, 40 days from extraction to analysis
R	PCBs	4							
Q	PCBs	32							

Table 4
Fill Areas Alluvial Groundwater Sampling – Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Parameters	Number of Environmental Samples per Site	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike/Matrix Spike Duplicates or Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
O,P,S	Metals	12	One per 10, or fraction of 10, samples collected (8)	One per 10, or fraction of 10, samples (8)	One per 20, or fraction of 20, samples collected (4)	NA	1-250 or 500 mL polyethylene or fluorocarbon (TFE or PFA) container	4°C HNO_3 to pH<2	180 days from collection
R	Metals	4							
Q	Metals	32							
O,P,S	Dioxin	3	One per 10, or fraction of 10, samples collected (2)	One per 10, or fraction of 10, samples (2)	One per 20, or fraction of 20, samples collected (1)	NA	2-one liter amber glass containers with Teflon™ lined screw caps	4°C FC	30 days from collection to extraction, 45 days from extraction to analysis
R	Dioxin	3							
Q	Dioxin	6							
O,P,S	ORP	12	One per 10, or fraction of 10, samples collected (8)	One per 10, or fraction of 10, samples (8)	One per 20, or fraction of 20, samples collected (4)	NA	250 mL plastic container	4°C	As soon as possible
R	ORP	4							
Q	ORP	32							
O,P,S	DO	12	One per 10, or fraction of 10, samples collected (8)	One per 10, or fraction of 10, samples (8)	One per 20, or fraction of 20, samples collected (4)	NA	100 mL plastic container	4°C	As soon as possible
R	DO	4							
Q	DO	32							
O,P,S	Ferrous Iron	12	One per 10, or fraction of 10, samples collected (8)	One per 10, or fraction of 10, samples (8)	One per 20, or fraction of 20, samples collected (4)	NA	250 mL plastic container	4°C HCl to pH<2	As soon as possible
R	Ferrous Iron	4							
Q	Ferrous Iron	32							
O,P,S	Manganese	12	One per 10, or fraction of 10, samples collected (8)	One per 10, or fraction of 10, samples (8)	One per 20, or fraction of 20, samples collected (4)	NA	1-250 or 500 mL polyethylene or fluorocarbon (TFE or PFA) container	4°C HNO_3 to pH<2	180 days from collection
R	Manganese	4							
Q	Manganese	32							

Table 4
Fill Areas Alluvial Groundwater Sampling – Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Parameters	Number of Environmental Samples per Site	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike/Matrix Spike Duplicates or Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
O,P,S	Nitrate	12	One per 10, or fraction of 10, samples collected (8)	One per 10, or fraction of 10, samples (8)	One per 20, or fraction of 20, samples collected (4)	NA	250 mL plastic container	4°C	48 hours
R	Nitrate	4							
Q	Nitrate	32							
O,P,S	Sulfate	12	One per 10, or fraction of 10, samples collected (8)	One per 10, or fraction of 10, samples (8)	One per 20, or fraction of 20, samples collected (4)	NA	250 mL plastic container	4°C	28 hours
R	Sulfate	4							
Q	Sulfate	32							
O,P,S	Alkalinity	12	One per 10, or fraction of 10, samples collected (8)	One per 10, or fraction of 10, samples (8)	One per 20, or fraction of 20, samples collected (4)	NA	250 mL plastic container	4°C	14 days from collection
R	Alkalinity	4							
Q	Alkalinity	32							
O,P,S	Methane	12	One per 10, or fraction of 10, samples collected (8)	One per 10, or fraction of 10, samples (8)	One per 20, or fraction of 20, samples collected (4)	NA	40 mL VOA vial	4°C	14 days
R	Methane	4							
Q	Methane	32							
O,P,S	Carbon Dioxide	12	One per 10, or fraction of 10, samples collected (8)	One per 10, or fraction of 10, samples (8)	One per 20, or fraction of 20, samples collected (4)	NA	40 mL VOA vial	4°C	14 days
R	Carbon Dioxide	4							
Q	Carbon Dioxide	32							
Total Number of Samples		1,422	(154)	(154)	(77)	(12)			

FC If free chlorine is present in samples, it must be removed by the appropriate addition of $Na_2S_2O_3$
* (x) Estimated number, criteria presented shall be used to determine actual numbers.

Table 5
Fill Areas Bedrock Well Sampling - Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Parameters	Number of Environmental Samples per Site	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
O,P,R,S	VOCs	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	One per sample cooler containing VOC analysis (1)	3-40 mL glass vials with Teflon™-lined septum caps	4°C HCl to pH<2 FC	14 days from collection
Q	VOCs	2							
O,P,R,S	SVOCs	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	2-one liter amber glass containers with Teflon™-lined screw caps	4°C FC	7 days from collection to extraction, 40 days from extraction to analysis
Q	SVOCs	2							
O,P,R,S	Pesticides	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	4-one liter amber glass containers with Teflon™-lines screw caps	4°C	7 days from collection to extraction, 40 days from extraction to analysis
Q	Pesticides	2							

Table 5
Fill Areas Bedrock Well Sampling - Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Parameters	Number of Environmental Samples per Site	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
O,P,R,S	Herbicides	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	4-one liter amber glass containers with Teflon™-lines screw caps	4°C	7 days from collection to extraction, 40 days from extraction to analysis
Q	Herbicides	2							
O,P,R,S	PCBs	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	2-one liter amber glass containers with Teflon™-lined screw caps	4°C	7 days from collection to extraction, 40 days from extraction to analysis
Q	PCBs	2							
O,P,R,S	Metals	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	1-250 or 500 mL polyethylene or fluorocarbon (TFE or PFA) container	4°C HNO_3 to pH<2	180 days from collection
Q	Metals	2							

Table 5
Fill Areas Bedrock Well Sampling - Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Parameters	Number of Environmental Samples per Site	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
O,P,R,S	Dioxin	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	2-one liter amber glass containers with Teflon™-lined screw caps	4°C FC	30 days from collection to extraction. 45 days from extraction to analysis
Q	Dioxin	2							
O,P,R,S	ORP	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	250 mL plastic container	4°C	As soon as possible
Q	ORP	2							
O,P,R,S	DO	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	100 mL plastic container	4°C	As soon as possible
Q	DO	2							

Table 5
Fill Areas Bedrock Well Sampling - Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Parameters	Number of Environmental Samples per Site	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
O,P,R,S	Ferrous Iron	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	250 mL plastic container	4°C HCl to pH<2	As soon as possible
Q	Ferrous Iron	2							
O,P,R,S	Manganese	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	1-250 or 500 mL polyethylene or fluorocarbon (TFE or PFA) container	4°C HNO_3 to pH<2	180 days from collection
Q	Manganese	2							
O,P,R,S	Nitrate	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	250 mL plastic container	4°C	48 hours
Q	Nitrate	2							

Table 5
Fill Areas Bedrock Well Sampling - Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Parameters	Number of Environmental Samples per Site	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
O,P,R,S	Sulfate	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	250 mL plastic container	4°C	28 days
Q	Sulfate	2							
O,P,R,S	Alkalinity	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	250 mL plastic container	4°C	14 days from collection
Q	Alkalinity	2							
O,P,R,S	Methane	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	40 mL VOA vial	4°C	14 days
Q	Methane	2							

Table 5
Fill Areas Bedrock Well Sampling - Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Parameters	Number of Environmental Samples per Site	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
O,P,R,S	Carbon Dioxide	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	40 mL VOA vial	4°C	14 days
Q	Carbon Dioxide	2							
Total Number of Samples		96	(16)	(16)	(16)	(1)			

Six samples of each of the following analytes will be collected from the open hole (collected as well is installed): VOCs, SVOCs, pesticides, herbicides, PCBs, metals, and each of the geochemical parameters.
No dioxin samples will be collected from the open hole.
Two samples of each of the analytes will be collected from the cased/screened hole (bedrock groundwater).
* (x) Estimated number, criteria presented shall be used to determine actual numbers.

Table 6
Fill Areas Surface Soil Sampling – Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Parameters	Number of Environmental Samples per Site	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
O	VOCs	3	One per 10, or fraction of 10, samples collected (3)	One per 10, or fraction of 10, samples (3)	One per 20, or fraction of 20, samples collected (2)	One per sample cooler containing VOC analysis (2)	3-Encore™ samplers (or in accordance with USEPA Method 5035)	4°C	Transferred to soil container or analyzed 48 hours from collection; For TCLP VOCs, 14 days from collection to TCLP extract generation, 14 days from TCLP extraction to analysis
P	VOCs	4							
Q	VOCs	13							
R	VOCs	4							
S	VOCs	2							
O	SVOCs	3	One per 10, or fraction of 10, samples collected (3)	One per 10, or fraction of 10, samples (3)	One per 20, or fraction of 20, samples collected (2)	NA	250 mL wide mouth glass container with Teflon™-lined lid	4°C	14 days from collection to extraction; 40 days from extraction to analysis; For TCLP-SVOCs, 14 days from collection to TCLP extract generation, 7 days from TCLP extract generation to extraction, 40 days from extraction to analysis
P	SVOCs	4							
Q	SVOCs	13							
R	SVOCs	4							
S	SVOCs	2							

Table 6
Fill Areas Surface Soil Sampling – Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Parameters	Number of Environmental Samples per Site	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
O	Pesticides	3	One per 10, or fraction of 10, samples collected (3)	One per 10, or fraction of 10, samples (3)	One per 20, or fraction of 20, samples collected (2)	NA	250 mL wide mouth glass container with Teflon™-lined lid	4°C	14 days from collection to extraction; 40 days from extraction to analysis; For TCLP, 14 days from collection to TCLP extract generation, 14 days from TCLP extract generation to extraction, 40 days from extraction to analysis
P	Pesticides	4							
Q	Pesticides	13							
R	Pesticides	4							
S	Pesticides	2							
O	Herbicides	3	One per 10, or fraction of 10, samples collected (3)	One per 10, or fraction of 10, samples (3)	One per 20, or fraction of 20, samples collected (2)	NA	250 mL wide mouth glass container with Teflon™-lined lid	4°C	14 days from collection to extraction; 40 days from extraction to analysis; For TCLP, 14 days from collection to TCLP extract generation, 14 days from TCLP extract generation to extraction, 40 days from extraction to analysis
P	Herbicides	4							
Q	Herbicides	13							
R	Herbicides	4							
S	Herbicides	2							

Table 6
Fill Areas Surface Soil Sampling – Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Parameters	Number of Environmental Samples per Site	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
O	PCBs	3	One per 10, or fraction of 10, samples collected (3)	One per 10, or fraction of 10, samples (3)	One per 20, or fraction of 20, samples collected (2)	NA	500 mL wide mouth glass container	4oC	14 days from collection to extraction; 40 days from extraction to analysis
P	PCBs	4							
Q	PCBs	13							
R	PCBs	4							
S	PCBs	2							
O	Metals	3	One per 10, or fraction of 10, samples collected (3)	One per 10, or fraction of 10, samples (3)	One per 20, or fraction of 20, samples collected (2)	NA	4 ounce wide mouth polyethylene or fluorocarbon (TFE or PFA) container	4°C	180 days from collection; For TCLP, 180 days from collection to TCLP extract generation, 180 days from extraction to analysis
P	Metals	4							
Q	Metals	13							
R	Metals	4							
S	Metals	2							
O	Dioxin	3	One per 10, or fraction of 10, samples collected (3)	One per 10, or fraction of 10, samples (3)	One per 20, or fraction of 20, samples collected (2)	NA	100 grams in 4 oz. Amber glass jar with Teflon™-lined lid	4°C	30 days from collection to extraction, 45 days from extraction to analysis
P	Dioxin	4							
Q	Dioxin	13							
R	Dioxin	4							
S	Dioxin	2							
Total Number of Samples		182	(35, 7)	(35, 7)	(21, 7)	(3)			

* (x) Estimated number, criteria presented shall be used ot determine actual numbers.

Table 7
Fill Areas Subsurface Soil Sampling – Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Parameters	Number of Environmental Samples per Site	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
O	VOCs	3	One per 10, or fraction of 10, samples collected (3)	One per 10, or fraction of 10, samples (3)	One per 20, or fraction of 20, samples collected (2)	One per sample cooler containing VOC analysis (2)	3-Encore™ samplers (or in accordance with USEPA Method 5035)	4°C	Transferred to soil container or analyzed 48 hours from collection; For TCLP VOCs, 14 days from collection to TCLP extract generation, 14 days from TCLP extraction to analysis
P	VOCs	4							
Q	VOCs	13							
R	VOCs	4							
S	VOCs	2							
O	SVOCs	3	One per 10, or fraction of 10, samples collected (3)	One per 10, or fraction of 10, samples (3)	One per 20, or fraction of 20, samples collected (2)	NA	250 mL wide mouth glass container with Teflon™-lined lid	4°C	14 days from collection to extraction; 40 days from extraction to analysis; For TCLP-SVOCs, 14 days from collection to TCLP extract generation, 7 days from TCLP extract generation to extraction, 40 days from extraction to analysis
P	SVOCs	4							
Q	SVOCs	13							
R	SVOCs	4							
S	SVOCs	2							

Table 7
Fill Areas Subsurface Soil Sampling – Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Parameters	Number of Environmental Samples per Site	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
O	Pesticides	3	One per 10, or fraction of 10, samples collected (3)	One per 10, or fraction of 10, samples (3)	One per 20, or fraction of 20, samples collected (2)	NA	250 mL wide mouth glass container with Teflon™-lined lid	4°C	14 days from collection to extraction; 40 days from extraction to analysis; For TCLP, 14 days from collection to TCLP extract generation, 14 days from TCLP extract generation to extraction, 40 days from extraction to analysis
P	Pesticides	4							
Q	Pesticides	13							
R	Pesticides	4							
S	Pesticides	2							
O	Herbicides	3	One per 10, or fraction of 10, samples collected (3)	One per 10, or fraction of 10, samples (3)	One per 20, or fraction of 20, samples collected (2)	NA	250 mL wide mouth glass container with Teflon™-lined lid	4°C	14 days from collection to extraction; 40 days from extraction to analysis; For TCLP, 14 days from collection to TCLP extract generation, 14 days from TCLP extract generation to extraction, 40 days from extraction to analysis
P	Herbicides	4							
Q	Herbicides	13							
R	Herbicides	4							
S	Herbicides	2							

Table 7
Fill Areas Subsurface Soil Sampling – Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Parameters	Number of Environmental Samples per Site	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
O	PCBs	3	One per 10, or fraction of 10, samples collected (3)	One per 10, or fraction of 10, samples (3)	One per 20, or fraction of 20, samples collected (2)	NA	500 mL wide mouth glass container	4oC	14 days from collection to extraction; 40 days from extraction to analysis
P	PCBs	4							
Q	PCBs	13							
R	PCBs	4							
S	PCBs	2							
O	Metals	3	One per 10, or fraction of 10, samples collected (3)	One per 10, or fraction of 10, samples (3)	One per 20, or fraction of 20, samples collected (2)	NA	4 ounce wide mouth polyethylene or fluorocarbon (TFE or PFA) container	4°C	180 days from collection; For TCLP, 180 days from collection to TCLP extract generation, 180 days from extraction to analysis
P	Metals	4							
Q	Metals	13							
R	Metals	4							
S	Metals	2							
O	Dioxin	3	One per 10, or fraction of 10, samples collected (3)	One per 10, or fraction of 10, samples (3)	One per 20, or fraction of 20, samples collected (2)	NA	100 grams in 4 oz. Amber glass jar with Teflon™-lined lid	4°C	30 days from collection to extraction, 45 days from extraction to analysis
P	Dioxin	4							
Q	Dioxin	13							
R	Dioxin	4							
S	Dioxin	2							
Total Number of Samples		182	(35, 7)	(35, 7)	(21, 7)	(3)			

* (x) Estimated number, criteria presented shall be used ot determine actual numbers.

Table 8
Air Sampling - Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Parameters	Number of Environmental Samples per Site	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
P	VOCs	4	One per 10, or fraction of 10, samples collected (3)	One per 10, or fraction of 10, samples (3)	One per 20, or fraction of 20, samples collected (2)	One per sample cooler containing VOC analysis (2)	Sample cartridge/filter as described in Method TO1	4°C	7 days from collection or analysis
O,R,&S	VOCs	4							
Q	VOCs	8							
P	SVOCs	4	One per 10, or fraction of 10, samples collected (3)	One per 10, or fraction of 10, samples (3)	One per 20, or fraction of 20, samples collected (2)	NA	Sample cartridge/filter as described in Method TO13	4°C	7 days from collection or analysis
O,R,&S	SVOCs	4							
Q	SVOCs	8							

Table 8
Air Sampling - Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Parameters	Number of Environmental Samples per Site	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
P	Pesticides	4	One per 10, or fraction of 10, samples collected (3)	One per 10, or fraction of 10, samples (3)	One per 20, or fraction of 20, samples collected (2)	NA	Sample cartridge/filter as described in Method TO13	4°C	7 days from collection or analysis
O,R,&S	Pesticides	4							
Q	Pesticides	8							
P	PCBs	4	One per 10, or fraction of 10, samples collected (3)	One per 10, or fraction of 10, samples (3)	One per 20, or fraction of 20, samples collected (2)	NA	Sample cartridge/filter as described in Method TO13	4°C	7 days from collection or analysis
O,R,&S	PCBs	4							
Q	PCBs	8							

Table 8
Air Sampling - Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Parameters	Number of Environmental Samples per Site	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
P	Metals	4	One per 10, or fraction of 10, samples collected (3)	One per 10, or fraction of 10, samples (3)	One per 20, or fraction of 20, samples collected (2)	NA	Sample cartridge/filter as described in Method 6010B *	4°C	7 days from collection or analysis
O,R,&S	Metals	4							
Q	Metals	8							
P	Dioxin	4	One per 10, or fraction of 10, samples collected (3)	One per 10, or fraction of 10, samples (3)	One per 20, or fraction of 20, samples collected (2)	NA	Sample cartridge/filter as described in Method TO9	4°C	7 days from collection or analysis
O,R,&S	Dioxin	4							
Q	Dioxin	8							
Total Number of Samples		(112)	(18)	(18)	(12)	(2)			

* (x) Estimated number, criteria presented shall be used to determine actual numbers.

Table 9
Fill Areas Stormwater Runoff Sampling - Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Parameters	Number of Environmental Samples per Site	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
R	VOCs	3	One per 10, or fraction of 10, samples collected (2)	One per 10, or fraction of 10, samples (2)	One per 20, or fraction of 20, samples collected (1)	One per sample cooler containing VOC analysis (1)	3-40 mL glass vials with Teflon™-lined septum caps	4°C HCl to pH<2 FC	14 days from collection
Q	VOCs	6							
R	SVOCs	3	One per 10, or fraction of 10, samples collected (2)	One per 10, or fraction of 10, samples (2)	One per 20, or fraction of 20, samples collected (1)	NA	2-one liter amber glass containers with Teflon™-lined screw caps	4°C FC	7 days from collection to extraction, 40 days from extraction to analysis
Q	SVOCs	6							
R	Pesticides	3	One per 10, or fraction of 10, samples collected (2)	One per 10, or fraction of 10, samples (2)	One per 20, or fraction of 20, samples collected (1)	NA	4-one liter amber glass containers with Teflon™-lines screw caps	4°C	7 days from collection to extraction, 40 days from extraction to analysis
Q	Pesticides	6							

Table 9
Fill Areas Stormwater Runoff Sampling - Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Parameters	Number of Environmental Samples per Site	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
R	Herbicides	3	One per 10, or fraction of 10, samples collected (2)	One per 10, or fraction of 10, samples (2)	One per 20, or fraction of 20, samples collected (1)	NA	4-one liter amber glass containers with Teflon™-lines screw caps	4°C	7 days from collection to extraction, 40 days from extraction to analysis
Q	Herbicides	6							
R	PCBs	3	One per 10, or fraction of 10, samples collected (2)	One per 10, or fraction of 10, samples (2)	One per 20, or fraction of 20, samples collected (1)	NA	*2-one liter amber glass containers with Teflon™-lined screw caps	4°C	7 days from collection to extraction, 40 days from extraction to analysis
Q	PCBs	6							
R	Metals	3	One per 10, or fraction of 10, samples collected (2)	One per 10, or fraction of 10, samples (2)	One per 20, or fraction of 20, samples collected (1)	NA	1-250 or 500 mL polyethylene or fluorocarbon (TFE or PFA) container	4°C HNO_3 to pH<2	180 days from collection
Q	Metals	6							

Table 9
Fill Areas Stormwater Runoff Sampling - Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Site	Parameters	Number of Environmental Samples per Site	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
R	Dioxin	3	One per 10, or fraction of 10, samples collected (2)	One per 10, or fraction of 10, samples (2)	One per 20, or fraction of 20, samples collected (1)	NA	2-one liter amber glass containers with Teflon™-lined screw caps	4°C FC	30 days from collection to extraction, 45 days from extraction to analysis
Q	Dioxin	6							
Total Number of Samples		63	(14)	(14)	(7)	(1)			

* (x) Estimated number, criteria presented shall be used to determine actual numbers.

Table 10
Upgradient Groundwater Sampling - Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Station	Parameters	Number of Environmental Samples per Station	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
1,2,3,4	VOCs	13	One per 10, or fraction of 10, samples collected (5)	One per 10, or fraction of 10, samples (5)	One per 20, or fraction of 20, samples collected (3)	One per sample cooler containing VOC analysis (3)	3-40 mL glass vials with Teflon™-lined septum caps	4°C HCl to pH<2 FC	14 days from collection
1,2,3,4	SVOCs	13	One per 10, or fraction of 10, samples collected (5)	One per 10, or fraction of 10, samples (5)	One per 20, or fraction of 20, samples collected (3)	NA	2-one liter amber glass containers with Teflon™-lined screw caps	4°C FC	7 days from collection to extraction, 40 days from extraction to analysis
1,2,3,4	Pesticides	4	One per 10, or fraction of 10, samples collected (2)	One per 10, or fraction of 10, samples (2)	One per 20, or fraction of 20, samples collected (1)	NA	4-one liter amber glass containers with Teflon™-lines screw caps	4°C	7 days from collection to extraction, 40 days from extraction to analysis
1,2,3,4	Herbicides	4	One per 10, or fraction of 10, samples collected (2)	One per 10, or fraction of 10, samples (2)	One per 20, or fraction of 20, samples collected (1)	NA	4-one liter amber glass containers with Teflon™-lines screw caps	4°C	7 days from collection to extraction, 40 days from extraction to analysis
1,2,3,4	PCBs	4	One per 10, or fraction of 10, samples collected (2)	One per 10, or fraction of 10, samples (2)	One per 20, or fraction of 20, samples collected (1)	NA	2-one liter amber glass containers with Teflon™-lined screw caps	4°C	7 days from collection to extraction, 40 days from extraction to analysis

Table 10
Upgradient Groundwater Sampling - Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Station	Parameters	Number of Environmental Samples per Station	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
1,2,3,4	Metals	4	One per 10, or fraction of 10, samples collected (2)	One per 10, or fraction of 10, samples (2)	One per 20, or fraction of 20, samples collected (1)	NA	1-250 or 500 mL polyethylene or fluorocarbon (TFE or PFA) container	4°C HNO_3 to pH<2	180 days from collection
2,3	Dioxin	3	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	2-one liter amber glass containers with Teflon™-lined screw caps	4°C FC	30 days from collection to extraction, 45 days from extraction to analysis
1,2,3,4	ORP	4	One per 10, or fraction of 10, samples collected (2)	One per 10, or fraction of 10, samples (2)	One per 20, or fraction of 20, samples collected (1)	NA	250 mL plastic container	4°C	As soon as possible
1,2,3,4	DO	4	One per 10, or fraction of 10, samples collected (2)	One per 10, or fraction of 10, samples (2)	One per 20, or fraction of 20, samples collected (1)	NA	100 mL plastic container	4°C	As soon as possible

Table 10
Upgradient Groundwater Sampling - Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Station	Parameters	Number of Environmental Samples per Station	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
1,2,3,4	Ferrous Iron	4	One per 10, or fraction of 10, samples collected (2)	One per 10, or fraction of 10, samples (2)	One per 20, or fraction of 20, samples collected (1)	NA	250 mL plastic container	4°C HCl to pH<2	As soon as possible
1,2,3,4	Manganese	4	One per 10, or fraction of 10, samples collected (2)	One per 10, or fraction of 10, samples (2)	One per 20, or fraction of 20, samples collected (1)	NA	1-250 or 500 mL polyethylene or fluorocarbon (TFE or PFA) container	4°C HNO_3 to pH<2	180 days from collection
1,2,3,4	Nitrate	4	One per 10, or fraction of 10, samples collected (2)	One per 10, or fraction of 10, samples (2)	One per 20, or fraction of 20, samples collected (1)	NA	250 mL plastic container	4°C	48 hours
1,2,3,4	Sulfate	4	One per 10, or fraction of 10, samples collected (2)	One per 10, or fraction of 10, samples (2)	One per 20, or fraction of 20, samples collected (1)	NA	250 mL plastic container	4°C	28 days

Table 10
Upgradient Groundwater Sampling - Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Station	Parameters	Number of Environmental Samples per Station	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
1,2,3,4	Alkalinity	4	One per 10, or fraction of 10, samples collected (2)	One per 10, or fraction of 10, samples (2)	One per 20, or fraction of 20, samples collected (1)	NA	250 mL plastic container	4°C	14 days from collection
1,2,3,4	Methane	4	One per 10, or fraction of 10, samples collected (2)	One per 10, or fraction of 10, samples (2)	One per 20, or fraction of 20, samples collected (1)	NA	40 mL VOA vial	4°C	14 days
1,2,3,4	Carbon Dioxide	4	One per 10, or fraction of 10, samples collected (2)	One per 10, or fraction of 10, samples (2)	One per 20, or fraction of 20, samples collected (1)	NA	40 mL VOA vial	4°C	14 days
Total Number of Samples		318	(37)	(37)	(20)	(2)			

* (x) Estimated nubmer, criteria presented shall be used to determine actual numbers.

Table 1A
Off-Site Surface Soil Sampling - Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Station	Parameters	Number of Environmental Samples per Station	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
1,2,3,4	VOCs	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	One per sample cooler containing VOC analysis (1)	3-Encore™ samplers (or in accordance with USEPA Method 5035)	4°C	Transferred to soil container or analyzed 48 hours from collection; For TCLP VOCs, 14 days from collection to TCLP extract generation, 14 days from TCLP extraction to analysis
1,2,3,4	SVOCs	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	3-Encore™ samplers (or in accordance with USEPA Method 5035)	4°C	14 days from collection to extraction, 40 days from extraction to analysis; For TCLP SVOCs, 14 days from collection to TCLP extract generation, 7 days from TCLP extract generation to extraction, 40 days from extraction to analysis
1,2,3,4	Pesticides	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	3-Encore™ samplers (or in accordance with USEPA Method 5035)	4°C	14 days from collection to extraction, 40 days from extraction to analysis; For TCLP, 14 days from collection to TCLP extract generation, 14 days from TCLP extract generation to extraction, 40 days from extraction to analysis
1,2,3,4	Herbicides	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	3-Encore™ samplers (or in accordance with USEPA Method 5035)	4°C	14 days from collection to extraction, 40 days from extraction to analysis; For TCLP, 14 days from collection to TCLP extract generation, 14 days from TCLP extract generation to extraction, 40 days from extraction to analysis

Table 11A
Off-Site Surface Soil Sampling - Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Station	Parameters	Number of Environmental Samples per Station	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
1,2,3,4	PCBs	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	3-Encore™ samplers (or in accordance with USEPA Method 5035)	4°C	14 days from collection to extraction, 40 days from extraction to analysis
1,2,3,4	Metals	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	3-Encore™ samplers (or in accordance with USEPA Method 5035)	4°C	180 days from collection; For TCLP, 180 days from collection to TCLP extract generation, 180 days from extraction to analysis
1,2,3,4	Dioxin	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	3-Encore™ samplers (or in accordance with USEPA Method 5035)	4°C	30 days from collection to extraction, 45 days from extraction to analysis
Total Number of Samples		(28)	(7)	(7)	(7)	(1)			

* (x) Estimated number, criteria presented shall be used to determine actual numbers.

Table 11B
Off-Site Subsurface Soil Sampling - Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Station	Parameters	Number of Environmental Samples per Station	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
1,2,3,4	VOCs	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	One per sample cooler containing VOC analysis (1)	3-Encore™ samplers (or in accordance with USEPA Method 5035)	4°C	Transferred to soil container or analyzed 48 hours from collection; For TCLP VOCs, 14 days from collection to TCLP extract generation, 14 days from TCLP extraction to analysis
1,2,3,4	SVOCs	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	3-Encore™ samplers (or in accordance with USEPA Method 5035)	4°C	14 days from collection to extraction, 40 days from extraction to analysis; For TCLP SVOCs, 14 days from collection to TCLP extract generation, 7 days from TCLP extract generation to extraction, 40 days from extraction to analysis
1,2,3,4	Pesticides	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	3-Encore™ samplers (or in accordance with USEPA Method 5035)	4°C	14 days from collection to extraction, 40 days from extraction to analysis; For TCLP, 14 days from collection to TCLP extract generation, 14 days from TCLP extract generation to extraction, 40 days from extraction to analysis

Table 11B
Off-Site Subsurface Soil Sampling - Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Station	Parameters	Number of Environmental Samples per Station	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
1,2,3,4	Herbicides	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	3-Encore™ samplers (or in accordance with USEPA Method 5035)	4°C	14 days from collection to extraction, 40 days from extraction to analysis; For TCLP, 14 days from collection to TCLP extract generation, 14 days from TCLP extract generation to extraction, 40 days from extraction to analysis
1,2,3,4	PCBs	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	3-Encore™ samplers (or in accordance with USEPA Method 5035)	4°C	14 days from collection to extraction, 40 days from extraction to analysis
1,2,3,4	Metals	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	3-Encore™ samplers (or in accordance with USEPA Method 5035)	4°C	180 days from collection; For TCLP, 180 days from collection to TCLP extract generation, 180 days from extraction to analysis
1,2,3,4	Dioxin	1	One per 10, or fraction of 10, samples collected (1)	One per 10, or fraction of 10, samples (1)	One per 20, or fraction of 20, samples collected (1)	NA	3-Encore™ samplers (or in accordance with USEPA Method 5035)	4°C	30 days from collection to extraction, 45 days from extraction to analysis

Table 11B
Off-Site Subsurface Soil Sampling - Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

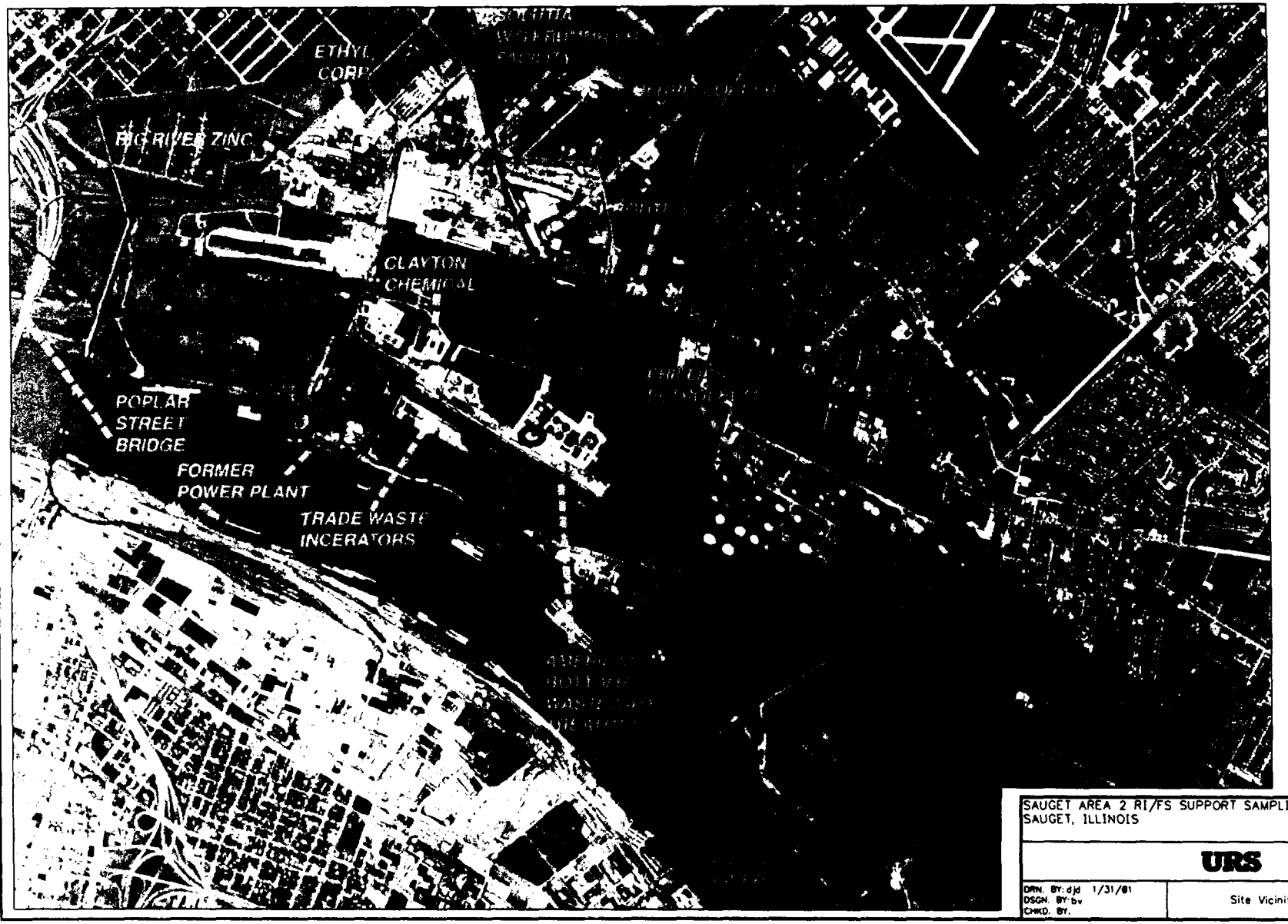
Station	Parameters	Number of Environmental Samples per Station	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
Total Number of Samples		(28)	(7)	(7)	(7)	(1)			

Notice there are no dioxin analyses in the subsurface background soil.
* (x) Estimated number, criteria presented shall be used to determine actual numbers.

Table 12
Fill Areas Soil Grain Size Analysis - Sample and Analysis Summary
Sauget Area 2 Field Sampling Plan

Deep Piezometer	Parameters	Number of Environmental Samples	Number of Field Blanks / Equipment Blanks	Number of Field Duplicates	Number of Matrix Spike / Matrix Spike Duplicates or Spike Spike Duplicates	Number of Trip Blanks	Sample Containers (number, size, type)	Preservation	Holding Time Extraction / Analysis
#1 - #9	Grain Size Particle Size Bulk Density Specific Gravity Moisture Content pH TOC	Every 5 feet and every change in formation to bottom of piezometer	One per 10, or fraction of 10, samples collected	One per 10, or fraction of 10, samples	One per 20, or fraction of 20, samples collected	N/A	4 ounce wide mouth glass container with Teflon™-lined lid; for pH, 100 mL plastic container	4°C	As soon as possible; for TOC, 28 days from collection

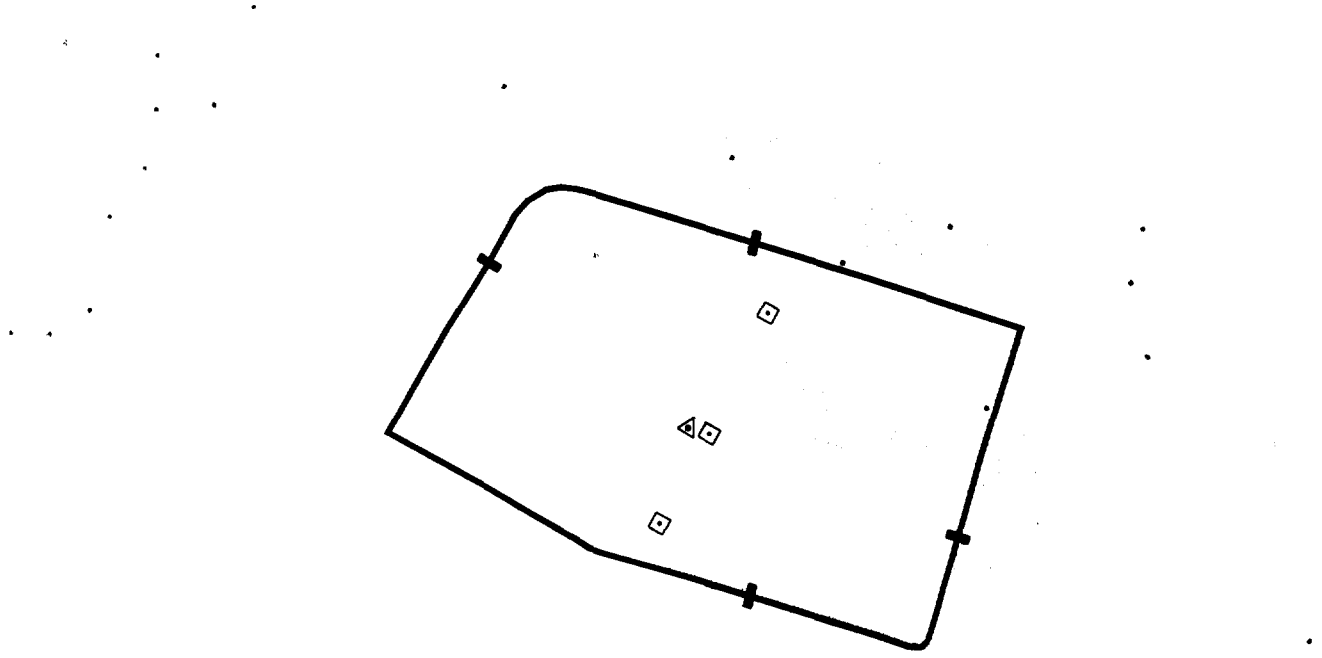
Figures

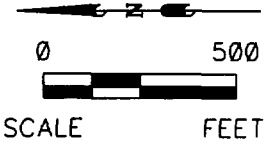


SAUGET AREA 2 RI/FS SUPPORT SAMPLING PLAN SAUGET, ILLINOIS	PROJECT NO. 2320010024.02
URS	
DRN. BY: djd 1/31/01 DSGN. BY: bv CHKD. BY.	Site Vicinity Map
	FIG NO 1

File: E:\2320010024.00\SITE MAP FIG_1.DWG Last edited: 05/29/01 @ 08:09 a.m. WC-ST.LOUIS, MO

File: E:\2320010024.02\EPA\TEST TRENCH.DWG Last edited: 04/10/02 @ 10:01 a.m. WC-ST.LOUIS, MO





LEGEND

- Leachate Monitoring Well
- Test Trench (Area Extent of Waste)
- Waste Characterization Boring

Note: Trench size not to scale; approximate length=20 feet

SAUGET AREA 2 RI/FS SUPPORT SAMPLING PLAN SAUGET, ILLINOIS	PROJECT NO. 2320010024.02
URS	
DRN. BY: djd 1/31/01 DSGN. BY: bv CHKD. BY:	Site O Waste, Soil, and Leachate Sampling Locations
FIG. NO. 2	

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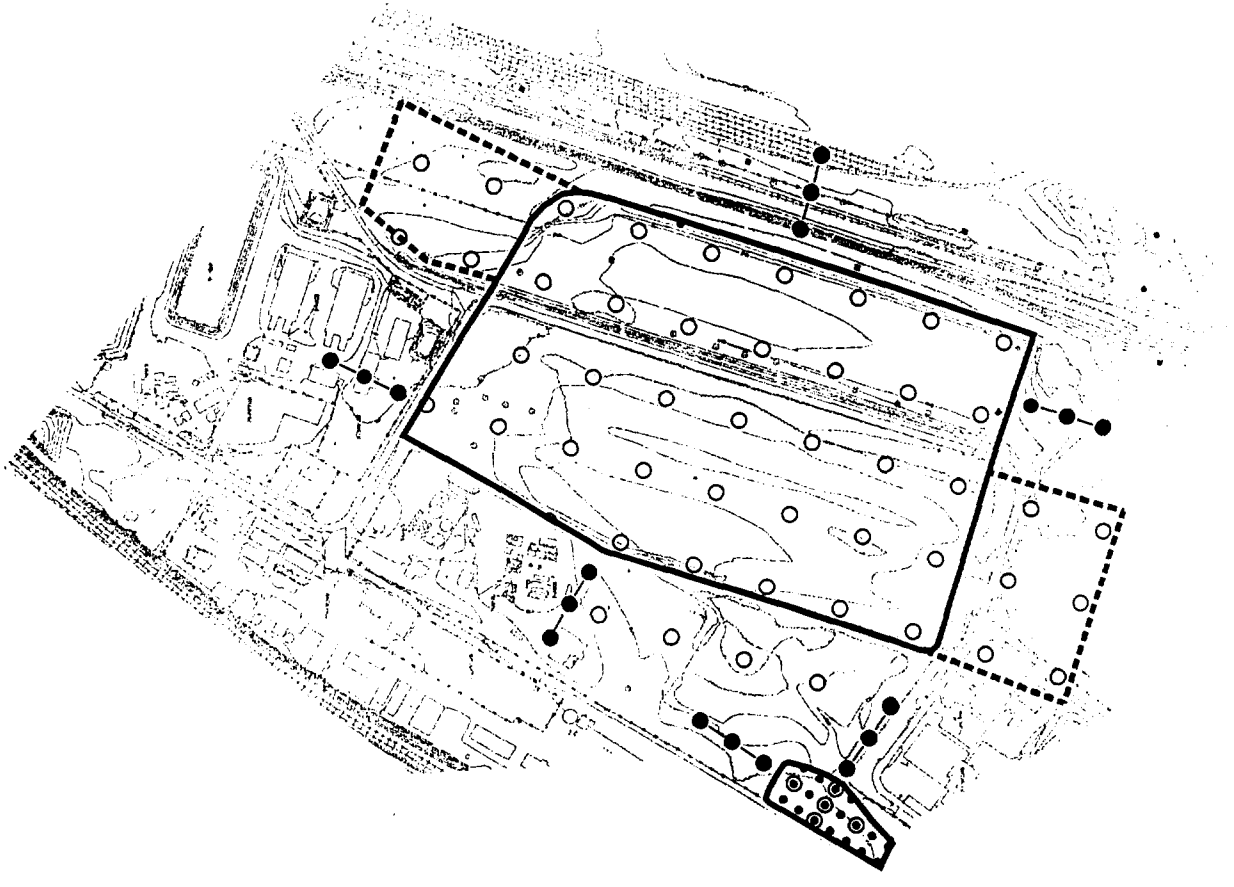


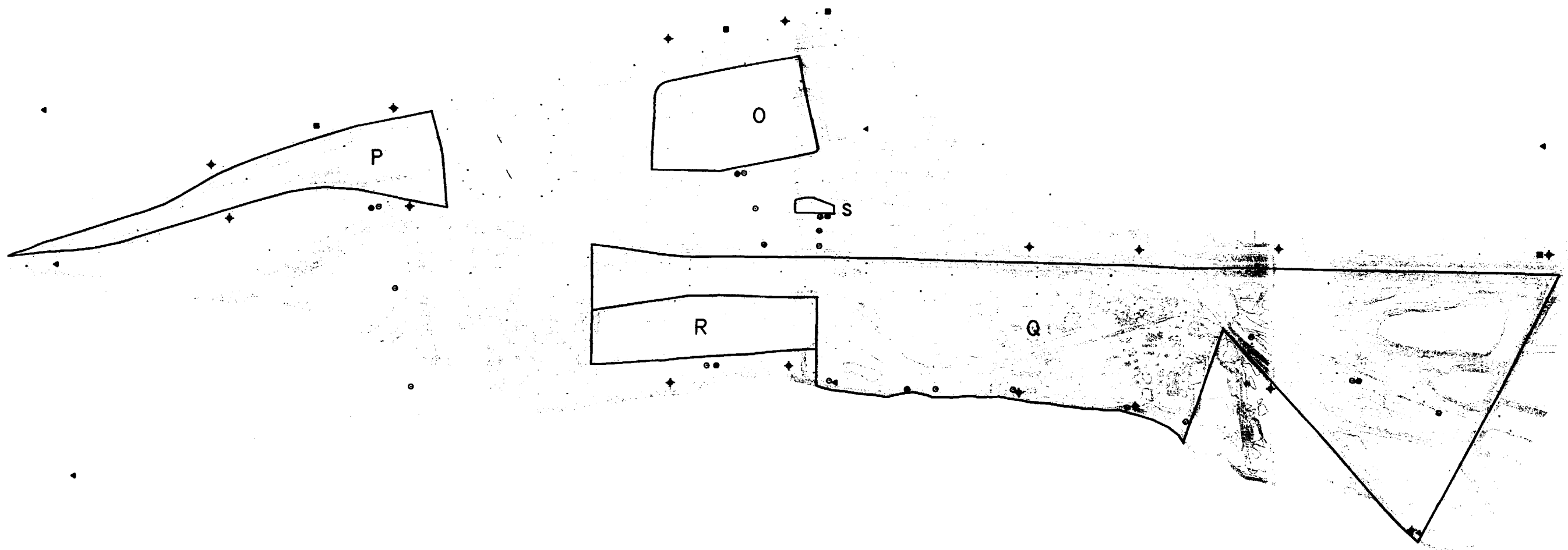
0 500

SCALE FEET

LEGEND

- Magnetometer Survey Locations
- Soil Gas Survey Locations
- Potential Soil Gas Survey Step Out Location

SAUGET AREA 2 RI/FS SUPPORT SAMPLING PLAN SAUGET, ILLINOIS	PROJECT NO. 2320010024.02
URS	
DRN. BY: djd 1/31/01 DSGN. BY: bv CHKD. BY:	Site O Soil Gas Sampling Locations
	FIG. NO. 3



LEGEND

- ■ Offsite Soil and Upgradient/Groundwater Sampling Locations
- ⊙ Site-Related Groundwater Sampling Locations
- ⊕ Bedrock Monitoring Well
- ▲ Piezometer Cluster
- ⌖ Air Sampling Location

Note: Data from Area 1 background locations will also be considered as background for Area 2

0 1000
SCALE FEET

SAUGET AREA 2 RI/FS SUPPORT SAMPLING PLAN SAUGET ILLINOIS	PROJECT NO. 2320010024.02
URS	
DRN. BY: djd 1/31/01 DSGN. BY: bv CHKD. BY:	Offsite Soil and Upgradient/Groundwater, Piezometer, Site-Related Groundwater, and Air Sampling Locations
	FIG. NO. 4

File: E:\2320010024.02\EPA\OFFSITE_SITE-RELATED FIG-4.DWG Last edited: 04/10/02 @ 10:38 a.m. WC-ST.LOUIS, MO

File: E:\2320010024.02\EPA\TEST TRENCH.DWG Last edited: 04/10/02 @ 10:01 a.m. WC-ST.LOUIS, MO

LEGEND

- Leachate Monitoring Well
- Test Trench (Area Extent of Waste)
- Test Trench (Buried tank/drum Confirmation)
- Waste Characterization Boring

N

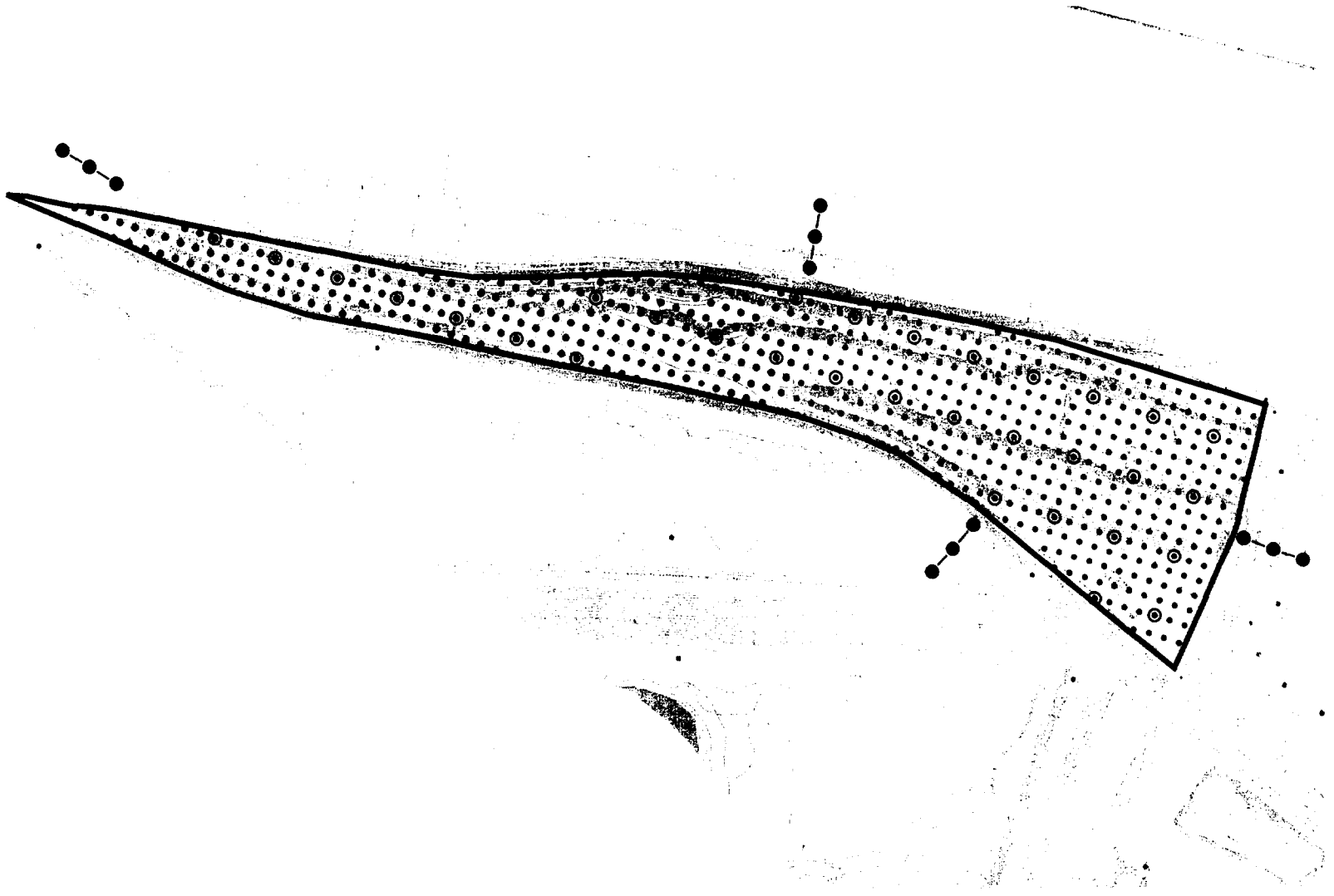
0 500

SCALE FEET

Note: Trench size not to scale; approximate length=20 feet

SAUGET AREA 2 RI/FS SUPPORT SAMPLING PLAN SAUGET, ILLINOIS	PROJECT NO. 2320010024.02
URS	
DRN. BY: djd 1/31/01 DSGN. BY: bv CHKD. BY:	Site P Waste, Soil, and Leachate Sampling Locations
	FIG. NO. 5

File: E:\2320010024.02\EPA\SOIL GAS.DWG Last edited: 04/10/02 @ 10:19 a.m. WC-ST.LOUIS, MO



LEGEND

- Magnetometer Survey Locations
- Soil Gas Survey Locations
- Potential Soil Gas Survey Step Out Location

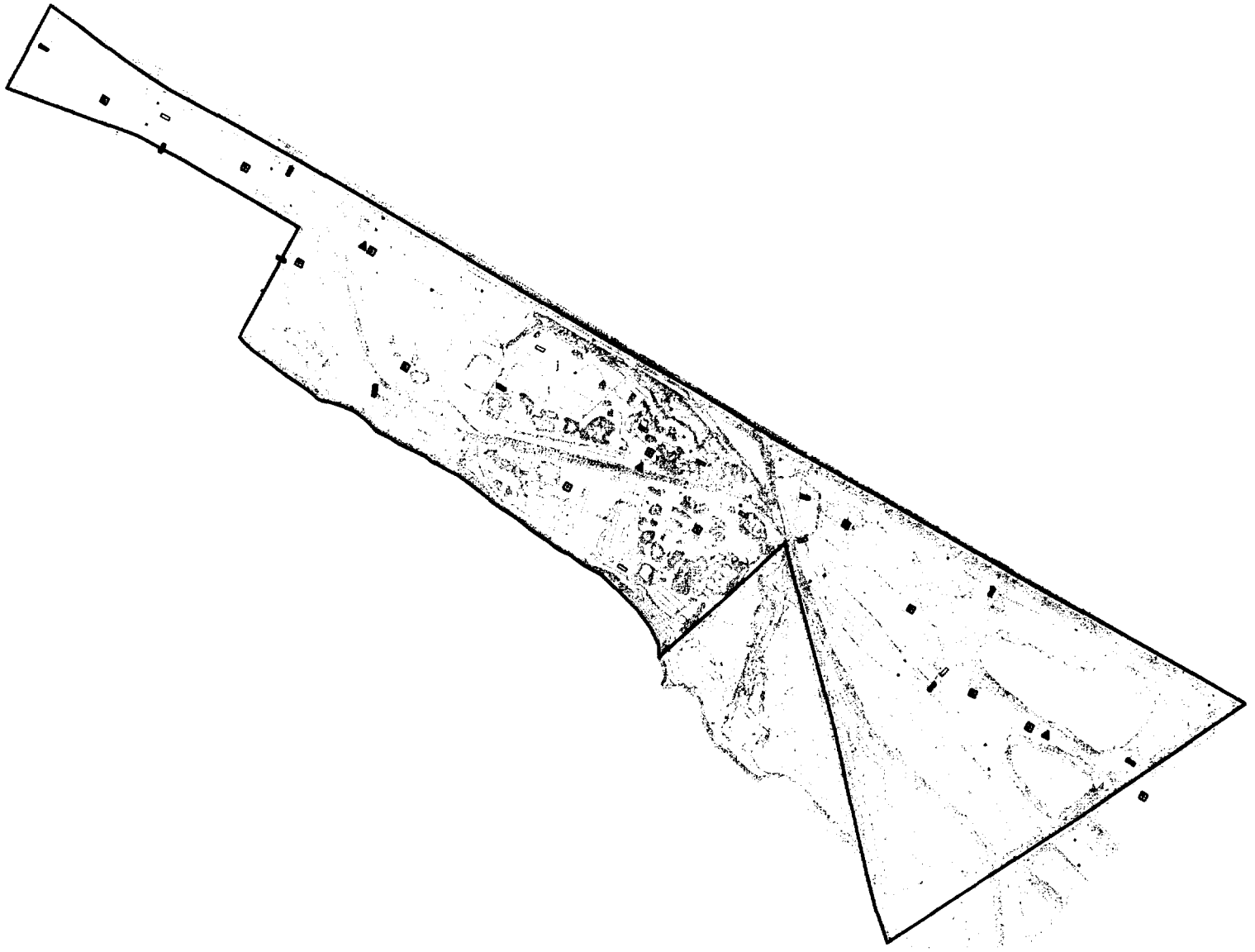
N

0 500

SCALE FEET

SAUGET AREA 2 RI/FS SUPPORT SAMPLING PLAN SAUGET, ILLINOIS		PROJECT NO. 2320010024.02
URS		
DRN. BY: djd 1/31/01 DSGN. BY: bv CHKD. BY:	Site P Soil Gas Sampling and Magnetometer Measurement Locations	FIG. NO. 6

File: E:\2320010024.02\EPA\TEST TRENCH.DWG Last edited: 04/10/02 @ 10:01 a.m. WC-ST.LOUIS, MO



LEGEND

- Leachate Monitoring Well
- Test Trench (Area Extent of Waste)
- Test Trench (Buried tank/drum Confirmation)
- Waste Characterization Boring

N

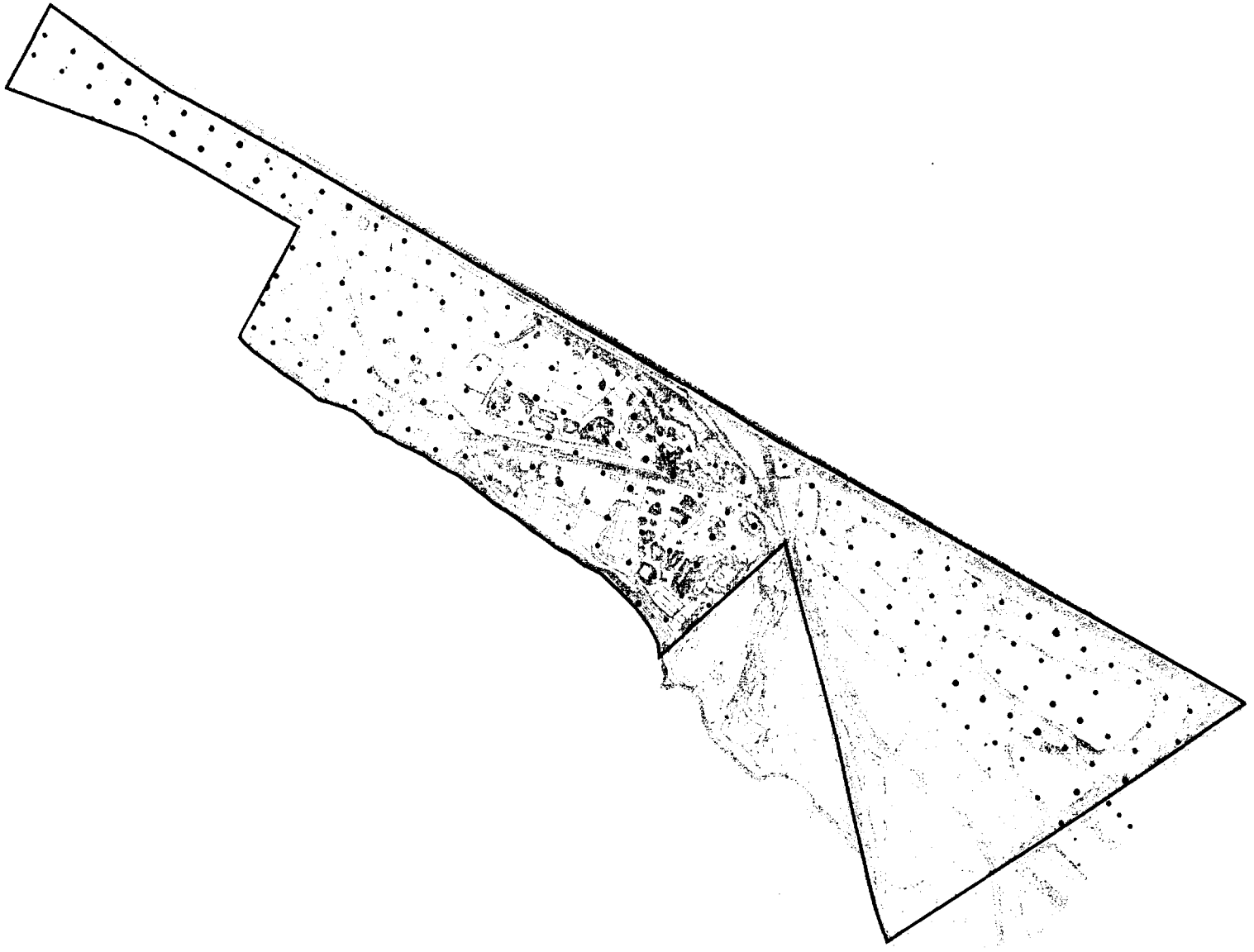
0 1000

SCALE FEET

Note: Trench size not to scale; approximate length=20 feet

SAUGET AREA 2 RI/FS SUPPORT SAMPLING PLAN SAUGET, ILLINOIS	PROJECT NO. 2320010024.02
URS	
DRN. BY:djd 1/31/01 DSGN. BY:bv CHKD. BY:	Site Q Waste, Soil, and Leachate Sampling Locations
	FIG. NO. 7

File: E:\2320010024.02\EPA\SOIL GAS.DWG Last edited: 04/10/02 @ 10:19 a.m. WC-ST.LOUIS, MO



LEGEND

- • Magnetometer Survey Locations
- O Soil Gas Survey Locations

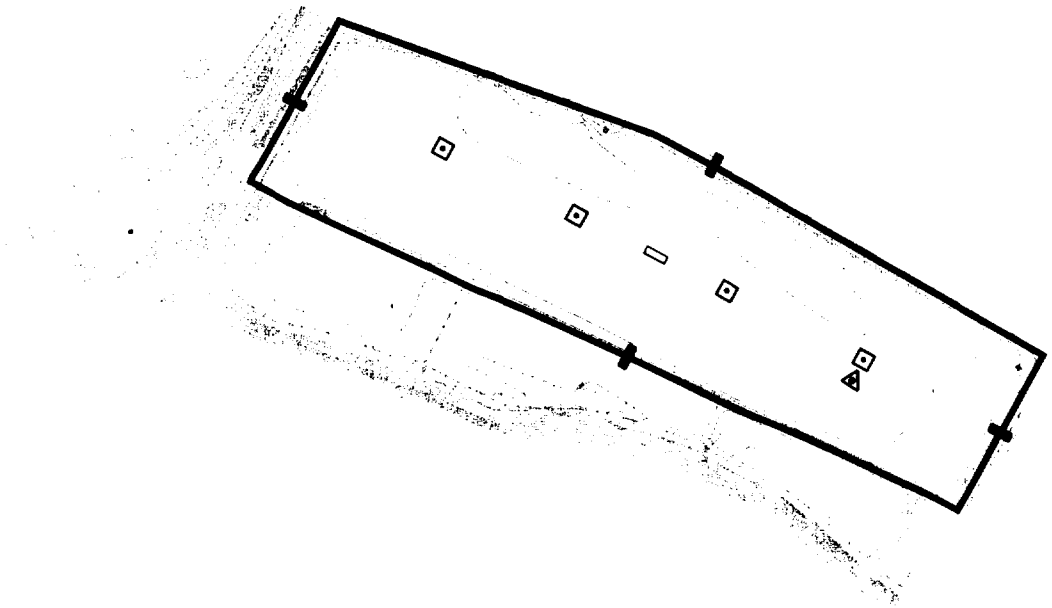
N

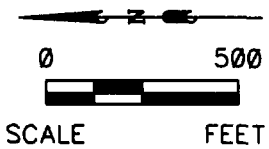
0 1000

SCALE FEET

SAUGET AREA 2 RI/FS SUPPORT SAMPLING PLAN SAUGET, ILLINOIS		PROJECT NO. 2320010024.02
URS		
DRN. BY:djd 1/31/01 DSGN. BY:bv CHKD. BY:	Site Q Soil Gas, XRF, and GC/MS Sampling and Magnetometer Measurement Locations	FIG. NO. 8

File: E:\2320010024.02\EPA\TEST TRENCH.DWG Last edited: 04/10/02 @ 10:01 a.m. WC-ST.LOUIS, MO





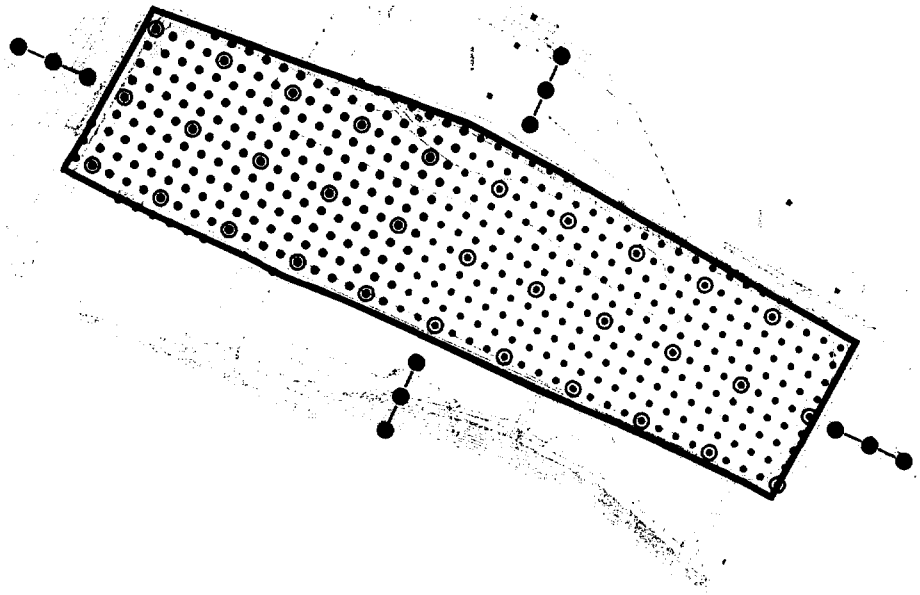
LEGEND

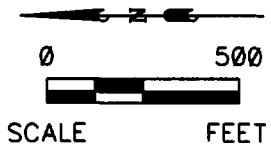
- Leachate Monitoring Well
- Test Trench (Area Extent of Waste)
- Test Trench (Buried tank/drum Confirmation)
- Waste Characterization Boring

Note: Trench size not to scale; approximate length=20 feet

SAUGET AREA 2 RI/FS SUPPORT SAMPLING PLAN SAUGET, ILLINOIS	PROJECT NO. 2320010024.02
URS	
DRN. BY: djd 1/31/01 DSGN. BY: bv CHKD. BY:	Site R Waste, Soil, and Leachate Sampling Locations
	FIG. NO. 9

File: E:\2320010024.02\EPA\SOIL GAS.DWG Last edited: 04/10/02 @ 10:19 a.m. WC-ST.LOUIS, MO

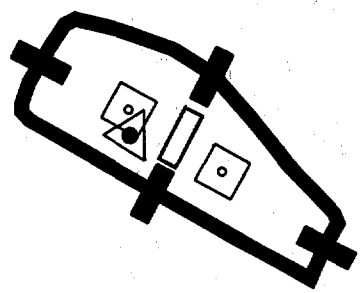


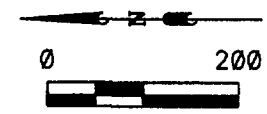


LEGEND

- • Magnetometer Survey Locations
- ○ Soil Gas Survey Locations
- ●–●–● Potential Soil Gas Survey Step Out Location

SAUGET AREA 2 RI/FS SUPPORT SAMPLING PLAN SAUGET, ILLINOIS	PROJECT NO. 2320010024.02
URS	
DRN. BY: djd 1/31/01 DSGN. BY: bv CHKD. BY:	Site R Soil Gas Sampling and Magnetometer Measurement Locations
	FIG. NO. 10





LEGEND

- Leachate Monitoring Well
- Test Trench (Area Extent of Waste)
- Test Trench (Buried tank/drum Confirmation)
- Waste Characterization Boring

Note: Trench size not to scale; approximate length=20 feet

SAUGET AREA 2 RI/FS SUPPORT SAMPLING PLAN SAUGET, ILLINOIS	PROJECT NO. 2320010024.0
URS	
DRN. BY: djd 1/31/01 DSGN. BY: bv CHKD. BY:	Site S Waste, Soil, and Leachate Sampling Locations
	FIG. NO. 11

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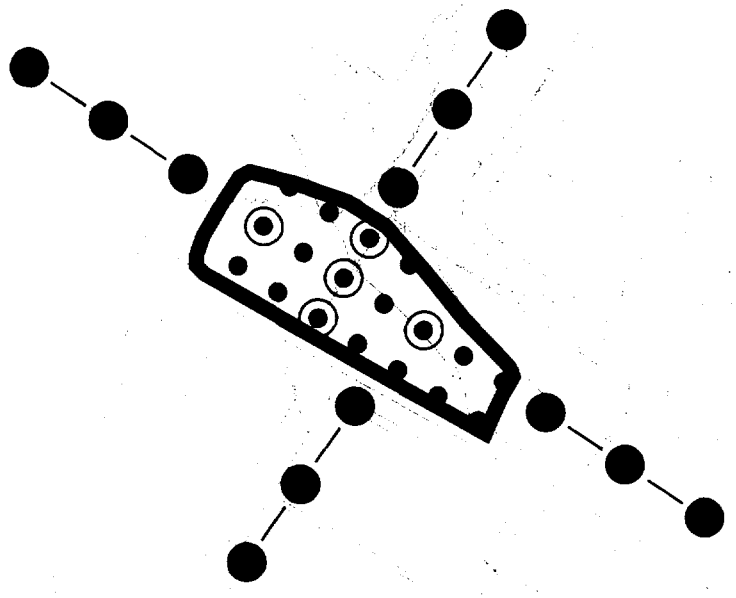

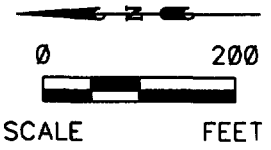

LEGEND

- Magnetometer Survey Locations
- Soil Gas Survey Locations
- Potential Soil Gas Survey Step Out Location

SAUGET AREA 2 RI/FS SUPPORT SAMPLING PLAN SAUGET, ILLINOIS	PROJECT NO. 2320010024.02
URS	
DRN. BY: djd 1/31/01 DSGN. BY: bv CHKD. BY:	Site S Soil Gas Sampling and Magnetometer Measurement Locations
	FIG. NO. 12

APPENDIX A

Static Head Space Gas Chromatography, GC/MS, and X-Ray Fluorescence Spectroscopy SOP

I. SCOPE AND APPLICATION

A. This method closely parallels EPA Method 3810 and is a static headspace technique for extracting volatile organic compounds (VOCs) from samples. It is a method that allows large numbers of samples to be screened in a relatively short period of time. Detection limits for this method may vary widely among samples because of the large variability and complicated matrices of waste samples. The method works best for compounds with boiling points of less than 125°C. The sensitivity of this method will depend on the equilibria of the various compounds between the vapor and dissolved phases.

B. Data generated by this method is ideal for characterizing the nature and extent of VOCs in soils and groundwater.

II. SUMMARY OF METHOD

A. The sample is collected in a sealed glass container and allowed to equilibrate at 90°C. A sample of the headspace gas is withdrawn with a gas-tight syringe for analysis by gas chromatography (G.C.).

III. INTERFERENCES

A. Contamination by carry-over can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carry-over, the sample syringe must be thoroughly cleaned between samples.

B. Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free.

IV. APPARATUS AND MATERIALS

A. Vials: 40 ml vials with open top screw caps and Teflon/silicone septa.

B. Gas Chromatograph: Shimadzu GC-14A or equivalent lab-grade unit.

C. Data System: Shimadzu CR4A or equivalent.

D. Detectors: Flame ionization and/or electron capture.

E. Column: Restek 502.2, 624, or equivalent middle-polarity phase.

F. Syringes: Hamilton syringes including 10-µL and 500-µL gas-tight.

G. Heating block.

V. PROCEDURE

A. Gas chromatographic conditions and calibration.

1. The following conditions are provided as a guide; optimum performance will depend on analytes of interest:

   a. Oven Temperature Program: 70°C (5 min)⇨ 10°C/min ⇨190°C (5 min)
   b. Injector Temperature = 275°C
   c. Detector Temperature = 290°C
   d. Carrier Gas = Nitrogen @ 19 ml/min (for 105 m column)
   e. Injection Amount = 350 µL
   f. Initial calibration should consist of at least three concentration levels for each target analyte.

B. Sample preparation and analysis.

1. Soil sample
   Place 20.0 g soil sample into a vial.
   Add 20.0 ml DI H2O (shown to be free of contamination) to vial and soil. Shake for 1 minute.

   OR

   Groundwater sample
   Place 20.0 ml groundwater sample into a vial

2. Place sample vial in heating block at 90°C for 1 hour.

3. Withdraw 350 µL of the headspace with a gas-tight syringe and analyze by direct injection into the G.C.

VI. QUALITY CONTROL

A. A three (or five) point calibration curve must be set-up before samples are analyzed.

B. A method blank must be analyzed at the start of each day and at a rate of one per every 10 samples, to show the system is interference-free.

C. A continuing calibration check must be analyzed at the start of each day and at a rate of one per every 10 samples to verify that the operation of the measurement system is in control and not varying.

APPENDIX A

Static Head Space Gas Chromatography, GC/MS, and X-Ray Fluorescence Spectroscopy SOP

URS

October 15, 2001

Mr. Mike Ribordy
U.S. EPA – Region 5
77 West Jackson Boulevard (SR-6J)
Chicago, IL 60604-3590

RE: Sauget Area 2 Sites Deliver by Overnight Mail

Dear Mike,

Enclosed please find several Standard Operating Procedures (SOPs) for your review in accordance with our discussions via conference call last week (10/9/01) on this topic. Severn Trent Laboratories, Inc. has been selected by the Sauget Area 2 Sites group to perform all non-biological analytical work for this effort, with the exception of the soil gas survey, which will be performed by HydroLOGIC, Inc. Therefore, all SOPs previously submitted for either Triangle Laboratories or Lancaster Laboratories should be disregarded. The SOPs that have been attached include the following:

Severn Trent Laboratories, On-Site Technologies Division (mobile laboratory for soil screening)

- SOP OSMV1007.R1, VOCs by GS/MS
- SOP OSMS1013.R1, SVOC's by GC/MS

Severn Trent Laboratories, Inc. (fixed laboratory, Sacramento CA)

- SOP SAC-ID-0011 Dioxins/Furans by EPA Method 8280A
- SOP SAC-ID-0005 Dioxins/Furans by EPA Method 8290

Hydro-LOGIC, Inc. (mobile laboratory for soil gas survey)

- Sample Collection SOP
- SOP HLI-SOP-A-015-R1 Organics by EPA Method 8021

Severn Trent (the On-Site Technologies Division) is currently modifying the SOP for metals by X-Ray refraction (XRF) to account for site-specific calibration procedures, based on the discussions held during the conference call on this topic. This will be provided under separate cover immediately upon completion, which is expected within a day or two.

The SOPs for the mobile laboratory analysis of soil samples by GS/MS are revisions to those presented previously. Provided below is a summary of the EPA comments and how those comments have been addressed in the revision.

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B Volatile Organic Compounds by GC/MS SOP 0SMV1007.RO

1) Section 6.0 - Will this SOP be using the modified preparation EPA Method 3810?

- *The laboratory will use EPA Method 5030 for sample introduction. The procedures are provided in section 6.8 of the SOP.*

2) Section 8.3 - Specify the concentration of the standards. The SOP appendices were not included.

- *Language has been added after section 8.3.3 to provide additional details regarding standard concentrations.*

3) Section 9.3.1 typo - Reference to Table 10, should be Table 2.

- *Corrected*

4) Section 9.4.2 - Table 11 and Table 12 were not included.

- *Deleted reference to tables and added text directly*

5) Section 10.6.1 typo - Reference to Table 9, should be Table 3

- *Corrected*

6) TABLE 1.0 - The Quantitation Limits (QLs) for Acetone, 2-butanone, 2-hexanone, carbon disulfide, and cis- & trans-dichloropropene should be included. See QAPP TABLE 5D. Include any missing compounds in Table 5.0 and Table 7.0.

- *Table updated to include reporting limits for these compounds. Limits in QAPP to apply to fixed, confirmatory lab*

C Semivolatile Organic Compounds (SVOCs) by GC/MS SOP OSMS1013.RO

1) Section 9.7.7 - Figure 7.0 (mass spectra review checklist) was not included.

- *Removed text - we do not use checklist specifically for mass spectra review. Review procedures related to this topic included in section 12.*

2) Section 9.9.1, typos - Reference to Figure 5.0, should be Figure 6.0. Reference to Tables 6.0 and 7.1, should be Tables 7.0 and 8.0.

- *Corrected*

3) Section 9.10.2, typo - Reference to 11.4.1, should be 9.9.3.

- *Corrected*

4) Section 9.11.2 - Figure 5.0 was not included.

- *Removed reference - maintenance information is recorded as journal entries on run log or separate "college-style" notebook.*

5) TABLE 1.0 - The Low Soil QLS (330 ug/Kg) are greater than the PQLs (170 ug/kg) specified in QAPP TABLE 5F. The compounds 2,6-Dinitrotoluene and Carbazole should be included in this table. Carbazole should be included in Tables 6.0 and 8.0.

- *No changes necessary. Limits in QAPP to apply to fixed, confirmatory lab*

The SOPs for dioxin analysis by Severn Trent and for static headspace GC/MS (soil gas survey) by HydroLOGIC, Inc. supercede those previously submitted. For the static headspace analysis, SOP HLI-SOP-A-015-R1 Organics by EPA Method 8021, the SOP will be modified to accommodate running for soil gas samples by direct-injection as specified in the sample collection SOP. A 3-point calibration curve will be employed, and results will be reported as total VOC's. Method blanks and calibration checks will be will be run throughout the project.

Please do not hesitate to call Steve Smith if you have any questions on this information.

Sincerely,

Robert B. Veenstra
Senior Program Manager

Cc: Steve Smith, SA2SG Project Manager

STL On-Site Technologies
STANDARD OPERATING PROCEDURE

TITLE : Volatile Organic Compounds (VOCs) by GC/MS

SUPERSEDES : (NONE)

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Approvals and Signatures

Division Manager: _____
Peter A. Law — Date

QA Manager: _____
Robert S. DeGaetano — Date

Technical Director: _____
John V. Hawkins — Date

1.0 SCOPE AND APPLICATION

1.1 This SOP provides detailed procedures for determining volatile organic compounds in multi-media, multi-concentration samples.

1.2 This method is applicable to nearly all types of samples, regardless of water content, including various air sampling trapping media, soil vapor, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils and sediments.

1.3 Compounds typically determined by this method and their MDL and PQL values are presented in Table 1 of this document.

1.4 It is the policy of STL and of the On-Site Technologies division to ensure that we administer contracts and orders for goods and services in a manner that is fully compliant with governmental laws and regulations, as well as the STL Policy Statement on Business Ethics and Conduct.

2.0 SUMMARY OF METHOD

2.1 Volatile compounds are introduced into the gas chromatograph by the purge and trap method. The components are separated via the chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information.

2.2 Aqueous and air samples are purged directly. Generally, soils are preserved by extracting the volatile analytes into methanol. If low detection limits are required, soil samples may be preserved with sodium bisulfate and purged directly.

2.3 In the purge and trap process, an inert gas is bubbled through the solution at ambient temperature or at 40°C (40°C required for low level soils) and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbant column where the volatile components are trapped. After purging is completed, the sorbant column (trap) is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is then heated to elute the components which are detected with a mass spectrometer.

2.4 Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing the resultant mass spectra and GC retention times.

3.0 DEFINITIONS

3.1 There are many definitions used within the laboratory that may be generic to all laboratory analyses or more specific for certain methods. For the most recent terms and definitions used within the laboratory, refer to the STL-OST Laboratory Quality Manual.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. The use of ultra high purity gases, pre-purged purified reagent water, and approved lots of purge and trap grade methanol will greatly reduce introduction of contaminants. In extreme cases the purging vessels may be pre-purged to isolate the instrument from laboratory air contaminated by solvents used in other parts of the laboratory.

4.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) into the sample through the septum seal during shipment and storage. A field blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

4.3 Matrix interferences may be caused by non-target contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source depending upon the nature and diversity of the site being sampled.

4.4 Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially or in the same purge position on an autosampler. Whenever an unusually concentrated sample is analyzed, it should be followed by one or more blanks to check for cross-contamination. The purge and trap system may require extensive bake-out and cleaning after a high-level sample.

4.5 Some samples may foam when purged due to surfactants present in the sample. When this kind of sample is encountered an antifoaming agent (e.g., J.T. Baker's Antifoam B silicone emulsion) can be used. A blank spiked with this agent must be analyzed with the sample because of the non-target interferences associated with the agent.

5.0 SAFETY

5.1 Procedures shall be carried out in a manner that protects the health and safety of all STL-OST associates.

5.2 The STL Chemical Hygiene Plan (CHP) gives details about the specific health and safety practices which are to be followed in the laboratory area. Personnel should receive training in the CHP, including the written Hazard Communication plan, prior to working in the laboratory.

5.3 The health and safety hazards of many of the chemicals used in this procedure have not been fully defined, therefore each chemical compound should be treated as a potential health hazard. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

5.3.1 Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include: Acrylonitrile, benzene, carbon tetrachloride, chloroform, 1,2-dibromo-3-chloropropane, 1,4-dichlorobenzene, and vinyl chloride.

5.3.2 Chemicals known to be flammable are: Methanol.

5.4 Exposure to chemicals must be maintained as low as reasonably achievable, therefore, unless they are known to be non-hazardous, all samples should be opened, transferred, and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5 The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.6 All work must be stopped in the event of a known or potential compromise to the health and safety of an STL-OST associate. The situation must be reported immediately to a laboratory supervisor.

6.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

6.1 Holding times for all volatile analysis are 14 days from sample collection.

6.2 Water samples are normally preserved at pH < 2 with 1:1 hydrochloric acid. If residual chlorine is present, 2 drops of 10% sodium thiosulfate are added.

6.3 Solid samples are field preserved with sodium bisulfate solution for low level analysis, or with methanol for medium level analysis. Soil samples can also be taken using the EnCore™ sampler and preserved in the lab within 48 hours of sampling. At specific client request, unpreserved soil samples may be accepted.

6.4 There are several methods of sampling soil. The recommended method, which provides the minimum of field difficulties, is to take an EnCore sample. (The 5 g or 25 g sampler can be used, depending on client preference). Following shipment back to the lab the soil is preserved in methanol. This is the medium level procedure. If very low detection limits are needed (< 50 µg/kg for most analytes) then it will be necessary to use two additional 5 g EnCore samplers or to use field preservation.

6.5 Sample collection for medium level analysis using EnCore samplers.

6.5.1 Ship one 5 g (or 25 g) EnCore sampler per field sample position. An additional bottle must be shipped for percent moisture determination.

6.5.2 When the samples are returned to the lab, extrude the (nominal) 5g (or 25 g) sample into a tared VOA vial containing 5 mL methanol (25 mL methanol for the 25 g sampler). Obtain the weight of the soil added to the vial and note on the label.

6.5.3 Add the correct amount of surrogate spiking mixture.

6.5.4 Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples.

6.5.5 Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol.

6.5.6 Shake the samples for two minutes to distribute the methanol throughout the soil.

6.5.7 Allow to settle, then remove a portion of methanol and store in a clean Teflon capped vial at 4+2°C until analysis.

6.6 Sample collection for medium level analysis using field methanol preservation

6.6.1 Prepare a 2 oz sample container by adding 25 mL purge and trap grade methanol. (If a 5 g sample is to be used, add 5 mL methanol to a 2 oz container or VOA vial VOA vial).

6.6.2 Seal the bottle and attach a label.

6.6.3 Weigh the bottle to the nearest 0.01g and note the weight on the label.

6.6.4 Ship with appropriate sampling instructions.

6.6.5 Each sample will require an additional bottle with no preservative for percent moisture determination.

6.6.6 At client request, the methanol addition and weighing may also be performed in the field.

6.6.7 When the samples are returned to the lab, obtain the weight of the soil added to the vial and note on the label.

6.6.8 Add the correct amount of surrogate spiking mixture.

6.6.9 Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples.

6.6.10 Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol.

6.6.11 Shake the samples for two minutes to distribute the methanol throughout the soil.

6.6.12 Allow to settle, then remove a portion of methanol and store in a clean Teflon capped vial at 4+2°C until analysis.

6.7 Low level procedure

6.7.1 If low detection limits are required (typically < 50 µg/kg) sodium bisulfate preservation must be used. However, it is also necessary to take a sample for the medium level (field methanol preserved or using the EnCore sampler) procedure, in case the concentration of analytes in the soil is above the calibration range of the low level procedure.

6.7.2 A purge and trap autosampler capable of sampling from a sealed vial is required for analysis of samples collected using this method. (Varian Archon or O.I. 4552).

6.7.3 The soil sample is taken using a 5g EnCore sampling device and returned to the lab. It is recommended that two EnCore samplers be used for each field sample position, to allow for any reruns than may be necessary. A separate sample for % moisture determination is also necessary.

6.7.4 Prepare VOA vials by adding a magnetic stir bar, approximately 1 g of sodium bisulfate and 5 mL of reagent water.

6.7.5 Seal and label the vial. It is strongly recommended that the vial is labeled with an indelible marker rather than a paper label, since paper labels may cause the autosampler to bind and malfunction. The label absolutely must not cover the neck of the vial or the autosampler will malfunction.

6.7.6 Weigh the vial to the nearest 0.1g and note the weight on the label.

6.7.7 Extrude the soil sample from the EnCore sampler into the prepared VOA vial. Reweigh the vial to obtain the weight of soil and note on the label.

6.7.8 Note: Soils containing carbonates may effervesce when added to the sodium bisulfate solution. If this is the case at a specific site, add 5 mL of water instead, and freeze at > -10°C until analysis.

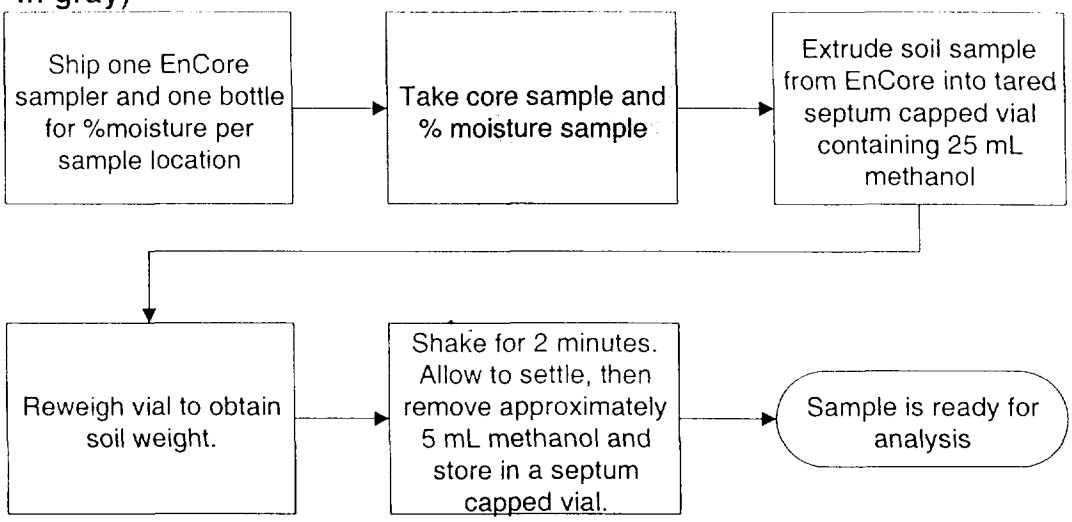
6.7.9 Alternatively the sodium bisulfate preservation may be performed in the field. This is not recommended because of the many problems that can occur in the field setting. Ship at least two vials per sample. The field samplers must determine the weight of soil sampled. Each sample will require an additional bottle with no preservative for percent moisture determination, and an additional bottle preserved with methanol for the medium level procedure. Depending on the type of soil it may also be necessary to ship vials with no or extra preservative.

6.8 Unpreserved soils

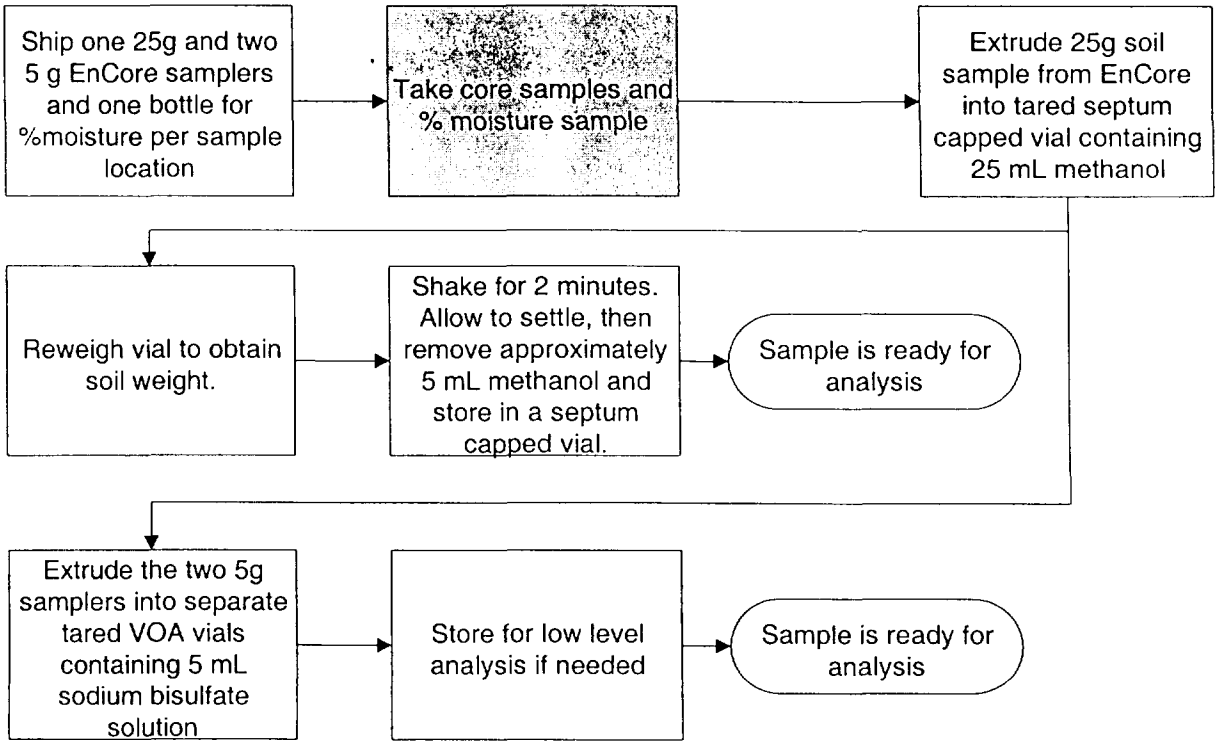
6.8.1 At specific client request unpreserved soils packed into glass jars or brass tubes may be accepted and subsampled in the lab. This is the old procedure based on method 5030A where an aliquot of soil, typically 5 grams, is added directly to the sparge vessel containing 5 – 10 mls of water. Alternatively, the soil may be extracted in 5 mL of methanol and a 100uL aliquot of the extract added to 5 – 10 mL of water in the sparge vessel for medium/high level analysis.

6.8.2 The maximum holding time is 14 days from sampling until the sample is analyzed.

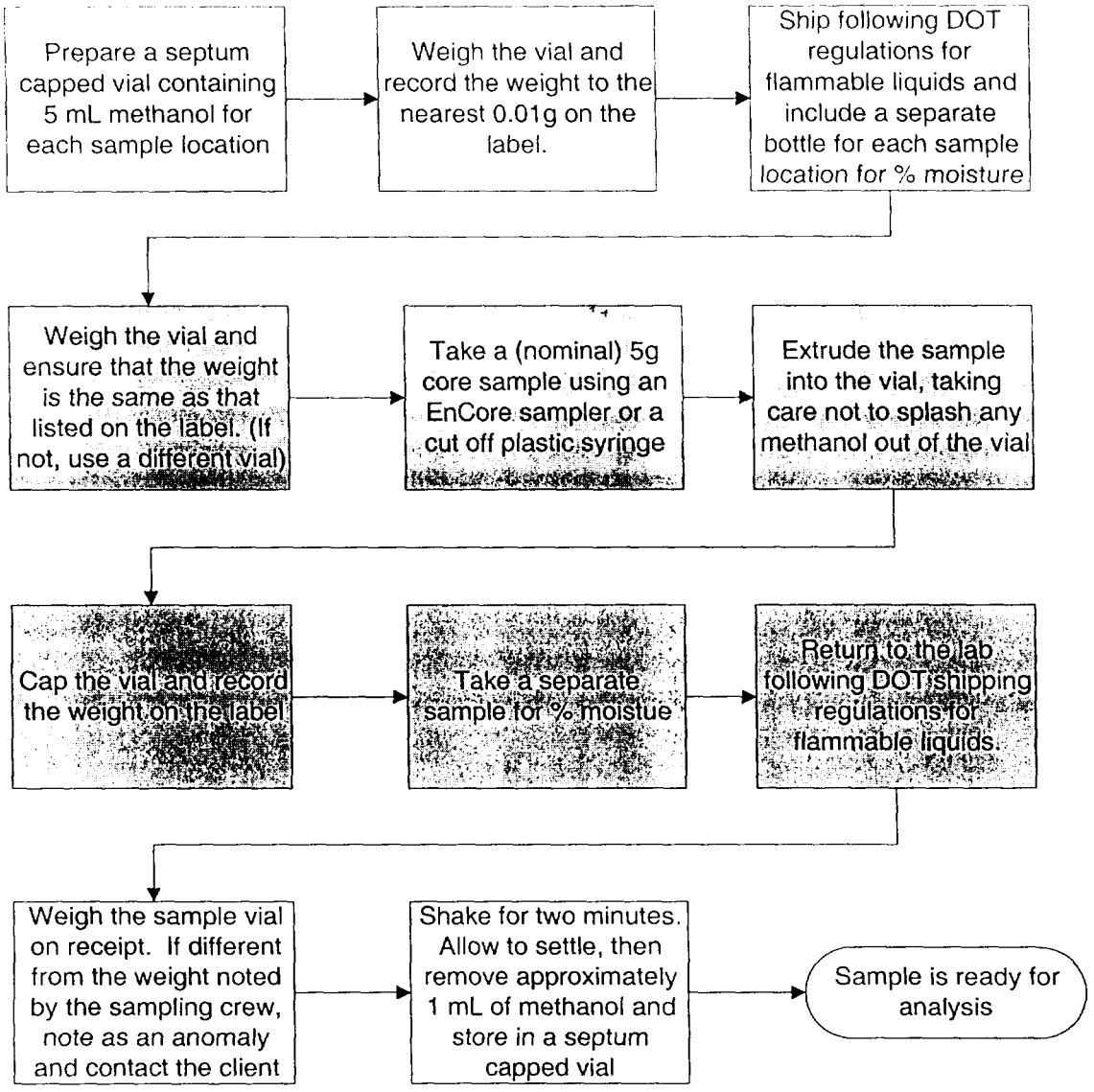
EnCore procedure when low level is not required (field steps in gray)



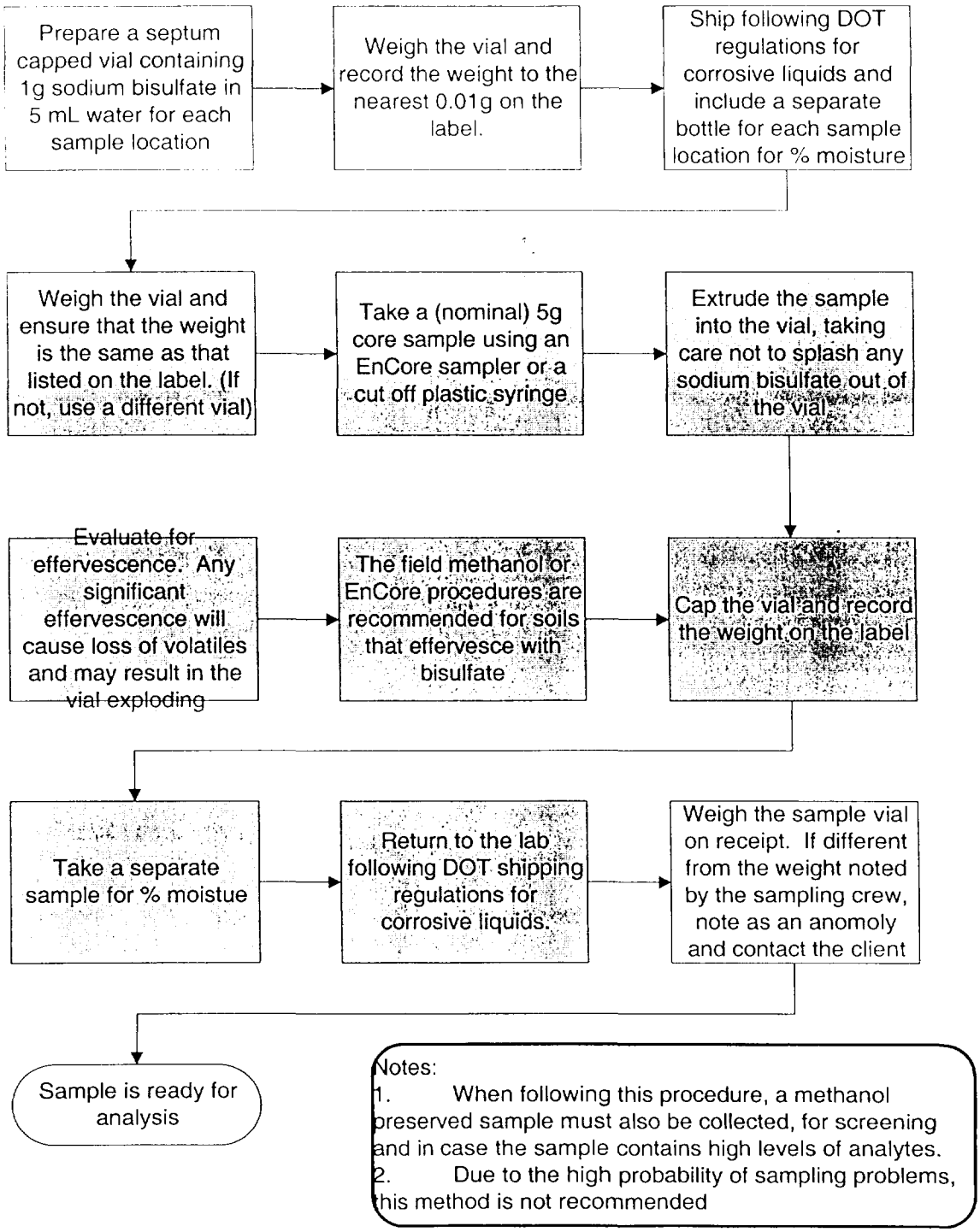
EnCore procedure when low level is required



Field methanol extraction procedure (field steps in gray)



Field bisulfate preservation procedure (field steps in gray)



7.0 EQUIPMENT AND MATERIALS

7.1 Microsyringes: 10 uL and larger, 0.006 inch ID needle.

7.2 Syringe: 5 or 25 mL glass with luerlok tip, if applicable to the purging device.

7.3 Balance: Analytical, capable of accurately weighing 0.0001 g, and a top-loading balance capable of weighing 0.1 g

7.4 Glassware:

7.4.1 Vials: 20 mL with screw caps and Teflon liners.

7.4.2 Volumetric flasks: 10 mL and 100 mL, class A with ground-glass stoppers.

7.5 Spatula: Stainless steel.

7.6 Disposable pipets: Pasteur.

7.7 pH paper: Wide range.

7.8 Gases:

7.8.1 Helium: Ultra high purity, gr. 5, 99.999%.

7.8.2 Nitrogen: Ultra high purity, from cylinders of gas generators, may be used as an alternative to helium for purge gas.

7.8.3 Compressed air: Used for instrument pneumatics.

7.9 Purge and Trap Device: The purge and trap device consists of the sample purger, the trap, and the desorber.

7.10 Gas Chromatograph/Mass Spectrometer System:

7.10.1 Gas Chromatograph: The gas chromatograph (GC) system must be capable of temperature programming. Most STL-OST laboratories utilize a Hewlett-Packard 5890 Series II gas chromatograph with 5972A Hewlett Packard Mass Selective Analyzer, or equivalent.

7.10.2 Chromatographic columns:

7.10.2.1 Column 1: DB-624 (J@W Scientific), 60 m x 0.32 mm ID

7.10.2.2 Column 2: VRX (J@W Scientific), 30m x 0.25mm ID

7.10.3 Sample concentrator:

7.10.3.1 OI Analytical model 4560 or model 4460A, or equivalent

7.10.4 Autosampler:

7.10.4.1 OI Analytical MPM-16 or DPM-16 Multiple Purging Modules (5030).

7.10.4.2 Varian Archon Purge and Trap Autosampler (5035).

7.10.5 Data acquisition system:

7.10.5.1 G1034C Operating Software and G1032C EnviroQuant Software, or equivalent, for data acquisition and reduction.

8.0 REAGENTS AND STANDARS

8.1 Methanol: Purge and Trap Grade, High Purity

8.2 Reagent Water: Purchased from Baxter or other equivalent vendor. Water is certified high purity, organic free, and is analyzed by STL-OST to show that it is free of interferences and therefore can be used for sample dilutions and as a lab blank.

8.3 Standards

8.3.1 Stock Solutions: Stock solutions may be purchased as certified solutions from commercial sources or prepared from pure standard materials as appropriate. These standards are prepared in methanol and stored in Teflon-sealed screw-cap bottles with minimal headspace at -10 to –20 °C.

8.3.2 Working standards: A working solution containing the compounds of interest prepared from the stock solution(s) in methanol. These standards are stored in the freezer or as recommended by the manufacturer.

8.3.2.1 Working standards are monitored by comparison to the initial calibration curve. If any of the calibration check compounds drift in response from the initial calibration by more than 20% then corrective action is necessary. This may include steps such as instrument maintenance, preparing a new calibration verification standard or tuning the instrument. If the corrective actions do not correct the problem then a new initial calibration must be performed.

8.3.3 Aqueous Calibration Standards are prepared in reagent water using the secondary dilution standards. These aqueous standards must be prepared daily. If stock or secondary dilution standards are purchased in sealed ampoules they may be used up to the manufacturers expiration date.

* Typically, stock calibration standard concentrations are 2000 ug/mL. However, the concentration may change based on availability of specific standards from approved vendors. From these stock solutions, an aliquot is taken and brought to volume in methanol to yield a final concentration of 25 ug/mL. Dilutions of the 25 ug/mL working standard are prepared in water at concentrations of corresponding to 5, 10, 20, 50 and 100 ug/L. Additional standard preparations may be required based on project specific data quality objectives. All preparation information is recorded in standard preparation logbooks.

8.3.4 Internal Standards: Internal standards are added to all samples, standards, and blank analyses. The internal standards utilized by this procedure are stated in method 8260B.

8.3.5 Surrogate Standards: Surrogate standards are added to all samples, standards, and blank analyses. The surrogates utilized by this procedure are stated in method 8260B.

* Typically, stock solutions of internal standard and surrogates are 2000 ug/mL. However, the concentration may change based on availability of specific standards from approved vendors. From these stock solutions, an aliquot is taken and brought to volume in methanol to yield a final concentration of 50 ug/mL. A total of 5 uL of the internal standard/surrogate working standard is added to 5 mL of sample to yield a final concentration of 50 ug/L.

8.3.6 Laboratory Control Sample (LCS) Spiking Solutions: Unless otherwise agreed upon as part of the project data quality objectives, the LCS spike mix will contain all target compounds for the particular investigation. The source of the LCS spiking solution is from a source other than the calibration standard, or from the same working standard as the calibration if an independent calibration verification sample from a different source was analyzed following initial calibration. The concentration levels and preparation procedures are identical to the calibration working standard with the final concentration at or near the midpoint of the initial calibration.

8.3.7 Matrix Spiking Solutions: Same as LCS

8.3.8 Tuning Standard: A standard made up that will deliver 50 ng on column upon injection. A working standard concentration of 25 ng/uL of 4-Bromofluorobenzene in methanol is recommended.

9.0 PROCEDURES

9.1 Prior to the analysis of samples and blanks, each GC/MS system must be tuned and calibrated. Hardware tuning is checked through the analysis of the 4-Bromofluorobenzene (BFB) to establish that a given GC/MS system meets the standard mass spectral abundance criteria. The GC/MS system must be calibrated initially at a minimum of five concentrations (analyzed under the same BFB tune), to determine the linearity of the response utilizing target calibration standards. Once the system has been calibrated, the calibration must be verified each twelve hour time period for each GC/MS system. The use of separate calibrations is required for water and low soil matrices.

9.2 Recommended Instrument Conditions

General:

Electron Energy:	70 volts (nominal)
Mass Range:	35–300 AMU
Scan Time:	to give at least 5 scans/peak, but not to exceed 2 second/scan
Injector Temperature:	200–250 °C
Source Temperature:	According to manufacturer's specifications
Transfer Line	Temperature: 250–300□C
Purge Flow:	40 mL/minute
Carrier Gas	Flow: 15 mL/minute
Make-up Gas Flow:	25–30 mL/minute

Gas chromatograph suggested temperature program:

BFB Analysis

Isothermal:	170 °C

Sample Analysis

Initial Temperature:	40 °C
Initial Hold Time:	4 minutes
Temperature Program:	8 °C/minute
Final Temperature:	184 °C
Second Temperature	Program: 40 °C/minute
Final Temperature:	240 °C
Final Hold Time:	2.6 minutes

9.3 Instrument Tuning

9.3.1 Each GC/MS system must be hardware-tuned to meet the abundance criteria listed in Table 2 for a maximum of a 50 ng injection or purging of BFB. Analysis must not begin until these criteria are met. These criteria must be met for each twelve-hour time period. The twelve-hour time period begins at the moment of injection of BFB.

9.4 Initial Calibration

9.4.1 A series of five initial calibration standards is prepared and analyzed for the target compounds and each surrogate compound. Typical calibration levels for a 5 mL purge are: 5, 20, 50, 100, and 200 ug/L. Certain analytes are prepared at higher concentrations due to poor purge performance.

9.4.2 Each calibration standard is analyzed and the response factors (RF) for each compound calculated using the area response of the characteristic ions against the concentration for each compound and internal standard.

9.4.2.1 The five system performance check compounds (SPCC) are checked for a minimum average response factor.

- System Performance Check Compounds (SPCC) average RF must be greater than or equal to 0.100 for chloromethane, 1,1-dichloroethane, and bromoform. SPCCs chlorobenzene and 1,1,2,2-tetrachloroethane average RF must be greater than or equal to 0.300.

9.4.2.2 The % RSD of the calibration check compounds (CCC) must be less than 30%.

- The CCC compounds are vinyl chloride, 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, and ethylbenzene.

9.4.2.3 If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

9.4.2.4 The average RF must be calculated for each compound. If the %RSD is < 15%, then the average response factor for calibration may be used. Alternatively, if the average %RSDs for all compounds in the calibration is < 15%, then all analytes may use average response factor for calibration. However, any detected compounds with %RSD > 15% must be noted in the report, or a linear curve generated with the correlation coefficient, r, > 0.995 (coefficient of determination, r^2 for non-linear curves > 0.990).

9.5 Continuing Calibration: The initial calibration must be verified every twelve hours. Continuing calibration begins with analysis of BFB as described above.

9.5.1 If the system tune is acceptable, the continuing calibration standard(s) are analyzed. The level 3, or mid-level calibration standard is used for the continuing calibration.

9.5.2 The RF data are compared with the average RF from the initial five-point calibration to determine the percent drift of the CCC compounds.

9.5.2.1 The % drift of the CCCs must be < 20% for the continuing calibration to be valid. The SPCCs are also monitored. The SPCCs must meet the criteria described above.

9.5.2.2 If the CCCs and or the SPCCs do not meet criteria, the system must be evaluated and corrective action must be taken. The BFB tune and continuing calibration must be acceptable before analysis.

9.6 Sample Analysis Procedures – Water Samples

9.6.1 Samples are removed from refrigerated storage and are signed out in the internal chain of custody form, or equivalent (if applicable). All samples are allowed to warm to room temperature.

9.6.2 Make sure all instrumental operating conditions are correctly set and BFB, calibration and blank criteria have been met.

9.6.3 In a gas tight 5-ml syringe, add 5-ml aliquot of sample that has been allowed to come to ambient temperature. Carefully pour the sample into the syringe barrel till just short of overflowing.

9.6.4 Replace the syringe plunger. After replacing the plunger, vent any residual air, then adjust the volume to 5.0 ml. Drop a few drops of the sample on narrow range pH paper (0-6pH range) and record the pH in the instrument logbook for all aqueous samples.

9.6.5 Next, add the internal standard and surrogate standards and load the syringe contents into the purge vessel (see SOP appendices for IS/SURR solution preparation and amount to add).

9.6.6 Water MS/MSD samples are prepared by spiking the sample aliquot with matrix spike standard in addition to internal standards and surrogate solutions (see SOP appendices for IS/SURR and MS/MSD/LCS solution preparation and amounts to add).

9.6.7 A method blank must be analyzed every 12 hours after the initial and/or continuing calibration criteria has been achieved. The method blank consists of 5 ml reagent water spiked with the internal standard and surrogate standards, and carried through the analytical procedure.

9.7 Sample Analysis Procedures – Low Level Soil Samples

9.7.1 Samples are removed from refrigerated storage and are signed out in the internal chain of custody form, or equivalent (if applicable). All samples are allowed to warm to room temperature.

9.7.2 Make sure all instrumental operating conditions are correctly set and BFB, calibration and blank criteria have been met.

9.7.3 Using a clean, dry culture tube, weigh out 5 grams of sample and add the internal standard and surrogate standards.

9.7.4 Add 5-ml reagent water to the culture tube in the same manner as a water sample. The sample is now ready for heated purge and analysis.

9.7.4.1 Low-level soil samples are analyzed using the same calibration curve as water samples (assuming the calibration curve was analyzed using a heated-purge).

9.8 Sample Analysis Procedures – Medium Level Soil Samples

9.8.1 If high levels of volatiles are expected, then the samples collected should be field preserved in methanol.

9.8.2 Alternatively, the client may request the EnCore sampler or equivalent. Therefore, the plug of soil from the EnCore sampler is placed into the pre-weighed VOA jar containing 10-mls of purge and trap grade methanol. Record the weight of the jar, soil and methanol. Record the soil weight on the jar. Swirl to mix the contents, then let the contents settle and transfer 1-2mls of the methanol extract into an extract vial. Store extract until time of analysis. It is also possible that a low-level soil is actually a high level soil. Therefore the methanol extraction is performed at the laboratory.

9.8.3 If the sample is extracted at the laboratory, the sample consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula.

9.8.4 A medium level soil extract is prepared by weighing out 5.0 grams of sample into a 20-ml extraction vial, record the weight to the nearest 0.1-gram. Determine the percent moisture (see SOP # OSS00803.MA).

9.8.5 Quickly add 5.0 ml of purge and trap grade methanol to the vial. Swirl the vial to mix contents and allow the soil to settle.

9.8.6 Using a disposable pipette, transfer about 1 ml of sample extract to a GC vial for storage. The remainder of the extract may be discarded. Transfer about 1 ml of the reagent methanol to a labeled GC vial for use as the method blank. These extracts may be stored in the dark at 4 ± 2 °C prior to analysis.

9.8.7 In a gas-tight 5-ml syringe, add 5 ml of reagent water and fortify it with the IS/Surrogate spiking solution using a 10 µl gas-tight syringe, and 100 µl of sample extract using a 250 µl gas tight syringe. Transfer the sample to the purge vessel on the autosampler.

9.8.8 If an extract is analyzed which contains target compounds at concentrations greater than the initial calibration upper limit, then the extract must be reanalyzed at an appropriate dilution. Volumes of less than 10 µl (i.e. 10 fold MLS dilution) shall be prepared diluting an aliquot of the methanol extract and then taking 100 µl for analysis. Add the volume of methanol extract from the sample and a volume of clean methanol to total 100 µl. The total methanol volume added shall be 100 µl, excluding the methanol in the standards.

9.9 Qualitative Analysis – Target Compounds

9.9.1 The relative retention time of a target compound must be within +/- 0.06 RRT units of the RRT of the calibration standard for a positive identification. For reference the standard must be analyzed within the same 12 hour time period as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT shall be assigned by using the extracted ion current profiles for ions unique to the component of interest.

9.9.2 In addition, a comparison must be made between the mass spectrum obtained in the sample analysis and the reference mass spectrum for that compound, which was obtained on that specific GC/MS system. The requirements for qualitative verification by comparison of mass spectra are as follows:

9.9.2.1 All ions present in the reference spectrum at an intensity greater than 10% must be present in the sample spectrum.

9.9.2.2 The relative intensities of the ions above 10% must agree with 20% between the reference and sample spectra.

9.9.2.3 Ions greater than 10% in the sample spectrum but not present in the reference spectrum must be considered and accounted for by the analyst.

9.9.2.4 If a compound cannot be verified by the above criteria, but in the technical judgment of the analyst, the identification is correct, then the compound shall be reported.

9.10 Tentatively Identified Compounds

9.10.1 If requested a library search shall be performed for non-target compounds in the sample for purposes of tentative identification. For this purpose, the most recent release of the NIST mass spectral library shall be used.

9.10.2 Up to 10 organic compounds of apparent concentration not listed in Table 1.0, shall be tentatively identified via a forward library search. Only compounds with responses greater than 10% of the closest IS exhibiting no interference are to be searched.

9.10.3 The ChemStation software is utilized to perform the automated library search. The program (TICS) is executed with the data file, quantitation file, and number of compounds to be searched, specified for each sample or blank. Prior to running the program, the analyst must delete from the quantitation file, using the QDEL program, the non-TCL compounds identified in the quantitation file. This will facilitate the automated search using the program. If the non-TCL positive hits are not removed prior to executing the program, they would be counted as target compounds and not be searched by the program, leading to false negatives.

9.10.4 A tentative identification will be made after a comparison between the mass spectrum obtained in the sample analysis and the library search mass spectra found for that compound. The requirements for tentative verification by comparison of mass spectra are as follows:

9.10.4.1 Ions present in the reference spectrum at an intensity greater than 10% should be present in the sample spectrum.

9.10.4.2 The relative intensities of the ions above 10% should agree with 20% between the reference and sample spectra.

9.10.5 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or coeluting compounds.

9.10.6 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible background subtraction by the data system.

9.10.7 If in the technical judgment of the mass spectral interpretation specialist, no valid tentative identification can be made, the compound shall be reported as unknown. Additional classification shall be made if possible (i.e. Unknown hydrocarbon).

10.0 QUALITY CONTROL

10.1 Initial Demonstration of Capability

10.1.1 For the standard analyte list, the initial demonstration of capability (IDOC) and method detection limit (MDL) studies must be acceptable before analysis of samples may begin. MDLs should be analyzed for low and medium soils and aqueous samples.

10.1.2 For non-standard analytes, a MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of a standard at the reporting limit and a single point calibration.

10.2 Control Limits

10.2.1 Historical control limits are determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be determined at least annually.

10.2.1.1 For new projects and/or sites without historical data, default limits of 70 – 130% for the LCS and MS recoveries will be used until enough data points are collected.

10.2.1.2 Alternatively, control limits may be determined and agreed upon with the client based on the data quality objectives of the project.

10.3 Surrogates

10.3.1 Every sample, blank, and QC sample is spiked with surrogates. Surrogate recoveries in samples, blanks, and QC samples must be assessed to ensure that recoveries are within established limits.

10.3.2 If any surrogates are outside limits, the following corrective actions must take place (except for dilutions):

10.3.2.1 Check all calculations for error.
10.3.2.2 Ensure that instrument performance is acceptable.
10.3.2.3 Recalculate the data and/or reanalyze if either of the above checks reveal a problem.
10.3.2.4 Reprepare and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem. The decision to reanalyze or flag the data should be made in consultation with the client. If the surrogates are out of control for the sample, matrix spike, and matrix spike duplicate, then matrix effect has been demonstrated for that sample and repreparation is not necessary.

10.4 Method Blanks

10.4.1 For each batch of samples, analyze a method blank. The method blank is analyzed after the calibration standards, normally before any samples.

10.4.1.1 For low-level volatiles, the method blank consists of reagent water.
10.4.1.2 For medium-level volatiles, the method blank consists of methanol.

10.4.2 Surrogates are added and the method blank is carried through the entire analytical procedure.

10.4.3 The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below), or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

10.4.3.1 If the analyte is a common laboratory contaminant (methylene chloride, acetone, 2-butanone) the data may be reported with qualifiers if the concentration of the analyte is less than five times the reporting limit. Such action must be taken in consultation with the client.

10.4.3.2 Reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples.

10.4.3.3 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 done in consultation with the client.

10.4.4 The method blank must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in the associated samples re-extraction of the blank and affected samples will normally be required. Consultation with the client should take place.

10.4.5 If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all associated samples are flagged with a "B," and appropriate comments may be made in a narrative to provide further documentation.

10.5 Laboratory Control Samples (LCS)

10.5.1 For each batch of samples, analyze a LCS. The LCS is analyzed after the calibration standard, and normally before any samples. The LCS contains a representative subset of the analytes of interest and must contain the same analytes as the matrix spike. If full analyte spike lists are used at client request, it will be necessary to allow a percentage of the components to be outside control limits as this would be expected statistically. These requirements should be negotiated with the client. If any analyte or surrogate is outside established control limits, the system is out of control and corrective action must occur. Corrective action will normally be repreparation and reanalysis of the batch.

10.5.1.1 If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report. (Examples of acceptable reasons for not reanalyzing might be that the matrix spike and matrix spike duplicate are acceptable, and sample surrogate recoveries are good, demonstrating that the problem was confined to the LCS.)

10.5.1.2 If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

10.6 Matrix Spikes

10.6.1 For each QC batch, analyze a matrix spike and matrix spike duplicate. Spiking compounds and levels are given in Table 3. Compare the percent recovery and relative percent difference (RPD) to that in the laboratory specific historically generated limits.

10.6.1.1 If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented.

10.6.1.2 If the recovery for any component is outside QC limits for both the matrix spike/ spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include reanalysis of the batch.

10.6.1.3 If a MS/MSD is not possible due to limited sample, then a LCS duplicate should be analyzed. RPD of the LCS and LCSD are compared to the matrix spike limits.

10.6.1.4 The matrix spike/duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

10.7 Nonconformance and Corrective Action

10.7.1 Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

11.0 CALCULATIONS

11.1 Response factor (RF):

Equation 1

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:

A_x = Area of the characteristic ion for the compound to be measured
A_{is} = Area of the characteristic ion for the specific internal standard
C_{is} = Concentration of the specific internal standard, ng
C_x = Concentration of the compound being measured, ng

11.2 Standard deviation (SD):

Equation 2

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(Xi - X)^2}{N-1}}$$

X_i = Value of X at i through N
N = Number of points
X = Average value of X_i

11.3 Percent relative standard deviation (%RSD):

Equation 3

$$\%RSD = \frac{\textbf{Standard Deviation}}{\overline{RF_i}} \times 100$$

$\overline{RF_i}$ = **Mean of RF values in the curve**

11.4 Percent drift between the initial calibration and the continuing calibration:

Equation 4

$$\%\ \text{Drift} = \frac{C_{expected} - C_{found}}{C_{expected}} \times 100$$

Where

$C_{expected}$ = Known concentration in standard
C_{found} = Measured concentration using selected quantitation method

11.5 Quantitative Analysis – Target Compounds

11.5.1 The relative response factor (RRF) from the initial calibration standard or the equation for linear regression is used to calculate the concentration in the sample depending on the percent RSD in the calibration curve.

11.5.2 Water Samples

Equation 5

$$\mu g/L = \frac{(Ax)(Is)(Df)}{(Ais)(RRF)(Vo)}$$

where,

Ax	=	area of the compound quantitation ion
Ais	=	area of IS quantitation ion
Is	=	IS amount in nanograms
RRF	=	Average Relative Response Factor from the Initial calibration curve
Vo	=	volume of water purged in ml's
Df =		Dilution factor.

11.5.3 Medium Level Soil Samples (dry weight basis)

Equation 6

$$\mu g/Kg = \frac{(Ax)(Is)(Vt)(1000)(Df)}{(Ais)(RRF)(Va)(Ws)(D)}$$

where,
Ax, Is, Ais and RRF are as given for water.

$$D = \frac{100 - \%\ moisture}{100}$$

RRF = Average Relative response factor from the ambient temperature purge of the initial calibration curve.

Ws = weight of sample extracted in grams
Vt = total volume of methanol extract in ml
Va = volume of the methanol extract added in μl
Df = Dilution factor. For medium level soils, the number of microliters (μl) of methanol added to the reagent water for purging (i.e. Va above) to the number of μl of the methanol extract of the sample contained in that volume Va. The dilution factor is equal to one in all cases other than those requiring dilution of the methanol extract.

11.6 MS/MSD Recovery

Equation 7

$$\textbf{Matrix Spike Recovery, } \% = \frac{SSR - SR}{SA} \times 100$$

SSR = Spike sample result

SR = Sample result

SA = Spike added

11.7 Relative % Difference calculation for the MS/MSD

Equation 8

$$\mathbf{RPD} = \frac{|\mathbf{MSR - MSDR}|}{\frac{1}{2}(\mathbf{MSR + MSDR})} \times 100$$

Where:

RPD = Relative percent difference

MSR = Matrix spike result

MSDR = Matrix spike duplicate result

11.8 Tentatively Identified Compounds

11.8.1 An estimated concentration for non-target compounds tentatively identified in the sample shall be determined by the internal standard method. For quantitation, the nearest IS free of interferences shall be used.

11.8.2 The equation used for calculating compound concentration is the same as above. Total area counts from the total ion chromatograms are used for both the IS and compound. A RRF of 1.0 is assumed and the resulting concentration shall be qualified as "J" (estimated), indicating the quantitative and qualitative uncertainties associated with this non-target compound.

11.8.3 meta and para Xylene isomers are to be reported as m&p-Xylene (total). The meta and para isomers coelute on the capillary column, therefore, special attention must be given to their quantitation. The area from the o-Xylene is quantitated separately. All three isomers must be present in the initial and continuing calibration standards.

11.8.4 If the on-column concentration of any compound in any sample exceeds the initial calibration range, a new aliquot of that sample must be diluted and purged. Guidance in performing dilutions, and exceptions to this requirement are as follows:

11.8.4.1 Use the results of the original analysis to determine the approximate dilution factor required for the largest analyte peak within the initial calibration range.

11.8.4.2 The dilution factor chosen shall keep the response of the largest analyte in the upper half of the calibration range of the instrument.

12.0 DATA REDUCTION and REVIEW

12.1 Hardcopies of all instrument calibration, calibration verification and daily analytical sequence raw data shall be assembled into "packages" for review.

12.1.1 A thorough review of all chromatograms and associated ion profiles is performed by qualified analysts to ensure retention times are correct and relative abundances match library and/or reference spectra.

12.2 Analysts are responsible for reviewing the packages to evaluate the accuracy of transcriptions, the instrument's performance, and the calculated results. Section 10 details the acceptance criteria and corrective actions for instrument/batch QA/QC.

12.3 All necessary documentation to support corrective actions performed shall be included with the packages and available for review.

12.4 Preliminary results may be reported to the client at this time.

13.0 REPORTING OF RESULTS

13.1 Prior to generating a final report of results, the data is reviewed a second time. In addition to the method review performed by the first chemist, the second review includes a verification of any project/client specific criteria and a sensibility check.

13.2 If for any reason there is a question regarding the technical soundness of the data, it is brought directly to the attention of the Technical Director and/or Quality Assurance Manager.

13.3 After completing the secondary review, the final results are reported to the client in hardcopy form and/or electronic deliverable, if requested.

14.0 POLLUTION PREVENTION

14.1 Where possible, all STL-OST methods utilize very small quantities of extraction solvents to minimize pollution.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N.W. Washington D.C. 20036, (202) 872-4477.

15.0 WASTE MANAGEMENT

15.1 Solvent waste must be disposed of in clearly labeled waste cans.

15.2 Acid waste must be collected in clearly labeled acid waste containers.

15.3 Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.4 Refer to the Laboratory Sample and Waste Disposal plan.

15.5 Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

16.0 SUPPLEMENTAL DOCUMENTS – N/A

17.0 REFERENCES

17.1 "Test Methods for Evaluating Solid Waste", USEPA-SW846, Third Edition, September 1986 with all current revisions, method 8260B.

18.0 SUBSTANTIVE REVISIONS

18.1 Original issue – 05/11/01

18.2 Revision – 10/15/01

TABLE 1.0
TARGET COMPOUNDS AND REPORTING LEVELS

Compound	Report Limit (ug/L)	Report Limit (ug/kg)
1,1,1,2-Tetrachloroethane	5	500
1,1,1-Trichloroethane	5	500
1,1,2,2-Tetrachloroethane	5	500
1,1,2-Trichloroethane	5	500
1,1,-Dichloropropene	5	500
1,1-Dichloroethane	5	500
1,1-Dichloroethene	5	500
1,2,3-Trichlorobenzene	5	500
1,2,3-Trichloropropane	5	500
1,2,4-Trichlorobenzene	5	500
1,2,4-Trimethylbenzene	5	500
1,2-Dibromo-3-chloropropane	5	500
1,2-Dibromoethane	5	500
1,2-Dichlorobenzene	5	500
1,2-Dichloroethane	5	500
1,2-Dichloropropane	5	500
1,3,5-Trimethylbenzene	5	500
1,3-Dichlorobenzene	5	500
1,3-Dichloropropane	5	500
1,4-Dichlorobenzene	5	500
2,2-Dichloropropane	5	500
2-Butanone	10	1000
2-Chloroethylvinylether	5	500
2-Chlorotoluene	5	500
4-Chlorotoluene	5	500
4-isopropyltoluene	5	500
Acetone	10	1000
Benzene	5	500
Bromobenzene	5	500
Bromochloromethane	5	500
Bromodichloromethane	5	500
Bromoform	5	500
Bromomethane	10	1000
Carbon Disulfide	5	500
Carbon tetrachloride	5	500
Chlorobenzene	5	500
Chloroethane	10	1000
Chloroform	5	500
Chloromethane	10	1000
cis-1,2-Dichloroethene	5	500
cis-1,3-Dichloropropene	5	500
Dibromochloromethane	5	500
Dibromomethane	5	500
Dichlorodifluoromethane	5	500
Ethylbenzene	5	500
Hexachlorobutadiene	5	500
Isopropylbenzene	5	500
m&p-Xylenes	5	500
Methyl t-butyl ether	5	500
Methylene chloride	5	500
Naphthalene	5	500
n-Butylbenzene	5	500
n-Propylbenzene	5	500
O-Xylene	5	500
sec-Butylbenzene	5	500
Styrene	5	500
tert-Butylbenzene	5	500
Tetrachloroethene	5	500
Toluene	5	500
trans,1,2-Dichloroethene	5	500
trans-1,3-Dichloropropene	5	500
Trichloroethene	5	500
Trichlorofluoromethane	5	500
Vinyl chloride	10	1000

TABLE 2.0
GC/MS INSTRUMENT PERFORMANCE CRITERIA
4-BROMOFLUOROBENZENE (BFB)

m/z	Ion Abundance Criteria
50	15-40% of mass 95
75	30-60% of mass 95
95	Base peak, 100% relative abundance
96	5-9% of mass 95
173	Less than 2 percent of mass 174
174	Greater than 50% of mass 95
175	5-9% of mass 174
176	95-101% of mass 174
177	5-9% of mass 176

TABLE 3.0
MATRIX SPIKE RECOVERY AND RELATIVE PERCENT DIFFERENCE LIMITS

Compound	% Recovery Water	RPD Water	% Recovery Soil	RPD Soil
1,1-Dichloroethane	61-145	14	59-172	22
Trichloroethene	71-120	14	62-137	24
Benzene	76-127	11	66-142	21
Toluene	76-125	13	59-139	21
Chlorobenzene	75-130	13	60-133	21

TABLE 4.0
SYSTEM MONITORING COMPOUND RECOVERY LIMITS

Compound	% Recovery Water	% Recovery Soil
Dibromofluoromethane	86 – 118	80 – 120
1,2-Dichloroethane-d_4	80 – 120	80 – 120
Toluene-d_8	88 - 110	81 - 117
Bromofluorobenzene	86 - 115	74 - 121

TABLE 5.0
VOLATILE INTERNAL STANDARDS WITH CORRESPONDING TARGET COMPOUNDS AND SYSTEM MONITORING COMPOUNDS ASSIGNED FOR QUANTITATION

Fluorobenzene	Chlorobenzene-d_5	1,4-Dichlorobenzene-d_4
Chloromethane	Dibromochloromethane	1,1,2,2-Tetrachloroethane
Bromomethane	Chlorobenzene	1,2,3-Trichloropropane
Vinyl Chloride	1,1,1,2-Tetrachloroethane	n-Propylbenzene
Chloroethane	Ethylbenzene	2-Chlorotoluene
Dichlorofluoromethane	m&p-Xylene	4-Chlorotoluene
Trichlorofluoromethane	o-Xylene	1,3,5-Trimethylbenzene
Methylene Chloride	Styrene	tert-Butylbenzene
1,1-Dichloroethene	Bromoform	1,2,4-Trimethylbenzene
1,2-Dichloroethene (cis, trans)	Isopropylbenzene	sec-Butylbenzene
1,1-Dichloroethane	Bromobenzene	1,3-Dichlorobenzene
Methyl tert-butyl ether	Toluene-d_8 (smc)	4-Isopropyltoluene
Bromochloromethane	4-Bromofluorobenzene (smc)	1,4-Dichlorobenzene
Chloroform		1,2-Dichlorobenzene
1,1,1-Trichloroethane		n-Butylbenzene
Carbon tetrachloride		1,2-Dibromo-3-chloropropane
Benzene		1,2,4-Trichlorobenzene
1,2-Dichloroethane		Hexachlorobutadiene
Trichloroethene		Naphthalene
1,2-Dichloropropane		1,2,3-Trichlorobenzene
Bromodichloromethane		
1,3-Dichloropropene (cis, trans)		
Toluene		
2-Chloroethylvinylether		
Tetrachloroethene		
Dibromofluoromethane (smc)		
1,2-Dichloroethane-d_4 (smc)		

TABLE 6.0
CHARACTERISTIC IONS FOR SYSTEM MONITORING COMPOUNDS AND INTERNAL STANDARDS FOR VOLATILE ORGANIC COMPOUNDS

System Monitoring Compounds	Primary Ion	Secondary Ion(s)
Dibromofluoromethane	113	111
1,2-Dichloroethane-d_4	65	67
Toluene-d_8	98	100
4-Bromofluorobenzene	95	174, 176

Internal Standards	Primary Ion	Secondary Ion(s)
Fluorobenzene	96	77
Chlorobenzene-d_5	117	119
1,4-Dichlorobenzene-d_4	152	151

TABLE 7.0 - CHARACTERISTIC IONS FOR VOLATILE TARGET COMPOUNDS

Analyte	Primary Ion*	Secondary Ion(s)
Chloromethane	50	52
Bromomethane	94	96
Vinyl Chloride	62	64
Chloroethane	64	66
Methylene Chloride	84	49, 51, 86
Acetone	43	58
Carbon Disulfide	76	78
1,1-Dichloroethene	96	61, 98
1,1-Dichloroethane	63	65, 83, 85, 98, 100
1,2-Dichloroethene	96	61, 98
Chloroform	83	85
1,2-Dichloroethane	62	64, 100, 98
2-Butanone	43**	57
1,1,1-Trichloroethane	97	99, 117, 119
Carbon Tetrachloride	117	119, 121
Bromodichloromethane	83	85
1,1,2,2-Tetrachloroethane	83	85, 131, 133, 166
1,2-Dichloropropene	75	77
Trichloroethene	130	95, 97, 132
Dibromochloromethane	129	208, 206
1,1,2-Trichloroethane	97	83, 85, 99, 132, 134
Benzene	78	----
cis-1,3-Dichloropropene	75	77
Bromoform	173	171, 175, 250, 252, 254, 256
2-Hexanone	43	58, 57, 100
4-Methyl-2-pentanone	43	58, 100
Tetrachloroethene	164	129, 131, 166
Toluene	91	92
Chlorobenzene	112	114
Ethylbenzene	106	91
Styrene	104	78, 103
Total Xylenes	106	91

STL On-Site Technologies
STANDARD OPERATING PROCEDURE

TITLE : Semivolatile Organic Compounds (SVOCs) by GC/MS

SUPERSEDES : (NONE)

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Approvals and Signatures

Division Manager: _____
Peter A. Law — Date

QA Manager: _____
Robert S. DeGaetano — Date

Technical Director: _____
John V. Hawkins — Date

1.0 SCOPE AND APPLICATION

1.1 The purpose of this SOP is to outline the techniques for determining the presence and concentration of various semivolatile organic target and non-target compounds. The standard 8270C target compounds are listed in Table 1.0. The method used in this procedure is solvent extraction and gas chromatograph/mass spectrometer analysis.

1.2 It is the policy of STL and of the On-Site Technologies Division to ensure that we administer contracts and orders for goods and services in a manner that is fully compliant with governmental laws and regulations, as well as the STL Policy Statement on Business Ethics and Conduct.

2.0 DEFINITIONS

2.1 There are many definitions used within the laboratory that may be generic to all laboratory analyses or more specific for certain methods. For the most recent terms and definitions used within the laboratory, refer to the STL-OST Laboratory Quality Manual.

3.0 SUMMARY OF METHOD

3.1 This method employs the technique of solvent extraction, coupled with a gas chromatograph/mass spectrometer analysis. An aliquot of sample extract is injected onto a gas chromatograph. The fused silica capillary column is then temperature programmed to separate the semi-volatiles organics prior to detection by the mass spectrometer.

3.2 This method is based on SW-846 Method 8270C and Method 8000B. The concentration of the solution used for the initial demonstration of precision and accuracy varies from that listed in the method. The lab uses a concentration of 20 ug/l , and the concentration listed in Table 6 of the method is 100 ug/l. Table 9 of this SOP reflects that change. When linear regression is used for quantitation the method calls for the use of percent drift to verify the validity of the continuing calibration. Because of software limitations the lab will use percent difference instead. The lab will use the criteria listed in the method.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, and laboratory solvent vapors. This can lead to discrete artifacts and/or elevated baseline in the gas chromatograph. All these materials must be demonstrated to be free from interferences by the running of laboratory reagent blanks.

5.0 SAFETY

5.1 Procedures shall be carried out in a manner that protects the health and safety of all STL-OST associates.

5.2 The STL Chemical Hygiene Plan (CHP) gives details about the specific health and safety practices which are to be followed in the laboratory area. Personnel should receive training in the CHP, including the written Hazard Communication plan, prior to working in the laboratory.

5.3 The health and safety hazards of many of the chemicals used in this procedure have not been fully defined, therefore each chemical compound should be treated as a potential health hazard. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

5.3.1 Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include: Acrylonitrile, benzene, carbon tetrachloride, chloroform, 1,2-dibromo-3-chloropropane, 1,4-dichlorobenzene, and vinyl chloride.

5.3.2 Chemicals known to be flammable are: Methanol.

5.4 Exposure to chemicals must be maintained as low as reasonably achievable, therefore, unless they are known to be non-hazardous, all samples should be opened, transferred, and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5 The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.6 All work must be stopped in the event of a known or potential compromise to the health and safety of an STL-OST associate. The situation must be reported immediately to a laboratory supervisor.

6.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

6.1 All sample extracts for semivolatile analysis must be protected from light and refrigerated at 4°C from the time of extraction until analysis.

6.2 All sample extracts for semivolatile analysis shall be analyzed within 40 days of following extraction.

7.0 APPARATUS AND MATERIALS

7.1 GC/MS/DS System

7.1.1 Gas Chromatograph - Hewlett-Packard Model 5890 GC, an analytical system which is temperature programmable with splitless injection and all required accessories including syringes, analytical columns, and gases.

7.1.2 GC Column - 30 m x 0.25 mm ID x 0.5 um film thickness RTX semivolatile column by Restek Corporation, or equivalent.

7.1.3 Mass Spectrometer - Hewlett-Packard 5970, capable of scanning from 35 to 500 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the EI ionization mode, and producing a mass spectrum which meets all the instrument performance criteria when 50 ng or less of DFTPP is injected through the GC inlet. Refer to Sections 10.3.1 for the performance criteria. Any samples analyzed when DFTPP criteria have not been met will require reanalysis.

7.1.4 GC/MS interface - any GC to MS interface that gives acceptable calibration points, at 50 ng or less per injection, for each of the parameters of interest, and achieves all acceptable performance criteria, may be used. GC to MS interfaces constructed of all-glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

7.1.5 Data system -Hewlett Packard DOS Chemstation with Enviroquant Software, capable of continuous acquisition and storage, on machine readable media, of all mass spectra obtained throughout the duration of the chromatographic program. The computer has software that allows searching any data file for ions of a specified mass and plotting such ion abundances versus time or scan number (EICP). Software also allows integrating the abundance in any EICP between specified time limits. Also, software allows for the comparison of sample non-target spectrum against reference library spectra. The most recent release of the NIST/EPA/NIH mass spectral library shall be used as the reference library. The DOS data systems will flag all manual edits with "M" qualifier.

7.1.6 Syringes -various volumes.

7.1.7 Micropipets - various volumes.

8.0 REAGENTS AND STANDARDS

8.1 Stock Standards - certified standards purchased from commercial sources in a semivolatile organics kit containing ampulated mixes of target compounds, matrix spike compounds, surrogates, and internal standards.

8.1.1 New ampules are opened every 12 months, or sooner, if the standard has degraded or evaporated.

8.2 Working Standards

8.2.1 Calibration Standard Solutions

8.2.2 Calibration standards at six concentration levels (10, 20, 50, 75, 100 and 200 total ng/ul) are prepared from the stock solutions. Each standard contains all the target compounds and surrogates.

8.2.3 Internal Standard (IS) Spiking Solution

8.2.4 A 400 ng/ul IS spiking solution containing the internal standards 1,4-dichlorobenzene-d4, naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12, is prepared from stock solutions every 12 months, or sooner, if the solution has degraded or evaporated. Add 10 ul of this solution to a 100 ul aliquot of extract for a concentration of 40 ng/ul (80 ng/2ul).

8.2.5 Surrogate (SU), Matrix Spike (MS), and Full Matrix Spike (FMS) Spiking Solution

8.2.6 The acid and base-neutral surrogate, matrix spike, and full matrix spike spiking solutions containing the appropriate compounds are prepared in methanol.

9.0 PROCEDURES

9.1 Instrumental Conditions

Gas Chromatograph	
Carrier Gas:	Helium
Flow Rate:	30 cm/sec
Initial Temp.:	40°C
Initial Hold:	4 min
Ramp Rate 1:	10°/min
Second Temp.:	270°C
Second Hold:	12 min
Ramp Rate 2:	8°/min
Final Temp.:	310°C
Final Hold:	10 min
Injector Temp.:	265°C
Transfer Temp:	310°C
Injector:	Grob-type, splitless
Sample Volume:	1 or 2 ul
EPC/EPP	99 mls/min to 40 psi for 0.3 min then 99 mls/min to 7.1 psi

9.2 Mass Spectrometer

Electron Energy:	70 eV
Mass Range:	35 - 500 amu
Scan Time:	less than 1 sec/scan

9.2.1 The mass spectrometer must be tuned to meet the instrument performance check criteria for 50 ng or less of DFTPP listed in Table 4.0.

9.3 Calibration Standards

9.3.1 Six initial calibration standards containing all the semivolatile target compounds and SU's are analyzed by injecting 1 or 2 ul of the calibration standards prepared in section 8.2.1. If a 2 ul injection is used, the resulting in final concentrations are 20, 40, 100, 150, 200, and 400 total ng/2 ul. The IS compounds are added to all calibration standards at a final concentration of 40 ng/uL (80 ng/2ul).

9.3.2 The working calibration range of this method is defined by the initial calibration curve, 10 to 200 ng (20 ng to 400 ng for a 2 uL injection). All extracts with target compounds exceeding 200 ng/uL (400 total ng for a 2 uL injection) must be diluted to within the upper half of the calibration range.

9.4 Initial Calibration

9.4.1 The calibration curve is prepared by adding the appropriate amount of each of the target analytes to an autosampler vial and adding 10 ul of Internal Standard Solution.

9.4.2 An initial calibration must be analyzed on each GC/MS system upon installation, whenever corrective action is taken which may affect the initial calibration criteria, or if the continuing calibration criteria can not be met.

9.4.3 The initial calibration can be performed only after the instrument performance is verified by meeting the DFTPP ion abundance criteria listed in Table 4.0. If less than 12 hours has expired since the tuning compound was injected, after meeting the initial calibration criteria, then samples may be analyzed. No continuing calibration is required. Quantitation is based on either the average RF in the curve or a linear regression line. If time does not remain in the 12 hour time period, a continuing calibration must be performed.

9.4.4 The response factors of the system performance check compounds (SPCC's) listed in Table 5.0 must have average relative response factors which are greater than or equal to 0.05, and the continuing calibration check compounds (CCC's) listed in Table 5.1 must have percent relative standard deviations (RSD's) less than or equal to 30.0 percent for the initial calibration to be acceptable.

9.4.5 There are three options that can be used to determine the acceptability of an initial calibration. They are listed below:

9.4.5.1 If the %RSD of any compound is ≤15%, the average RF from the curve for that compound may be used for quantitation.

9.4.5.2 If the %RSD for one or more analytes is greater than 15%, the mean %RSD for all compounds will be calculated. If the mean %RSD is ≤15%, the average RF may be used for all compounds.

9.4.5.3 If the mean %RSD is greater than 15%, quantitation from the regression line must be used for those compounds whose %RSD is greater than 15%.

9.5 Continuing Calibration

9.5.1 The continuing calibration can be performed only after the instrument performance is verified by meeting the DFTPP ion abundance criteria listed in Table 4.0. The calibration is verified by injecting a standard containing 50 ng/uL (100 total ng for a 2 uL injection) or less of DFTPP. The standard must be analyzed every 12 hours.

9.5.2 The response factors of the system performance check compounds (SPCC's) listed in Table 5.0 must have response factors greater than 0.05, and the continuing calibration check compounds (CCC's) listed in Table 5.1 must be less than or equal to 20.0 percent difference (%D) for the continuing calibration to be acceptable. The calculations are listed in Section 13.0. If the continuing calibration does not meet the above criteria the standard must be reinjected. If in the judgment of the analyst routine maintenance will solve the problem it can be performed prior to re-injection of the standard. Examples of routine maintenance include cutting the column, cleaning the injection port, and changing the injection port liner. Repeated failure may require corrective actions and reanalysis of the initial calibration.

9.6 Sample Analysis Procedures

9.6.1 Sample Extract Analysis

9.6.2 Sample extracts are removed from refrigerated storage and are signed out on the chain of custody form. All sample extracts are signed back in after they returned to storage.

9.6.3 Make sure all instrumental operating conditions are correctly set and DFTPP and calibration criteria have been met.

9.6.4 In an autosampler vial, load a measured aliquot of sample extract and spike with 10 ul of IS spiking solution.

9.6.5 The prepared extracts are then loaded into the HP autosampler carousel tray and the sequence is set up in the software to match the injection sequence on the autosampler tray.

9.6.6 If a sample is analyzed which contains target compounds at concentrations greater than the initial calibration upper limit, then the sample must be reanalyzed at an appropriate dilution.

9.7 Qualitative Analysis - Target Compounds

9.7.1 The relative retention time of a target compound must be within +/- 0.06 RRT units of the RRT of the calibration standard for a positive identification. For reference the standard must be analyzed within the same 12 hour time period as the sample. If the sample is analyzed within the same 12 hour time period as the initial calibration, then use the 50 ng standard as the reference. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT shall be assigned by using the extracted ion current profiles for ions unique to the component of interest.

9.7.2 In addition, a comparison must be made between the mass spectrum obtained in the sample analysis and the reference mass spectrum for that compound, which was obtained on that specific GC/MS system. The requirements for qualitative verification by comparison of mass spectra are as follows:

9.7.3 All ions present in the reference spectrum at an intensity greater than 10% must be present in the sample spectrum.

9.7.4 The relative intensities of the ions above 10% must agree with 20% between the reference and sample spectra.

9.7.5 Ions greater than 10% in the sample spectrum but not present in the reference spectrum must be considered and accounted for by the analyst.

9.7.6 If a compound cannot be verified by the above criteria, but in the technical judgment of the analyst, the identification is correct, then the compound shall be reported.

9.8 Qualitative Analysis - Tentatively Identified Compounds

9.8.1 A library search may be performed upon request for non-target compounds in the sample for purposes of tentative identification. For this purpose, the most recent release of the NIST mass spectral library shall be used. Pesticide and PCB confirmation is also done by tentatively identified compound search if needed to prove the presence of these compounds from a GC analysis.

9.8.2 Up to 20 non-target organic compounds of highest apparent concentration shall be tentatively identified via a forward library search. Only compounds with responses greater than 10% of the closest IS exhibiting no interference are to be searched. Peaks suspected of being aldol-condensation reaction products shall be searched and reported as such, but not counted as part of the 20 most intense non-target compounds. Solvent peaks which may be detected due to an early scan start time shall not be counted as a library search compound. All solvent peaks shall be labeled on the chromatogram as such.

9.8.3 A tentative identification will be made after a comparison between the mass spectrum obtained in the sample analysis and the library search mass spectra found for that compound. The requirements for tentative verification by comparison of mass spectra are as follows:

9.8.4 Ions present in the reference spectrum at an intensity greater than 10% should be present in the sample spectrum.

9.8.5 The relative intensities of the ions above 10% should agree with 20% between the reference and sample spectra.

9.8.6 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or coeluting compounds.

9.8.7 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible background subtraction by the data system.

9.8.8 If in the technical judgment of the mass spectral interpretation specialist, no valid tentative identification can be made, the compound shall be reported as unknown. Additional classification shall be made if possible (i.e. unknown hydrocarbon).

9.9 Quantitative Analysis - Target Compounds

9.9.1 Target compounds are quantitated by the internal standard technique. The associated internal standard used is listed in Table 6.0. The EICP area of the quantitation ions of compounds listed in Tables 7.0 and 8.0 are used.

9.9.2 All manual integrations must be initialed and dated by the analyst. The average relative response factor (RRF) from the curve or the linear regression line from the curve is used to calculate the concentration in the sample. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion. If secondary ion quantitation is performed, document the reasons in the SDG narrative. The area of a secondary ion can not be substituted for the primary ion unless a RRF is calculated using the secondary ion.

9.9.3 When compound concentrations are below the EQL, but the compound meets identification criteria, report the concentration with a "J" qualifier.

Water Samples

$$\text{Concentration ug/L} = \frac{(Ax)(Is)(Vt)(Df)}{(Ais)(RRF)(Vo)(Vi)}$$

where,
Ax = area of the compound quantitation ion
Ais = area of IS quantitation ion
Is = IS amount in nanograms
RRF = average RRF from curve
Vo = volume of water extracted in ml's
Vi = volume of extract injected in ul's
Vt = volume of the concentrated extract in ul's

Df = Dilution factor. The dilution factor for the analysis of water samples for semi-volatiles organics by this method is defined as follows:

$$\frac{\text{uL most conc. extract used to make dilution} + \text{uL clean solvent}}{\text{uL most conc. extract used to make dilution}}$$

If no dilution is performed, Df = 1.0.

Soil Samples

$$\text{Concentration ug/Kg (dry weight basis)} = \frac{(Ax)(Is)(Vt)(Df)(2.0)}{(Ais)(RRF)(Vi)(Ws)(D)}$$

where,
Ax, Is, Ais, Vt, Vi, Df, and RRF are as given for water.

$$D = \frac{100 - \%\ \text{moisture}}{100}$$

Ws = weight of sample extracted in grams

9.10 Tentatively Identified Compounds

9.10.1 An estimated concentration for non-target compounds tentatively identified in the sample shall be determined by the internal standard method. For quantitation, the nearest IS free of interferences shall be used.

9.10.2 The equation for calculating concentrations are the same as in 9.9.3. Total area counts from the total ion chromatograms are used for both the IS and compound. A RRF of 1.0 is assumed and the resulting concentration shall be qualified as "J" (estimated) and "N"(presumptive evidence of presence), indicating the quantitative and qualitative uncertainties associated with this non-target compound. [14]

9.10.3 If the on-column concentration of any compound in any sample extract exceeds the initial calibration range, that sample extract must be diluted, the IS concentration readjusted, and the sample extract reanalyzed. Guidance in performing dilutions, and exceptions to this requirement are as follows:

9.10.3.1 Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

9.10.3.2 The dilution factor chosen shall keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument.

9.10.3.3 Data for more than two analyses shall not be submitted.

9.10.3.4 Do not dilute MS/MSD samples to get either spiked or non-spiked analytes within the calibration range. If the sample from which the MS/MSD aliquots were taken contains high levels of the spiked analytes, run the MS/MSD at the same dilution as the unspiked sample.

9.11 Instrument Maintenance

9.11.1 All instrumentation is covered by a service contract with an external instrumentation service vendor, or by STL personnel trained in preventative maintenance.

9.11.2 Preventative Maintenance

9.11.2.1 Preventative maintenance is performed at routine intervals. All instrument preventative maintenance is performed according the manufacturers recommended procedures, by trained personnel. All preventative maintenance shall be thoroughly documented in the maintenance log, as to a description of the maintenance performed, the date performed, and the personnel performing the maintenance.

9.11.3 Corrective Maintenance Determinants and Procedures

9.11.3.1 Corrective maintenance is deemed necessary when the analytical system, after reanalysis, can not meet tune, calibration, or other protocol specific QC criteria. Corrective maintenance may include, but is not limited to, decontamination of the system, source cleaning, replacing the electron multiplier, column replacement or filament replacement. All corrective maintenance is performed according the manufacturers recommended procedures, by trained personnel. All corrective maintenance shall be thoroughly documented in the maintenance log, as to a description of the maintenance performed, the date performed, and the personnel performing the maintenance.

9.11.4 Maintenance Authorization

9.11.4.1 All preventative and corrective maintenance is authorized by the laboratory manager, or designee. When maintenance is deemed necessary, a service call is placed for all equipment covered under a service contract, by the department's manager, or designee.

10.0 QUALITY CONTROL

10.1 Initial Demonstration of Precision and Accuracy

10.1.1 Prepare four aliquots of the QC Check Standard in reagent water. Process the samples through the whole analytical procedure.

10.1.2 Calculate the average recovery (x) in ug/L and the standard deviation (s) in ug/L for each parameter from the four results. Compare the s and x with the criteria listed in Table 4.0. If all parameters meet the acceptance criteria, analysis of samples can begin. If any parameter fails, the cause for the failure must be determined and the test must be repeated for that parameter.

10.1.3 The demonstration of precision and accuracy will be verified on an annual basis.

10.2 Method detection limits (MDL's) for this method will be verified on an annual basis as detailed in the latest version of the SOP on MDL's.

10.3 Daily Performance Tests

10.3.1 Prior to initiating any data collection activities it is necessary to establish that a given GC/MS system meets the instrument performance criteria. This is accomplished through the analysis of 50 ng or less of decafluorotriphenylphosphine (DFTPP).

10.3.1.1 DFTPP must be analyzed at the start of every 12 hour sequence and can be a component in the 50 ng/uL (100 total ng/2ul) calibration standard.

10.3.1.2 The key ions produced during the analysis of DFTPP and their respective ion abundance criteria are given in Table 3.0. This criteria must be met before any calibration standards, blanks, or samples may be analyzed.

10.3.1.3 If the criteria is not met, the DFTPP must be reanalyzed. Repeated failure shall require the instrument to be manually tuned. After manual tuning, the DFTPP must be reinjected and the abundance criteria must be met before proceeding.

10.3.2 The 12 hour time period for a GC/MS system instrument performance check and standards calibration (initial or continuing calibration criteria) begins at the moment of injection of the DFTPP analysis that is submitted as documentation of a compliant instrument performance check. The time period ends after 12 hours have elapsed according to the system clock.

10.3.3 After the instrument performance criteria is met, the initial calibration curve must be verified through the analysis of a continuing calibration at 50 ng/uL (100 total ng/2uL). The continuing calibration criteria must be met before any method blank or sample analyses may proceed.

10.3.4 A method blank spiked with surrogates is extracted with every batch of samples and must be analyzed with the sample extracts after calibration criteria has been met. An acceptable method blank must meet the following:

10.3.4.1 Less than or equal to 5X the PQL for the phthalate esters.

10.3.4.2 Less than or equal to the PQL for each of the other target compounds.

10.3.4.3 If the method blank exceeds the above criteria, the analytical system is considered to be out of control. The source of the contamination must be investigated and appropriate corrective measures must be taken and documented before further sample analysis proceeds. All samples analyzed with a method blank that is out of control must be re-extracted and reanalyzed. The problems and solutions must be addressed in the SDG narrative.

10.4 Matrix Spike, Matrix Spike Duplicates and Matrix Spike Blanks

10.4.1 An MS and MSD must be extracted and analyzed for each group of samples of a similar matrix within each case, 20 samples, group of samples of a similar concentration level (soils only), or each 7 calendar day period; whichever is more frequent.

10.4.2 The limits for matrix spike compound recovery and relative percent difference (RPD) are given in Table 2.0. These limits are only advisory; therefore, no further action is required if the criteria limits are not achieved. However, frequent failures shall be investigated for possible laboratory generated error. The NYSDEC MSB has mandatory acceptance criteria. The MSB is evaluated against the Water % Recoveries listed in Table 2.0. If the MSB does not meet criteria, a QCDF is written, and the project manager is informed.

10.5 QC Check Samples

10.5.1 A QC Check Sample must be extracted with each extraction preparation batch for each group of samples of a similar matrix and concentration level (soils only). The QC Check Sample is analyzed with the associated batch of samples.

10.5.2 The limits for the spike compound recoveries are given in Table 9.0. These limits are only advisory; therefore no further action is required if the criteria limits are not achieved. However, frequent failures shall be investigated for possible laboratory generated error.

10.6 Surrogates

10.6.1 The surrogates Phenol-d5, 2,4,6-Tribromophenol, 2-Fluorophenol, Nitrobenzene-d5, Terphenyl-d14, and 2-Fluorobiphenyl are added to each sample, blank, standard, and MS/MSD, prior to extraction. The acid surrogates are added at 100 ug and the base-neutrals at 50 ug for waters and soils.

10.6.2 Surrogate recoveries must be within the QC limits given in Table 3.0 which were determined from multi-laboratory data. If the recovery for any two acid surrogates (phenol-d5, 2-fluorophenol, and 2,4,6-tribromophenol) or BN surrogates (nitrobenzene-d5, 2-fluorobiphenyl, and terphenyl-d14) are not within the QC limits defined in Table 2.0, or if any one of these surrogate recoveries are below 10%, the following actions are required:

10.6.2.1 Check all calculations for accuracy, spiking solutions, and internal standards

10.6.2.2 Reanalyze the sample if none of the above steps reveal a problem

10.6.2.3 Do not reanalyze dilutions if surrogate recoveries are outside limits

10.6.2.4 There is no need to reanalyze the MS or MSD, even if the surrogate recoveries are outside the limits

10.6.2.5 If the sample associated with the MS/MSD does not meet specifications, it should be reanalyzed only if the MS/MSD surrogate recoveries are within the limits

10.6.3 If the reanalysis of the sample solves the problem, then only submit the second analysis. If the reanalysis does not solve the problem, then re-extract and reanalyze the sample.

10.6.4 If the re-extraction and reanalysis of the sample solves the problem, contact the client by a QCDF and find out what they want submitted. If the re-extraction and reanalysis does not solve the problem, then both sets of results may be reported. Re-extraction and reanalysis shall be decided on a project specific basis and may not be requested by the client.

10.6.5 If the recovery of the surrogates in a method blank are not acceptable, as defined in section 10.6.2 above, then the method blank and all associated samples must be re-extracted and reanalyzed.

10.7 Internal Standards

10.7.1 Internal standards are added to each sample, blank, standard, and MS/MSD, at 40 ng prior to injection. Injection of 2 uL of the extract will result in a 80 ng on-column injection of all the internal standards.

10.7.2 The retention times (RT) and extracted ion current profile (EICP) of each IS must be evaluated for all standards immediately after the data acquisition. The IS EICP areas must be monitored and evaluated for each sample, blank, MS, MSD. If the IS EICP changes by more than a factor of 2 (-50% to +100%) from the latest (12 hour) calibration standard, the mass spectrometric system must be inspected for malfunctions, and corrections made as required. If the RT for any IS changes by more than 30 seconds from the latest (12 hour) calibration standard, the chromatographic system must be inspected for malfunctions, and corrections made as required. When corrections are made, reanalysis of the samples analyzed while the system was malfunctioning is necessary. If no system malfunctioning occurred, then document the matrix interference problem via a corrective action report. If the sample associated with the MS/MSD does not meet specifications, it should be reanalyzed only if the MS/MSD IS criteria is within limits.

10.7.3 If the reanalysis of the sample solves the problem, then only submit the second analysis.

10.8 Manual Integrations and Editing Flags

10.8.1 Manual integrations are required when the automated software does correctly integrate extracted ion current profiles (EICP). Manual integrations are flagged by the data system with the "M" qualifier beside any manually integrated area on the hardcopy quant report. The analyst shall initial and date the hardcopy report for the manual integrations performed.

10.9 Analytical Documentation Procedures

10.9.1 Instrument Batches

10.9.2 An instrument batch is created for each analytical sequence to organize all the associated data. Batch designations are of the format:

MMDDYY-X

where X = instrument identifier
MMDDYY = Month, Day, Year
(i.e. 021500-1)

10.9.3 Instrument batches are number sequentially so each analytical sequence is identified by a unique batch identifier. The batch consists of a file folder with all the associated QC information for the analytical sequence. The raw data is then bound together with the file folder to complete the batch.

10.10 Filing System

10.10.1 All active batches are filed chronologically according to instrument. The batches are transferred to file boxes for long term storage once all the associated data within a batch has been completed.

10.11 Data Archiving

10.11.1 The data files and method files on the server are archived on a daily basis.

10.12 Instrument Run Logs

10.12.1 It is STL's policy that all measurement data be recorded in logbooks or on preprinted log sheets in permanent ink. Transcriptions shall be avoided whenever possible. The record shall reflect the measurement performed and all appropriate details for conclusions related to the measurement. The record shall be signed and dated by the individual performing the measurement on the day the measurement is performed. Corrections shall be made by drawing a single line through the error, and initialing and dating the correction. A secondary authorization of the logbook is required and shall be performed by the department's manager or designee.

10.12.2 Each instrument has its own set of bound run logs which are sequentially number and paginated. Run logs are filed in the laboratory once they have been filled, for future reference. Each analytical sequence shall be started on a new page of the log and continued on the next page, if necessary. The header information designating the standard codes used shall be completed for each sequence. All standards used are recorded in this field for future traceability. The data file, job number, sample number, quantitation factor, dilution factor, analyst's signature, and date are recorded.

10.13 Initial data review sheet

10.13.1 The initial data review sheet (IDRS) is a computerized review sheet which is used to check the key quality control criteria for compliance. The IDRS is used to check that all samples have been analyzed with the required calibration time frame, if the IS's meet RT and EICP area criteria, and if the ID file being utilized was correctly updated. The IDRS is also used as the initial data review tool. Each sample is listed on the sheet and it is either accepted or rejected in the right hand column, by the analyst performing the data review. If reruns are required for dilutions, then the analyst shall indicate the proper dilution required for reanalysis. The data reviewer initial's and dates the IDRS. The batch is then secondary reviewed by another analyst to ensure that no oversight errors were made during the initial review. The batch is then filed for use during deliverables preparation. Refer to Figure 3.0 for an example of the IDRS.

10.14 Quality Control Deviation Form

10.14.1 A quality control deviation form (QCDF) is issued when a problem is encountered during analysis, data reduction or deliverables preparation, data validation, or when any deviations from this SOP occur. The QCDF is prepared by the analyst first identifying the problem and is then submitted to the department's manager for approval. The manager shall submit the QCDF to the QA/QC department where the QCDF will be recorded, copied and distributed to the necessary departments. A copy shall be placed in the job file by the project manager.

10.14.2 The lower portion of the QCDF is for the corrective actions taken, and is completed by the department or project manager when a corrective action decision has been made. The QCDF is then redistributed to all the departments and individuals involved.

10.15 Chain of Custody Record

10.15.1 When samples are removed from storage for preparation or analysis they must be signed out utilizing the chain of custody record (COC). The samples shall then be signed back in on the COC upon their return to storage or designated "used" if the sample volume is consumed during the preparation or analysis.

10.16 Sample Extraction Log

10.16.1 Samples are tracked on the Semivolatile Sample Extraction Log. As the extraction is being completed, the extraction information is entered into the extraction log. Samples requiring reanalysis are also tracked with the reason for the reanalysis (i.e. dilution, I.S. confirmation, etc). If a re-extraction is required, a QCDF is issued.

11.0 CALCULATIONS

11.1 Relative Response Factor (RRF)

$$RRF = \frac{(Ax)(Cis)}{(Ais)(Cx)}$$

where,

Ax = area of the compound quantitation ion

Ais = area of IS quantitation ion

Cis = IS concentration

Cx = compound concentration

An average RRF is calculated for each compound and surrogate from the initial calibration.

11.2 Percent Relative Standard Deviation (%RSD)

$$\%RSD = \frac{\text{Standard Deviation}}{\text{mean}} \times 100$$

11.3 Percent Difference (%D)

$$\%D = \frac{(\text{Average RRFi}) - (\text{RRFc})}{(\text{Average RRFi})} \times 100$$

where,

Average RRFi = Average RRF from the initial calibration

RRFc = RRF from the continuing calibration standard

11.4 Percent Moisture

$$\% \text{ moisture} = \frac{\text{g of Wet Sample - g of Dry Sample}}{\text{g of Wet Sample}} \times 100$$

11.5 Target Compound Concentrations

The calculations used to determine the target compound concentrations are described in the sections above.

11.6 Surrogate Percent Recovery

$$\% \text{ Recovery} = \frac{\text{Concentration Found}}{\text{Concentration Spiked}} \times 100$$

11.7 Matrix Spike Recovery/Matrix Spike Duplicate Recovery/Full Matrix Spike Recovery

$$\% \text{ Recovery} = \frac{\text{SSR - SR}}{\text{SA}} \times 100$$

where,

SSR = spiked sample result

SR = sample result

SA = spike added

11.8 Relative Percent Difference

$$\text{RPD} = \frac{\text{Absolute (MSR - MSDR)}}{(1/2)(\text{MSR+MSDR})} \times 100$$

where,

MSR = matrix spike recovery

MSDR = matrix spike duplicate recovery

The absolute value of the recovery difference is used in the above equation.

11.9 Adjusted Estimated Quantitation Limit for Samples

$$\text{Adjusted EQL} = \frac{(\text{EQL}) \times \text{Df}}{\text{D}}$$

where,

$$\text{D} = \frac{100 - \%\ \text{Moisture}}{100}$$

Df = Dilution Factor

12.0 DATA REDUCTION and REVIEW

12.1 Hardcopies of all instrument calibration, calibration verification and daily analytical sequence raw data shall be assembled into "packages" for review.

12.2 Analysts are responsible for reviewing the packages to evaluate the accuracy of transcriptions, the instrument's performance, and the calculated results. Section 10 details the acceptance criteria and corrective actions for instrument and batch QA/QC.

12.3 All necessary documentation to support corrective actions performed shall be included with the packages and available for review.

12.4 Preliminary results may be reported to the client at this time.

13.0 REPORTING OF RESULTS

13.1 Prior to generating a final report of results, the data is reviewed a second time. In addition to the method review performed by the first chemist, the second review includes a verification of any project/client specific criteria and a sensibility check.

13.2 If for any reason there is a question regarding the technical soundness of the data, it is brought directly to the attention of the Technical Director and/or Quality Assurance Manager.

13.3 After completing the secondary review, the final results are reported to the client in hardcopy form and/or electronic deliverable, if requested.

14.0 POLLUTION PREVENTION

14.1 Where possible, all STL-OST methods utilize very small quantities of extraction solvents to minimize pollution.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N.W. Washington D.C. 20036, (202) 872-4477.

15.0 WASTE MANAGEMENT

15.1 Solvent waste must be disposed of in clearly labeled waste cans.

15.2 Acid waste must be collected in clearly labeled acid waste containers.

15.3 Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.4 Refer to the Laboratory Sample and Waste Disposal plan.

15.5 Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

16.0 SUPPLEMENTAL DOCUMENTS – N/A

17.0 REFERENCES

17.1 "Test Methods for Evaluating Solid Waste", USEPA-SW846, Third Edition, September 1986 with all current revisions, method 8270C.

18.0 SUBSTANTIVE REVISIONS

18.1 Original issue – 05/15/01

18.2 Revision – 10/15/01

TABLE 1.0
TARGET COMPOUNDS AND REPORTING LEVELS

Semi-Volatile Organics	Quantitation Limits*	
	Water µg/L	Low Soil (µg/Kg)
Phenol	10	330
bis(2-Chloroethyl)ether	10	330
2-Chlorophenol	10	330
1,2-Dichlorobenzene	10	330
1,4-Dichlorobenzene	10	330
Benzyl Alcohol	10	330
1,3-Dichlorobenzene	10	330
2-Methylphenol	10	330
2,2'oxybis(1-Chloropropane)#	10	330
4-Methylphenol	10	330
N-Nitroso-di-n-propylamine	10	330
Hexachloroethane	10	330
Nitrobenzene	10	330
Isophorone	10	330
2-Nitrophenol	10	330
2,4-Dimethylphenol	10	330
Benzoic Acid	50	1600
bis(2-Chloroethoxy)methane	10	330
2,4-Dichlorophenol	10	330
1,2,4-Trichlorobenzene	10	330
Naphthalene	10	330
4-Chloroaniline	10	330
Hexachlorobutadiene	10	330
4-Chloro-3-methylphenol	10	330
2-Methylnaphthalene	10	330
Hexachlorocyclopentadiene	10	330
2,4,6-Trichlorophenol	25	800
2,4,5-Trichlorophenol	25	800
2-Chloronaphthalene	10	330
2-Nitroaniline	25	800
Dimethylphthalate	10	330
Acenaphthylene	10	330
3-Nitroaniline	25	800
Acenaphthene	10	330
2,4-Dinitrophenol	25	800
4-Nitrophenol	25	800
Dibenzofuran	10	330
2,4-Dinitrotoluene	10	330
Diethylphthalate	10	330
4-Chlorophenyl-phenylether	10	330
Fluorene	10	330
4-Nitroaniline	20	ND
4,6-Dinitro-2-methylphenol	25	800
N-nitrosodiphenylamine	10	330
4-Bromophenyl-phenylether	10	330
Hexachlorobenzene	10	330
Pentachlorphenol	25	800
Phenanthrene	10	330
Anthracene	10	330
Di-n-butylphthalate	10	ND
Fluoranthene	10	330
Pyrene	10	330
Butylbenzylphthalate	10	330
3,3'dichlorobenzidine	10	330
Benzo(a)anthracene	10	330
Chrysene	10	330
bis(2-Ethylhexyl)phthalate	10	330
Di-n-octylphthalate	10	330
Benzo(b)fluoranthene	10	330
Benzo(k)fluoranthene	10	330
Benzo(a)pyrene	10	330
Indeno(1,2,3-cd)pyrene	10	330
Dibenzo(a,h)anthracene	10	330
Benzo(g,h,i)perylene	10	330

*Quantitation limits listed for soil/sediment are based on wet weight. The quantitation limits calculated by the laboratory for soil/sediment, calculated on dry weight basis as required by the contract, will be higher.
#Perviously known as bis(2-chloroisopropyl)ether.

TABLE 2.0
MATRIX SPIKE RECOVERY AND RELATIVE PERCENT DIFFERENCE LIMITS

Compound	% Recovery Water	RPD Water	% Recovery Soil	RPD Soil
Phenol	12-110	42	26-90	35
2-Chlorophenol	27-123	40	25-102	50
1,4-Dichlorobenzene	36-97	28	28-104	27
N-Nitroso-di-n-propylamine	41-116	38	41-126	38
1,2,4-Trichlorobenzene	39-98	28	38-107	23
4-Chloro-3-methylphenol	23-97	42	26-103	33
Acenaphthene	46-118	31	31-137	19
4-Nitrophenol	10-80	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 3.0
SURROGATE RECOVERY LIMITS

Compound	% Recovery Water	% Recovery Soil
Nitrobenzene-d_5	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
Terphenyl-d_{14}	33-141	18-137
Phenol-d_5	10-110	24-113
2-Fluorophenol	21-110	25-121
2,4,6-Tribromophenol	10-123	19-122

TABLE 4.0
DFTPP KEY IONS AND ION ABUNDANCE CRITERIA FOR QUADRAPOLE MASS SPECTROMETERS

Mass	Ion Abundance Criteria
51	30.0 - 60 percent of mass 198
68	Less than 2.0 percent of mass 69
69	Present
70	Less than 2.0 percent of mass 69
127	40-60 percent of mass 198
197	Less than 1.0 percent of mass 198
198	Base peak, 100 percent relative abundance (see note)
199	5.0-9.0 percent of mass 198
275	10.0 - 30.0 percent of mass 198
365	Greater than 1 percent of mass 198
441	Present, but less than mass 443
442	40.0 - 100.0 percent of mass 198
443	17 - 23 percent of mass 442

TABLE 5.0

Calibration Check Compounds (ccc)	
Phenol	Acenaphthene
1,4-Dichlorobenzene	N-Nitrosodiphenylamine
2-Nitrophenol	Pentachlorophenol
2,4-Dichlorophenol	Fluoranthene
Hexachlorobutadiene	Di-n-octylphthalate
4-Chloro-3-methylphenol	Benzo(a)pyrene
2,4,6-Trichlorophenol	

TABLE 5.1

System Performance Check Compounds (spcc)	
N-Nitroso-di-n-propylamine	Hexachlorocyclopentadiene
2,4-Dinitrophenol	4-Nitrophenol

TABLE 6.0 - SEMI-VOLATILE INTERNAL STANDARDS WITH CORRESPONDING TARGET COMPOUNDS AND SURROGATES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}	Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
Phenol	Nitrobenzene	Hexachlorocyclopentadiene	4,6-Dinitro-2-methylphenol	Pyrene	Di-n-octylphthalate
bis(2-Chloroethyl)ether	Isophorone	2,4,6-Trichlorophenol	N-Nitrosodiphenylamine	Butylbenzylphthalate	Benzo(b)fluoranthene
2-Chlorophenol	2-Nitrophenol	2-Chloronaphthalene*	4-Bromophenyl phenyl ether	3,3'-Dichlorobenzidine	Benzo(k)fluoranthene
1,3-Dichlorobenzene	2,4-Dimethyl-phenol	2-Nitroaniline	Hexachlorobenzene	Benzo(a)anthracene	Benzo(a)pyrene
1,4-Dichlorobenzene	bis(2-Chloroethoxy)methane	Dimethylphthalate	Pentachlorophenol	bis(2-Ethylhexyl)phthalate	Indeno(1,2,3-cd)pyrene
1,2-Dichlorobenzene	2,4-Dichlorophenol	Acenaphthylene	Phenanthrene	Chrysene	Dibenz(a,h)anthracene
2-Methylphenol	1,2,4-Trichlorobenzene	3-Nitroaniline	Anthracene	Terphenyl-d_{14} (surr)	Benzo(g,h,i)perylene
2,2'-oxybis-(1-Chloropropane)	Naphthalene	Acenaphthene	Di-n-butylphthalate		
4-Methylphenol	4-Chloroaniline	2,4-Dinitrophenol	Fluoranthene		
N-Nitroso-di-n-propylamine	Hexachlorobutadiene	4-Nitrophenol			
Hexachloroethane	4-Chloro-3-methylphenol	Dibenzofuran			
2-Fluorophenol (surr)	2-Methylnaphthalene	2,4-Dinitrotoluene			
Phenol-d_5 (surr)	Nitrobenzene-d_5 (surr)	2,6-Dinitrotoluene			
		Diethylphthalate			
		4-Chlorophenyl phenyl ether			
		Fluorene			
		4-Nitroaniline			
		2-Fluorobiphenyl (surr)			
		2,4,6-Tribromophenol (surr)			

TABLE 7.0
CHARACTERISTIC IONS FOR INTERNAL STANDARDS
FOR SEMI-VOLATILE COMPOUNDS

Internal Standards	Primary Ion	Secondary Ions
1,4-Dichlorobenzene-d_4	152	115
Naphthalene-d_8	136	68
Acenaphthene-d_{10}	164	162, 160
Phenanthrene-d_{10}	188	94, 80
Chrysene-d_{12}	240	120, 236
Perylene-d_{12}	264	260, 265

TABLE 8.0

CHARACTERISTIC IONS FOR TARGET COMPOUNDS, INTERNAL STANDARDS AND SYSTEM MONITORING COMPOUNDS

Parameter	Primary Ion	Secondary Ion(s)
Phenol	94	65, 66
bis(2-Chloroethyl)ether	93	63, 95
2-Chlorophenol	128	64, 130
1,3-Dichlorobenzene	146	148, 113
1,4-Dichlorobenzene	146	148, 113
1,3-Dichlorobenzene	146	148, 113
2-Methylphenol	108	107
2,2'oxybis(1-Chloropropane)#	45	77, 79
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
1,2,4-Trichlorobenzene	180	182, 145
Naphthalene	128	129, 127
4-Chloroaniline	127	129
Hexachlorobutadiene	225	223, 227
4-Chloro-3-methylphenol	107	144, 142
2-Methylnaphthalene	142	141
Hexachlorocyclopentadiene	237	235, 272
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 200
2-Chloronaphthalene	162	164, 127
2-Nitroaniline	65	92, 138
Dimethylphthalate	163	194, 164
Acenaphthylene	152	151, 153
3-Nitroaniline	138	108, 92
Acenaphthene	153	152, 154
2,4-Dinitrophenol	184	63, 154
4-Nitrophenol	109	139, 65
Dibenzofuran	168	139
2,4-Dinitrotoluene	165	63, 182
2,6-Dinitrotoluene	165	89, 121
Diethylphthalate	149	177, 150
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
Pentachlorphenol	266	264, 268
Phenanthrene	178	179, 176
Anthracene	178	179, 176
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-octylphthalate	149	---
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, 227
Dibenzo(a,h)anthracene	278	139, 279
Benzo(g,h,i)perylene	276	138, 277

SURROGATES

Phenol-d5	99	42, 71
2-Fluorophenol	112	64
2,4,6-Tribromophenol	330	332, 141
Nitrobenzene-d5	82	128, 54
2-Fluorobiphenyl	172	171
Terphenyl	244	122, 212

TABLE 9.0 - QC ACCEPTANCE CRITERIA - METHOD 8270

Semi-Volatile Organics	Limit for s (ug/l)	Range for X (ug/l)	Range for %Recovery
Phenol	22.6	8.8 - 50	5 - 112
Bis(2-Chloroethyl)ether	55.0	21.4 - 63	12 - 158
2-Chlorophenol	8.7	18.1 - 60.2	23 - 134
1,2-Dichlorobenzene	30.9	4.3 - 56	32 - 129
1,4-Dichlorobenzene	32.1	18.6 - 52.8	20 - 124
Benzidine	N.L.	N.L.	N.L.
1,3-Dichlorobenzene	41.7	8.35 - 76.9	D - 172
2,6-Dinitrotoluene	29.6	34 - 68.3	50 - 158
2,2'-oxybis(1-Chloropropane)#	46.3	31.4 - 69.3	36 - 166
N-nitrosodimethylamine	N.L.	N.L.	N.L.
N-Nitroso-di-n-propylamine	100	6.8 - 98.9	D - 230
Hexachloroethane	24.5	27.6 - 50	40 - 113
Nitrobenzene	39.3	27.1 - 78.8	35 - 180
Isophorone	63.3	23.3 - 90.1	21 - 196
2-Nitrophenol	35.2	22.5 - 83.3	29 - 182
2,4-Dimethylphenol	26.4	20.9 - 54.5	32 - 119
bis(2-Chloroethoxy)methane	34.5	24.6 - 82.3	33 - 184
2,4-Dichlorophenol	26.4	26.5 - 60.8	39 - 135
1,2,4-Trichlorobenzene	28.1	28.6 - 64.6	44 - 142
Naphthalene	30.1	17.8 - 59.8	21 - 133
Hexachlorobutadiene	26.3	18.9 - 51.1	24 - 116
4-Chloro-3-methylphenol	37.2	20.4 - 63.9	22 - 147
Hexachlorocyclopentadiene	N.L.	N.L.	N.L.
2,4,6-Trichlorophenol	31.7	26.2 - 64.6	37 - 144
2-Chloronaphthalene	13.0	32.2 - 56.7	60 - 118
Dimethylphthalate	23.2	D - 50	D - 112
Acenaphthylene	40.2	26.7 - 63	33 - 145
Acenaphthene	27.6	30.0 - 66.1	47 - 145
2,4-Dinitrophenol	49.8	D - 86.4	D - 191
4-Nitrophenol	47.2	6.5 - 53.2	D - 132

TABLE 9.0 (continued)

Semi-Volatile Organics	Limits for s (ug/l)	Range for X, (ug/l)	Limits for % Recovery
2,4-Dinitrotoluene	21.8	23.7 - 63.4	39 - 139
Diethylphthalate	26.5	D - 50	D - 114
4-Chlorophenyl-phenylether	33.4	19.2 - 72.3	25 - 158
Fluorene	20.7	35.8 - 53.2	59 - 121
4,6-Dinitro-2-methylphenol	93.2	26.5 - 50	D - 181
N-nitrosodiphenylamine	N.L.	N.L.	N.L.
4-Bromophenyl-phenylether	23.0	32.4 - 57.2	53 - 127
Hexachlorobenzene	24.9	3.9 - 70.7	D - 152
Pentachlorophenol	48.9	19.0 - 75.9	14 - 176
Phenanthrene	20.6	32.6 - 54.3	54 - 120
Anthracene	32.0	21.7 - 59.0	27 - 133
Di-n-butylphthalate	16.7	4.2 - 55.5	1 - 118
Fluoranthene	32.8	21.4 - 60.6	26 - 137
Pyrene	25.2	34.8 - 50	52 - 115
Butylbenzylphthalate	23.4	D - 69.9	D - 152
3,3'-Dichlorobenzidine	71.4	4.1 - 106.2	D - 262
Benzo(a)anthracene	27.6	20.9 - 66.5	33 - 143
Chrysene	48.3	22.0 - 69.9	17 - 168
bis(2-Ethylhexyl)phthalate	41.1	14.4 - 68.4	8 - 158
Di-n-octylphthalate	31.4	9.3 - 65.9	4 - 146
Benzo(b)fluoranthene	38.8	21.0 - 70.2	24 - 159
Benzo(k)fluoranthene	32.3	12.6 - 72.8	11 - 162
Benzo(a)pyrene	39.0	15.8 - 74.0	17 - 163
Indeno(1,2,3-cd)pyrene	44.6	D - 75.4	D - 171
Dibenzo(a,h)anthracene	70.0	D - 99.8	D - 227
Benzo(g,h,i)perylene	58.9	D - 97.5	D - 219

#Previously known as bis(2-chloroisopropyl)ether.
All test concentrations at 20 ug/l.

OPERATION-SPECIFIC STANDARD OPERATING PROCEDURE

TITLE: EXTRACTION AND ANALYSIS OF POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS BY DFLM01.0, INCLUDING REVISION DFLM01.1 (SEPTEMBER 1991) AND METHOD 8280A

(SUPERSEDES: SAC-ID-0011, REVISION 1.0, APRIL 10, 1998)

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1. SCOPE AND APPLICATION

1.1. This method is appropriate for the extraction and determination of tetra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in water, soil, sediment, fly ash, and chemical waste samples. The analytical method requires the use of high resolution gas chromatography and low resolution mass spectrometry on sample extracts that have been subjected to specified cleanup procedures.

1.2. The calibration range is dependent on the compound and sample size. The sample size varies by sample matrix. The upper limit of the calibration range for each is compound is 20 times the Contract Required Quantitation Limits (CRQLs). See TABLE 1 for list of compounds and their CRQLs.

1.3. Analysis time takes approximately 50 minutes for a GC/MS run.

1.4. Typically, the lowest calibration standard is used as the reporting and flagging limit. See Table 4, standard CC1.

2. SUMMARY OF METHOD

2.1. Soil/Sediment Extraction

2.1.1. A 10 g aliquot of soil/sediment sample is spiked with the internal standard solution and extracted with toluene in a combination of Soxhlet extractor and a Dean Stark water separator (SDS).

NOTE: The sample should not contain an obvious liquid phase. If an obvious liquid phase exists, notify the project manager for consultation with the client.

2.2. Water Extraction

2.2.1. Approximately 1 L of the water sample is spiked with the internal standard solution and filtered to separate the aqueous and particulate fractions. The filtered aqueous fraction is extracted with methylene chloride using a separatory funnel. The particulate fraction is extracted with toluene in a SDS extractor. The extracts of the two fractions are combined for cleanup.

NOTE: Multiple phases should not be present. Consult with the client if multiple phases are present.

2.3. Fly Ash Extraction

2.3.1. A 10 g aliquot of the fly ash is washed with dilute hydrochloric acid, spiked with the internal standard solution, and extracted with toluene in a SDS extractor.

NOTE: The sample must not contain an obvious liquid phase.

2.4. Chemical Waste Sample Extraction

2.4.1. A 1g aliquot of stillbottom/oil/oily sludge/oil-laced soil sample is spiked with the internal standard solution and extracted with toluene in a combination of Soxhlet extractor and a Dean Stark water separator (SDS).

2.5. Cleanup

2.5.1. Immediately prior to cleanup, all extracts are spiked with a ^{37}Cl-2,3,7,8-TCDD standard. The addition of this standard differentiates between losses of analytes or internal standards during extraction and losses that occur during the various cleanup procedures.

2.5.2. The extracts are subjected to an acid-base washing treatment and dried. Following a solvent exchange step, the extract is cleaned up by a column chromatographic procedures including: silica gel, acid alumina, and charcoal/silica columns, to eliminate sample components that may interfere with the detection and measurement of PCDDs/PCDFs. The extracts are concentrated and the solvent is exchanged to tetradecane. The recovery standards are added to a 50 µL aliquot of the extract and the aliquot is reduced to a final volume of 50 µL. The remaining 50 µL of extract is retained in the event that dilutions or reanalysis are required.

2.6. Analysis

2.6.1. A 2 µL aliquot is injected into a fused silica capillary column in a gas chromatograph (GC) interfaced to a mass spectrometer (MS). Identification of PCDDs/PCDFs is based on the detection of the ions specified in TABLE 2, and the measurement of the appropriate relative abundance (ratio) of two characteristic ions in the molecular ion cluster. The PCDDs/PCDFs are quantitated by comparing the MS response of the detected analyte relative to the MS response of the appropriate internal standard.

3. DEFINITIONS

3.1. Definitions of terms used in this SOP may be found in the glossary of the Quality Assurance Management Plan (QAMP).

3.2. Soil/Sediment Sample: A portion of wet soil/sediment, which does not contain an obvious liquid phase.

3.3. Water Sample: A single phase system that is primarily clean water but may contain very small amounts of floating, suspended, and settled particulate matter.

3.4. Fly Ash Sample: A solid matrix from an incineration or other combustion process, which may contain water and other solids.

3.5. Chemical Waste Sample: Sample matrices of oils, stillbottoms, oily sludge, oil-laced soil, and surface water heavily contaminated with the matrices mentioned previously.

3.6. Concentration Calibration Solution (TABLE 4): Solutions (tetradecane) containing known amounts of selected analytes, five internal standards and two recovery standards that are analyzed prior to sample analysis. The solutions are used to determine the ratio of the instrument response of the analytes to that of the appropriate internal standard and the internal standards to that of the recovery standards.

3.7. Internal Standards (TABLE 8): 13C-2,3,7,8-TCDD, 13C-1,2,3,6,7,8-HxCDD, 13C-OCDD, 13C-2,3,7,8-TCDF and 13C-1,2,3,4,6,7,8-HpCDF (in isooctane) are added to every sample and are present at the same concentration in every blank, quality control sample, and concentration calibration solution. The internal standards are added to the sample before extraction and are used to measure the concentrations of the analytes.

3.8. Recovery Standard (TABLE 8): 13C-1,2,3,4-TCDD and 13C-1,2,3,7,8,9-HxCDD are added to every blank, quality control sample, and sample extract aliquot prior to analysis. Recovery standards are used to measure the recovery of the internal standards.

3.9. Cleanup Standard: ^{37}Cl-2,3,7,8-TCDD is added to every sample, blank, quality control sample, and concentration calibration solution. It is added to the samples after extraction but prior to cleanup.

3.10. Response Factor: The ratio of the response of the mass spectrometer to a known amount of an analyte relative to that of a known amount of an internal standard as measured in the initial and continuing calibrations. It is used to determine instrument performance and it is used in the quantitation calculations.

3.11. Signal-to-noise: The ratio of analyte signal to random background signal.

3.12. Estimated Detection Limit (EDL): The concentration of an analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. The EDL is calculated for each 2,3,7,8-substituted isomer for which the response of the quantitation and confirmation ions is less than 2.5 times the background level. (See TABLE 1 Reporting Limits).

3.13. Estimated Maximum Possible Concentration (EMPC): The concentration of a given analyte that would produce a signal with a given peak area. The EMPC is calculated for 2,3,7,8-substituted isomers for which the quantitation and/or the confirmation ion(s) has signal-to-noise in excess of 2.5 but does not meet all of the other identification criteria.

3.14. Window Defining Mix: A solution which contains the first and last eluting isomer of each homologue and is used to verify that the switching times between the descriptors have been properly set.

3.15. Homologous Series: A series of organic compounds in which each successive member has one more atom or group of atoms than the preceding member.

3.16. 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 structural isomers.

3.17. Congener: Any member of a particular homologous series, for example, pentachlorinated dibenzofurans.

3.18. Continuing Calibration Solution (Daily Standard): A solution analyzed every 12 hours to demonstrate continued acceptable GC/MS performance. The solution is the same as the Mid-Level concentration calibration solution, CC3.

3.19. Column Performance Check Mixture (CPSM): A mixture of TCDD isomers (including the 2,3,7,8-TCDD isomer) known to elute near each other on an SP-2331 column. This mixture demonstrates acceptable resolution between the 2,3,7,8-TCDD isomer and all other TCDD isomers on the SP-2331 column (valley $\leq$ 25%).

4. INTERFERENCES

4.1. Sample components may interfere with the detection and measurement of PCDDs/PCDFs. To eliminate interference, the extract is cleaned up by column chromatographic procedures.

4.2. Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines, which may cause misinterpretation of chromatographic data. All of these materials shall be demonstrated to be free from interferents under the conditions of analysis by running laboratory method blanks.

> ***NOTE:*** *Analysts must avoid using PVC gloves due to the possibility of contamination.*

4.3. The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all glass systems may be necessary.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL Sacramento associates.

5.2. Eye protection that satisfied ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and chemically resistant gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.2.1. N-Dex nitrile gloves provide varying degrees of intermittent splash protection against those chemicals listed. Refer to permeation/degradation charts for the actual data.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

5.3.1. Chemicals that have been classified as **carcinogens**, or **potential carcinogens**, under OSHA include: Methylene chloride, dibenzo-p-dioxins and dibenzofurans. 2,3,7,8-TCDD is a carcinogen, teratogen, and mutagen. Other PCDDs and PCDFs with chlorine atoms in positions 2,3,7,8 are known to have toxicities comparable to that of 2,3,7,8-TCDD. Exposure to these chemicals must be kept to a minimum by whatever means available. Methylene chloride.

5.3.2. The following materials are known to be **flammable**: Methanol, Toluene, Hexane, Acetone, isooctane, cyclohexane.

> **NOTE:** Methanol will readily absorb via the skin.

5.3.3. The following chemical is known to be a **neurotoxic agent:** Hexane.

5.3.4. The following chemicals are known to be **corrosive:** Sodium hydroxide, sulfuric acid, hydrochloric acid.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL Sacramento associate. The situation must be reported **immediately** to a laboratory supervisor.

5.7. Material Safety Data Sheets (MSDSs) are available to lab personnel, and must be read before samples or chemicals are handled.

6. EQUIPMENT AND SUPPLIES

6.1. Filters

6.1.1. Glass wool, rinsed with methylene chloride

6.1.2. Glass fiber filter: 15 cm, used with Buchner funnel

6.1.3. Whatman #1 (or equivalent)

6.1.4. White quartz sand. 60/70 mesh, used in the SDS extractor.

6.2. Glass wool, silanized.

6.3. Miscellaneous clean glassware

6.4. Dean Stark Water Separator Apparatus.

6.5. Concentrator tubes, 15 mL conical centrifuge tubes.

6.6. Separatory funnels, 500 mL and 2 L separatory funnels with a Teflon stopcock.

6.7. Soxhlet apparatus, 500 mL flask, all glass - Complete with glass extractor body, condenser, heating mantle and variable transformer for heat control.

6.8. Boiling chips

6.9. Buchner funnel, 15 cm

6.10. Filtration flask, 1 L capacity

6.11. Gas Chromatograph/Mass Spectrometer/Data System (GC/MS/DS) - Microcmass magnetic sector VG/Autospec or equivalent.

6.11.1. The GC must be capable of temperature programming and equipped with all required accessories, such as syringes, gases, and a capillary column. The GC injection port is designed for capillary columns; a splitless or an on-column injection technique is recommended.

6.11.2. The mass spectral data is obtained by using a low resolution instrument, utilizing 70 volts (nominal) electron energy in the electron impact mode. The system is capable of selected ion monitoring (SIM) for at least 18 ions simultaneously, with a cycle time of 1 second or less. Minimum integration time for SIM is 25 millisecond per m/z. The integration time used to analyze samples is identical to the time used to analyze the calibration solutions and QC samples. Total data acquisition time per cycle (18 ions) must not exceed 1 second.

6.11.3. An interfaced data system is present to acquire, store, reduce, and output mass spectral data.

6.11.4. GC Columns:

6.11.4.1. Fused silica capillary columns are required. The columns shall demonstrate the required separation of all 2,3,7,8-specific isomers whether a dual column or a single column is chosen. Column operating conditions shall be evaluated at the beginning and end of each 12 hour period during which samples or concentration calibration solutions are analyzed.

6.11.4.2. Isomer specificity for all 2,3,7,8-substituted PCDDs/PCDFs cannot be achieved on the 60 m DB-5 column. In order to determine the

concentration of the individual 2,3,7,8-substituted isomers, if the toxicity equivalence is greater than 0.7 ppb (solids), 7 ppt (aqueous), or 7 ppb (chemical waste), the sample extract shall be reanalyzed on a 60 m SP-2331 (or equivalent) GC column.

6.11.4.3. For any sample analyzed on a DB-5 (or equivalent) column in which either 2,3,7,8-TCDD or 2,3,7,8-TCDF is reported as an Estimated Maximum Possible Concentration, regardless of TEF-adjusted concentration or matrix, analysis of the extract is required on a second GC column which provides better specificity for these two isomers.

6.11.4.4. **For Method 8280A, the following conditions <u>may</u> require second column analysis:** *Second column analysis is dependent upon client requirements and site history.*

1) The criteria listed in Section 6.11.4.2 must be met <u>and</u> 2,3,7,8-TCDF must be detected or reported as an EMPC, or

2) If 2,3,7,8-TCDF is reported as an EMPC that is above the quantitation limit for the matrix.

7. REAGENTS AND STANDARDS

7.1. Solvents

7.1.1. High purity, distilled-in-glass: hexane, methanol, methylene chloride, toluene, isooctane, cyclohexane, acetone, tetradecane.

7.2. Sodium Sulfate: granular, anhydrous

7.2.1. Rinse with methylene chloride.

7.3. Sodium Hydroxide, ACS grade

7.3.1. Prepare a 10N solution in distilled water.

7.4. Sulfuric Acid, concentrated ACS grade, specific gravity 1.84

7.5. Hydrochloric Acid, concentrated ACS grade, specific gravity 1.17.

7.5.1. Prepare a 1N solution in distilled water for pretreatment of fly ash samples.

7.6. Column chromatography reagents

7.6.1. Alumina, acidic: ICN activated AA, Super I, ICN Biomedical or equivalent

7.6.2. Activated Charcoal: EM Science.

7.6.3. Silica gel: High purity grade Kiesel Gel 60, 70-230 mesh

7.6.3.1. Activate for up to 12 hours at 190°C before use. Store at 190°C in a covered flask.

7.6.4. Charcoal/Silica gel

7.6.4.1. Mix 5.0 g charcoal and 95 g activated silica gel. Activate mix for 12 hours at 190°C before use. Store at 190°C in a covered flask.

7.6.5. H_2SO_4 Silica gel

7.6.5.1. Mix 24 mL (44g) concentrated H_2SO_4 and 56g activated silica gel. Stir and shake until free flowing. Store at room temperature.

7.6.6. NaOH/Silica gel

7.6.6.1. Mix 34 mL 1N NaOH and 67g activated silica gel. Stir and shake until free flowing. Store at room temperature.

7.7. Calibration Solutions

All PCDD/PCDF calibration, internal standard, clean-up recovery standards, and spiking solutions are stable for one year from preparation. After one year, solutions may be revalidated. The revalidated solution may be used for an additional year or until there is evidence of compound degradation or concentration. The revalidation must be performed using an unexpired, not previously validated solution from a second lot or second vendor.

7.7.1. Five tetradecane solutions (CC1-CC5) containing 10 unlabeled and 7 carbon-labeled PCDDs/PCDFs at known concentrations are used to calibrate the instrument. One of these five solutions (CC3) is used as the continuing calibration solution and contains 7 additional unlabeled 2,3,7,8-substituted isomers that are

commercially supplied. The concentration ranges are homologue-dependent with the lowest concentrations associated with tetrachlorinated dioxins and furans (0.1-2.0 ng/µL), and higher concentrations associated with the penta- through octachlorinated homologues (0.5-10.0 ng/µL).

7.8. Internal Standard Solution

7.8.1. The solution contains the five internal standards in isooctane at the nominal concentrations listed in TABLE 8.

7.9. Recovery Standard Solution

7.9.1. The isooctane solution contains the recovery standards, 13C-1,2,3,4-TCDD and 13C-1,2,3,7,8,9-HxCDD, at concentrations of 0.5 ng/µL.

7.10. Continuing Calibration Solution

7.10.1. A solution containing standards to be used for the identification and quantitation of target analytes (CC3).

7.11. Window Defining Mix

7.11.1. A solution obtained by the laboratory through a commercial vendor. This solution contains the first and last eluting isomer of each homologue (See TABLE 6) and is used to verify that the switching times between the descriptors have been properly set.

7.11.2. The window defining mix need not contain any of the labeled internal or recovery standards, as no quantitative measurements are based on this mixture.

7.12. Cleanup Standard

7.12.1. A solution containing ^{37}Cl-2,3,7,8-TCDD at concentration of 0.25 ng/µL (0.25 µg/mL) in isooctane and is added to all sample extracts prior to cleanup. The recovery of this compound is used to judge the efficiency of the cleanup procedures.

7.13. Matrix Spiking Standard

7.13.1. A solution containing 10 of the 2,3,7,8-substituted isomers at the concentrations listed in TABLE 7 in isooctane, and is used to prepare the spiked sample aliquot. Dilute 50 µL of this standard to 1.0 mL with acetone and add to the aliquot chosen for spiking.

7.14. Column Performance Solution

7.14.1. The laboratory obtains this solution through commercial vendors. The solution contains 2,3,7,8-TCDD and the other TCDD isomers (1,4,7,8-TCDD and the 1,2,3,7/1,2,3,8-TCDD pair) that elute closest to 2,3,7,8-TCDD on the SP-2331 (or equivalent) GC column. The concentrations of these isomers should be approximately 0.5 ng/µL in tetradecane.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Water Samples

8.1.1. Each water sample received will consist of at least two 1-liter (or quart) amber glass bottles. Store at 4 ± 2°C from collection until extraction. Do not freeze. After a portion of the sample is removed for analysis, the unused portion of the sample is stored at 4 ± 2°C in a locked, limited access area for at least 60 days from the date of data submission.

8.2. Soil/Fly Ash/Chemical Waste Samples

8.2.1. Each soil/fly ash/chemical waste sample received will be contained in a 1-pint glass jar. Until a portion is removed for analysis, the sealed sample must be stored in a locked, limited access area at room temperature. Do not freeze. After a portion is removed for analysis, the unused portion of the sample is returned to its original container and stored at room temperature for at least 60 days from the date of data submission.

8.3. Protect samples from light at the time of receipt until extraction to minimize the potential for photodecomposition.

8.4. **For Method 8280A:**

8.4.1. All samples should be stored at 4° ± 2° C in the dark, for at least 30 days from the date of data submission, extracted within 30 days of collection and completely analyzed within 45 days of extraction. Whenever samples are analyzed after the

holding time expiration date, the results should be considered to be minimum concentrations and should be identified as such.

NOTE: *The holding times listed in Section 8.4.1 are recommendations. PCDDs and PCDFs are very stable in a variety of matrices, and holding times under the conditions listed in Section 8.4.1 may be as high as a year for certain matrices. Sample extracts, however, should always be analyzed within 45 days of extraction.*

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 laboratory matrix (e.g. water, Ottawa sand, sodium sulfate, etc.) 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 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. See STL Sacramento QA Policy 003 for specific acceptance criteria.

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, Ottawa sand, sodium sulfate, etc.) spiked 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. 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. See STL Sacramento QA Policy 003 for specific acceptance criteria.

9.3. A Matrix Spike and Duplicate Analysis (MS and DU) set must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. A MS is an aliquot of a selected field sample spiked with analytes of known identity and concentration. The MS and duplicate set must be processed in the same manner and at the same time as the associated samples. Spiked analytes with recoveries or precision outside control limits must be within control limits in the LCS. Corrective actions must be documented on a Non-Conformance memo, then implemented when recoveries of any spike analyte is outside control limits provided on the LIMS or by the client. Re-extraction of the blank, an LCS, the selected field sample, the MS and DU may be required after evaluation and review.

9.3.1. **For Method 8280A:** A Matrix Spike and Matrix Spike Duplicate set must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples.

9.4. A duplicate control sample (LCSD or DCS) must be substituted when insufficient sample volume is provided to process an MS/DU or MS/MSD set. The LCSD is evaluated in the same manner as the LCS. See STL Sacramento QA Policy 003 for specific acceptance criteria.

10. CALIBRATION AND STANDARDIZATION

10.1. Mass Calibration

10.1.1. Mass calibration of the mass spectrometer is recommended prior to analyzing the continuing calibration solution or samples each day. It is desirable to tune the instrument to greater sensitivity in the high mass range to achieve better response to the later eluting compounds. (See Appendix II for instrument tuning instructions.)

10.2. Window Defining Mix (WDM)

10.2.1. Prior to the calibration of the GC/MS system, it is necessary to establish the appropriate switching times for the SIM descriptors and to verify the chromatographic resolution. The switching times are determined by the analysis of the window defining mix, which contains the first and last eluting isomer in each homologue. (See TABLE 6)

10.2.2. The window defining mix must be analyzed at the following frequency:

10.2.2.1. Before initial calibration or the initial continuing calibration on each instrument and GC column used for analysis.

10.2.2.2. Each time a new initial calibration is performed, regardless of reason.

10.2.2.3. Each time adjustments or instrument maintenance activities are performed that may affect retention times.

10.2.2.4. Any time the retention time of either 13C-1,2,3,4,-TCDD or 13C-1,2,3,7,8,9-HxCDD recovery standards, in <u>any</u> analysis, varies by more than 10 seconds from its retention time in the most recent continuing calibration standard. **For Method 8280A, this section is not applicable.**

10.3. Chromatographic Resolution

10.3.1. For analyses on a DB-5 (or equivalent) GC column, the chromatographic resolution is evaluated by the analysis of the CC3 standard during both the initial and continuing calibration procedures.

10.3.2. For analyses on an SP-2331 (or equivalent) GC column, the chromatographic resolution is evaluated before the analysis of any calibration standards by the analysis of a commercially available column performance mixture that contains the TCDD isomers that elutes most closely with 2,3,7,8-TCDD on this GC column (1,4,7,8-TCDD and the 1,2,3,7/1,2,3,8-TCDD pair).

10.3.2.1. Analyze a 2 µL aliquot of this solution, using the column operating conditions and descriptor switching times previously established.

10.3.3. GC Resolution Criteria for SP-2331 or equivalent column. The chromatographic peak separation between unlabeled 2,3,7,8-TCDD and the peaks representing all other unlabeled TCDD isomers shall be resolved with a valley of ≤ 25%

$$\text{Valley} = \frac{X}{Y} \times (100)$$

Where:

X=the distinction from the baseline to the bottom of the valley between adjacent peaks.

Y=the peak height of any isomer.

10.3.3.1. The resolution criteria must be evaluated using measurements made on the selected ion current profile for the appropriate ions for each isomer. Measurements are not made from total ion current profiles.

10.3.3.2. Further analyses must not proceed until the GC resolution criteria have been met.

10.3.4. GC Resolution for DB-5 or equivalent column. The chromatographic peak separation between 13C-2,3,7,8-TCDD peak and 13C-1,2,3,4-TCDD isomers shall be resolved with a valley of ≤ 25%, in all calibration standards

$$\text{Valley} = \frac{X}{Y} \times (100)$$

Where:

X=the distinction from the baseline to the bottom of the valley between adjacent peaks.

Y=the peak height of any isomer.

10.3.4.1.In addition, the chromatographic peak separation between 1,2,3,4,7,8-HxCDD and 1,2,3,6,7,8-HxCDD in the CC3 solution shall be resolved with a valley of $\leq$ 50%, calculated in a similar fashion as above. The resolution criteria must be evaluated using measurements made on the SICP for the appropriate ions for each isomer. Measurements are not made from total ion current profiles.

10.3.4.2.The relative ion abundance criteria for PCDDs/PCDFs listed in TABLE 5, must be met for all PCDD/PCDF peaks, including the labeled internal and recovery standards, in all solutions. The lower and upper limits of the ion abundance ratios represent a $\pm$ 15% window around the theoretical abundance ratio for each pair of selected ions. The ^{37}Cl-2,3,7,8-TCDD cleanup standard contains no ^{35}Cl, thus the ion abundance ratio criterion does not apply to this compound.

10.3.4.3.For all calibrations solutions, the retention times of the isomers must fall within the appropriate retention time windows established by the window defining mix analysis. In addition, the absolute retention times of the recovery standards 13C-1,2,3,4-TCDD and 13C-1,2,3,7,8,9-HxCDD shall not change by more than 10 seconds between the initial CC3 analysis and the analysis of any other standard. **For Method 8280A, this section is not applicable.**

10.3.4.4.MS Sensitivity: For all calibration solutions, including the CC1 solution, the signal-to-noise ratio (S/N) must be greater than 2.5 for the unlabeled PCDD/PCDF ions and greater than 10 for the internal standard and recovery standard ions.

10.4. Five-Point Initial Calibration

10.4.1. The five calibration solutions outlined in TABLE 4 must be analyzed prior to any sample analyses. The solutions must be analyzed in the following order: CC3, CC1, CC2, CC4, CC5.

10.4.2. Analyze a 2 µL aliquot of each of the five concentration calibration solutions. The identical GC/MS/DS conditions used for the WDM or CPSM solution must also be used for the concentration calibration solutions.

10.4.3. The laboratory must not proceed with the sample analyses until an acceptable initial calibration is determined and documented according to the following criteria:

10.4.3.1.The relative ion abundance criteria listed for PCDDs/PCDFs in TABLE 5, must be met using areas to calculate the ratios.

10.4.3.2. All the analytes must fall within the appropriate retention time windows established by the GC Window Defining Mix. In addition, the absolute retention times of the recovery standards 13C-1,2,3,4-TCDD and 13C-1,2,3,7,8,9-HxCDD shall not change by more than 10 seconds between the initial CC3 analysis and the analysis of any other standard. **For Method 8280A, this section is not applicable.**

10.4.3.3.MS Sensitivity: The signal-to-noise (S/N) ratio must be greater than 2.5 for the unlabeled PCDD/PCDF ions and greater than 10 for the internal standard and recovery standard ions.

10.5. Relative Response Factors

10.5.1. Calculate the relative response factors (RRFs) for the 17 unlabeled target analytes relative to their appropriate internal standards (RRF_n) according to the formula in Section 10.5.5. For the seven unlabeled analytes and the ^{37}Cl-2,3,7,8-TCDD cleanup standard that are found only in the CC3 solution, only one RRF is calculated for each analyte. For the other 10 unlabeled analytes, calculate the RRF of each analyte in each calibration standard.

10.5.2. Calculate the RRFs for the five labeled internal standards and the cleanup standard relative to the appropriate recovery standard (RRF_{is}) in each calibration standard according to the formula in Section 10.5.5.

10.5.3. There is only one quantitation ion for the ^{37}Cl cleanup standard. Calculate the relative response factor as described for RRF_{is}, using one area for the cleanup standard and the sum of the areas of the ions from the recovery standard.

10.5.4. The RRF_n and the RRF_{is} are dimensionless quantities; therefore, the units used to express the Q_n, Q_{is}, and Q_{rs} must be the same.

NOTE: *This protocol is based on the assumption that if the 10 unlabeled 2,3,7,8-substituted isomers provided in the calibration solutions meet linearity criteria, then the seven additional 2,3,7,8-substituted isomers and the cleanup standard in CC3 solution may be assumed to have a sufficiently linear response to be used for quantitation. These eight RRFs cannot be used to determine relative standard deviation, but are used for percent difference determinations and quantitation of target analytes.*

10.5.5. Calculations are outlined below:

$$RRF_n = \frac{(A_{n1} + A_{n2}) \times Q_{is}}{(A_{is1} + A_{is2}) \times Q_n}$$

$$RRF_{is} = \frac{(A_{is1} + A_{is2}) \times Q_{rs}}{(A_{rs1} + A_{rs2}) \times Q_{is}}$$

Where:

A_{n1}, A_{n2}	=	integrated areas of the two quantitation ions of the isomer of interest (TABLE 2).
A_{is1}, A_{is2}	=	integrated areas of the two quantitation ions of the appropriate internal standard (TABLE 2)
A_{rs1}, A_{rs2}	=	integrated areas of the two quantitation ions of the appropriate recovery standard (TABLE 2).
RRF_n	=	the response factor of the quantitation ions of the isomer of interest relative to that of the appropriate internal standard.
RRF_{is}	=	the response factor of the internal standard relative to that of the appropriate internal standard

Q_n = quantity of unlabeled PCDD/PCDF analyte injected (ng).

Q_{is} = quantity of appropriate internal standard injected (ng).

Q_{rs} = quantity of appropriate recovery standard injected (ng).

10.5.6. Calculate the relative response factors for the native PCDDs/PCDFs relative to the recovery standards (RRF_{rs}):

Where;

$$RRF_{rs} = RRF_n \times RRF_{is}$$

10.5.6.1. This is used when the sample is diluted to the extent that the MS response of the internal standard is less than 10% of its MS response in the continuing calibration standard (See Section 12.3)

10.5.6.1.1. **For Method 8280A:** The RRF_{rs} method of quantitation is only used when the sample is diluted to the extent that the S/N ratio for the internal standard is less than 10.0.

10.5.7. Response Factor Criteria

10.5.7.1. Calculate the mean RRF (RRF_{ave}) and percent relative standard deviation (%RSD) of the five RRFs for the unlabeled PCDDs/PCDFs (CC1-CC5) and labeled internal standards present in all five concentration calibration solutions.

10.5.7.2. No mean RRF or %RSD calculations are possible for the 2,3,7,8-substituted isomers or the cleanup standard found only in the CC3 solution.

$$\%RSD = \frac{\text{Standard Deviation}}{\text{Mean RRF}} \times 100$$

10.5.7.3. The %RSD of the RRFs for the unlabeled PCDDs/PCDFs (CC1-CC5) and the internal standards must not exceed 15 percent.

10.5.8. If the initial calibration curve requirements are not met, the following suggestions may be useful:

- Check and adjust the GC and/or MS operation conditions,
- Adjust or replace the GC column,
- Adjust the MS for greater or lesser resolution using FC-43. Recalibrate.

10.6. Continuing Calibration (i.e. Daily Standard)

10.6.1. Inject a 2 µL aliquot of the continuing CC3 calibration solution. The continuing calibration solution must be analyzed at the beginning of each 12-hour period to evaluate chromatographic resolution and verify the RRF values used in quantitation.

10.6.2. The identical GC/MS/DS conditions used for the WDM and the initial calibration solutions must also be used for the continuing calibration solution.

10.6.3. GC Column Resolution Criteria. The chromatographic resolution on the DB-5, SP-2331 (or equivalent) columns must meet the QC criteria in Sections 10.3.3 and 10.3.4.

10.6.4. Ion Abundance Criteria. The relative ion abundances listed in TABLE 5 must be met for all PCDD/PCDF peaks, including the labeled internal and recovery standards.

10.6.5. Instrument Sensitivity Criteria. For the CC3 solution, the S/N ratio must be greater than 2.5 for the unlabeled PCDD/PCDF ions, and greater than 10.0 for the labeled internal and recovery standards.

10.6.6. Response Factor Criteria. The measured RRFs of each analyte and internal standard in the CC3 solution must be within ± 30.0% of the mean RRFs established during initial calibration.

$$\% \text{ Difference} = \frac{(RRF_i - RRF_c)}{RRF_i} \times 100$$

Where:

RRF_i=Relative response factor established during initial calibration.

RRF_c=Relative response factor established during continuing calibration.

10.6.7. If any of the criteria listed are not met, the Contractor must take corrective actions and reanalyze the continuing calibration standard (CC3). If the criteria are met after corrective action has been taken, then the sample analysis may proceed.

10.6.8. If the criteria are not met after corrective actions have been taken, then a new initial calibration must be performed, beginning with the analysis of the window defining mix. The new initial calibration must meet all of the QC criteria in Section 10.4 before sample analysis may proceed.

10.7. Instrument Sensitivity Check. In order to demonstrate that the GC/MS/DS system has retained adequate sensitivity during the course of sample analyses, the contractor must analyze the lowest of the standards (CC1) at the end of each 12-hour period during which samples and standards are analyzed.

10.7.1. Analyze a 2 µL aliquot of the CC1 solution, using the identical instrumental conditions used for analysis of samples and standards.

10.7.2. The CC1 solution analyzed at the end of the 12-hour period must meet the following criteria:

- Retention Time Criteria: The absolute retention time of the recovery standards 13C-1,2,3,4-TCDD and 13C-1,2,3,7,8,9-HxCDD shall not change more than 10 seconds between the initial CC3 analysis and then ending CC1 analysis. If the retention times of either of these standards change by more than ± 10 seconds, the contractor must adjust the switching times of the descriptors and analyze the window defining mix before proceeding with further analyses. **For Method 8280A, this section is not applicable.**

- All the analytes in the CC1 solution must meet the ion abundance ratio criteria in TABLE 5.

- Instrument Sensitivity Criteria: For the CC1 solution, the S/N ratio must be greater than 2.5 for the unlabeled PCDD/PCDF ions and greater than 10.0 for the labeled internal and recovery standards.

10.7.3. If the analysis of the CC1 solution at the end of the 12-hour period fails either the ion abundance or S/N criteria above, the laboratory must take corrective action which may include:

- Performing a new initial calibration, beginning with the analysis if the window defining mix
- Starting a new analytical sequence (See TABLE 9)
- Reanalyzing all samples originally analyzed in the preceding 12-hour time period in which:

  a) No PCDDs/PCDFs were detected

  b) Neither 2,3,7,8-TCDD or 2,3,7,8-TCDF were detected, even if other PCDDs or PCDFs were detected

  c) Any 2,3,7,8-substituted PCDD or PCDF is reported as an Estimated Maximum Possible Concentration

  d) These reanalysis are necessary because poor S/N ratios indicate a loss of sensitivity that could lead to false negative results, underestimation of concentration, or could cause ion abundance ratios to fall outside the QC limits.

For Method 8280A: If the CC1 analysis fails either the ion abundance or S/N criteria, then any samples analyzed during that 12-hour period that indicated the presence of any PCDDs/PCDFs below the method quantitation limit or where EMPC concentrations were reported must be reanalyzed. Samples with positive results above the method quantitation limit need not be reanalyzed.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.1.1. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.1.2. Soxhlet-Dean Stark (SDS) Extraction

11.1.2.1.Do not bake the components of the SDS apparatus as part of routine cleaning. Repeated baking of glassware can cause active sites on the glass surface to absorb PCDDs/PCDFs and other analytes. All glass parts of the SDS apparatus, including the thimbles, must be pre-extracted with toluene for approximately three hours prior to use. Pre-extraction will ensure that the glassware is as clean as possible and minimize cross contamination problems. Discard the used toluene, or pool it for later analysis to verify the cleanliness of the glassware.

11.1.2.2.The extraction of soil/sediment, fly ash, and particulates from water samples will require the use of a Soxhlet thimble. Prior to pre-extraction, prepare the thimble by adding 5g of 70/230 mesh silica gel to the thimble to produce a thin layer in the bottom of the thimble. This layer will trap fine particles in the thimble. Add 15-20g of quartz sand on top of the silica gel and place the thimble in the extractor.

11.1.2.3.After pre-extraction for three hours, allow the apparatus to cool and remove the thimble. Mix the appropriate weight of sample with the sand in the thimble, being careful not to disturb the silica gel layer.

11.1.2.3.1.If the sample aliquot to be extracted contains large lumps or is otherwise not easily mixed in the thimble, the sand and sample may be mixed in another container. Transfer approximately 2/3 of the sand from the thimble to a clean container, being careful not to disturb the silica gel, and the sample and a clean spatula, and transfer the sand/sample mixture to the thimble.

11.1.2.3.2.If a sample with particularly high moisture content is to be extracted, it may be helpful to leave a small conical depression in the material in the thimble. This procedure will allow the water to drain through the thimble more quickly during the early hours of the extraction. As the moisture is removed during the first few hours of extraction, the depression will collapse, and the sample can be uniformly extracted.

11.2. Chemical Waste Sample Extraction

11.2.1. Assemble a flask (125 mL), a Dean Stark trap, and a condenser, and pre-extract with toluene for three hours. Pre-extraction will ensure that the glassware is as clean

as possible and minimize cross-contamination problems. Discard the used toluene, or pool it for later analysis to verify cleanliness of the glassware.

11.2.2. Oily Sludge/Wet Fuel Oil: Weigh about 1g of sample to two decimal place into a tarred pre-extracted 125 mL flask. Add internal standard solution (TABLE 8) to the sample in the flask. Attach the pre-extracted Dean Stark water separator and condenser to the flask, and extract the sample by refluxing it with 50 mL of toluene for at least three hours

11.2.2.1. Continue refluxing the sample until all the water has been removed. Cool the sample, and filter the toluene extract through a rinsed glass fiber filter into a 100 mL round bottom flask. Rinse the filter with 10 mL of toluene, and combine the extract and rinsate. Concentrate the combined solution to approximately 10 mL using a rotary evaporator as described in Section 11.2.7.

11.2.2.2. Prepare a sample aliquot for the duplicate sample analysis and a sample aliquot for the spiked sample analysis.

11.2.2.2.1. **For Method 8280A:** Prepare sample aliquots for the matrix spike/matrix spike duplicate analysis.

11.2.3. Stillbottom/Oil: Weigh about 1g of sample to two decimal places into a tarred pre-extracted 125 mL flask. Add internal standard solution (See TABLE 8) to the sample in the flask. Attach the pre-extracted Dean Stark water separator and condenser to the flask, and extract the sample by refluxing it with 50 mL of toluene for at least three hours.

11.2.3.1. Cool the sample, and filter the toluene extract through a rinsed glass fiber filter into a 100 mL round bottom flask. Rinse the filter with 10 mL of toluene, and combine the extract and rinsate. Concentrate the combined solution to approximately 10 mL using a rotary evaporator as described in Section 11.2.7.

11.2.3.2. Prepare a sample aliquot for the duplicate sample analysis and a sample aliquot for the spiked sample analysis.

11.2.3.2.1. **For Method 8280A:** Prepare sample aliquots for the matrix spike/matrix spike duplicate analysis.

11.2.4. Fly Ash Sample Extraction

11.2.4.1. Weigh about 10g of the fly ash to two decimal places and transfer to an extraction jar. Add internal standard solution (See TABLE 8) to the sample.

11.2.4.2. Add 150 mL of 1N HCl to the fly ash sample in the jar. Seal the jar with the Teflon-lined screw cap, place on a mechanical shaker, and shake for three hours at room temperature..

11.2.4.3. Rinse a Whatman #1 (or equivalent) filter paper with toluene, and then filter the sample through the filter paper in a Buchner funnel into a 1L receiving flask. Wash the fly ash with approximately 500 mL distilled water.

11.2.4.4. Mix the fly ash with the sand in a pre-extracted thimble and place the filter paper on top of the sand. Place the thimble in a SDS extractor, add 200 mL toluene, and extract for 16 hours.

11.2.4.4.1. The solvent must cycle completely through the system 5-10 times per hour. Cool and filter the toluene extract through a rinsed glass fiber filter into a 500 mL round bottom flask. Rinse the filter with 10 mL of toluene. Concentrate the extract as described in Section 11.2.7.

NOTE: A blank must be analyzed using a piece of filter paper handled in the same manner as the fly ash sample.

11.2.4.5. Prepare a sample aliquot for the duplicate sample analysis and a sample aliquot for the spiked sample analysis.

11.2.4.5.1. **For Method 8280A:** Prepare sample aliquots for the matrix spike/matrix spike duplicate analysis.

11.2.5. Soil/Sediment Sample Extraction

11.2.5.1. An extremely wet sample may required centrifugation to remove standing water before extraction.

11.2.5.2. Weigh about 10g of soil to two decimal places and transfer to a pre-extracted thimble (See Section 11.1.2). Mix the sample with the quartz sand and add internal standard solution (see TABLE 8) to the sample/sand

mixture. Add small portions of the solution at several sites on the surface of the sample/sand mixture.

11.2.5.3. Place the thimble in the SDS apparatus. Add 200-250 mL toluene to the SDS apparatus and reflux for 16 hours. The solvent must cycle completely through the system 5-10 times per hour.

11.2.5.4. Estimate the percent solids content of the soil/sediment sample by measuring the volume of water evolved during the SDS extraction procedure. For extremely wet samples, the Dean Stark trap may need to be drained one or more times during the 16-hour extraction. Collect the water from the trap and measure its volume to the nearest 0.1 mL. Assume a density of 1.0 g/mL and calculate the percent solids content according to the following formula:

$$\text{Percent Solids} = \frac{\text{(Wet weight of sample - Weight of water)}}{\text{Wet weight of sample}} \times 100$$

11.2.5.5. Concentrate this extract as described in Section 11.2.7.

11.2.5.6. Prepare a sample aliquot for the duplicate sample analysis and a sample aliquot for the spiked sample analysis.

11.2.5.6.1. **For Method 8280A:** Prepare sample aliquots for the matrix spike/matrix spike duplicate analysis.

11.2.6. Water Sample Extraction

11.2.6.1. Allow the sample to reach ambient temperature. Add 1 mL of the acetone-diluted internal standard solution (See TABLE 8) to the sample bottle. Cap the bottle and mix the sample by gently shaking for 30 seconds. Filter the sample through a glass fiber filter that has been rinsed with toluene.

NOTE: *Reagent water used as a blank must also be filtered in a similar fashion and subjected to the same cleanup analysis as the water samples.*

11.2.6.1.1. If the total dissolved and suspended solids contents are too much to filter through the glass fiber filter, centrifuge the sample, decant, and then filter the aqueous phase. Combine the solids from

the centrifuge bottle(s), the particulate on the filter, and the filter itself and proceed with the SDS extraction in Section 11.2.6.2.

11.2.6.1.2.The filtered aqueous sample is poured into a 2 L separatory funnel. Add 100 mL methylene chloride to the sample bottle, seal, and shake for 60 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and 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 shall employ mechanical techniques to complete the phase separation (i.e. glass stirring rod). Drain the methylene chloride extract into a 500 mL round bottom flask by passing the extract through a funnel packed with a glass wool plug and half-filled with anhydrous sodium sulfate. Extract the water sample two more times using 100 mL of fresh methylene chloride each time. Drain each extract through the funnel into round bottom flask. After the third extraction, rinse the sodium sulfate with at least 30 mL of fresh methylene chloride. Concentrate this extract as described in Section 11.2.7.

11.2.6.2.Combine the filtered particulate portion of the sample with the quartz sand in the extraction thimble. Add the filter on top of the particulate/sand mixture and place the thimble into a pre-extracted SDS apparatus.

11.2.6.2.1.Add 200-250 mL of toluene to the SDS apparatus and reflux for 16 hours. The solvent must cycle completely through the system 5-10 time per hour. Concentrate this extract as described in Section 11.2.7.

11.2.6.3.Determine the original sample volume by weighing the empty sample container and assume the specific gravity of the sample to be 1.0 g/mL. Record the sample volume.

11.2.6.4.Prepare a sample aliquot for the duplicate sample analysis and a sample aliquot for the spiked sample analysis.

11.2.6.4.1.**For Method 8280A:** Prepare sample aliquots for the matrix spike/matrix spike duplicate analysis.

11.2.7. Macro-Concentration Procedures (All Matrices)

11.2.7.1. Prior to cleanup, extracts from all matrices must be concentrated to approximately 2 mL (near dryness). In addition, the concentrated extracts from the aqueous filtrate and the filtered particulates must be combined prior to cleanup. Prior to concentrating all extracts add 200 µL of tetradecane.

11.2.7.2. Concentration by Rotary Evaporator

11.2.7.2.1. According to manufacturer's instructions, assemble the rotary evaporator and warm the water bath to 65°C. Between samples, rinse 2-3 mL aliquots of toluene down the feed tube into a waste beaker.

11.2.7.2.2. 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.

11.2.7.2.3. Lower the flask into the water bath and adjust the speed of rotation and the temperature as required to complete the concentration in 15-20 minutes. At the proper rate of concentration, the flow of solvent into the receiving flask should be steady and no bumping or visible boiling of the extract shall occur.

NOTE: *If the rate of concentration is too fast, analyte loss may occur.*

11.2.7.2.4. When the liquid in the concentration flask has reached an apparent volume of 2 mL, remove the flask from the water bath, and stop the rotation. Slowly and carefully emit air into the system. Be sure not to open the valve so quickly that the sample is blown out of the flask. Detach the flask from the rotary evaporator. Rinse the feed tube with approximately 2 mL of toluene and hexane prior to attaching the next extract.

11.2.7.3. Extracts of Chemical Waste, Fly Ash, and Soil/Sediment Samples

11.2.7.3.1. For chemical waste, fly ash, and soil/sediment samples, the extract must be concentrated to approximately 2 mL prior to acid-

base washing treatment. Concentrate the extract as described above.

11.2.7.3.2. Transfer the concentrated extract to a 500 mL separatory funnel. Rinse the flask with toluene and add the rinse to the separatory funnel. Proceed with acid-base washing treatment per Section 11.2.8.

11.2.7.4. Extracts of Aqueous Filtrates

11.2.7.4.1. Extracts of the aqueous filtrate of water samples are in methylene chloride which are concentrated to approximately 2 mL by rotary evaporator prior to combining with the toluene extract of the particulates.

11.2.7.4.2. Combine the extract of the filtrate with the extract of the particulates as described in Section 11.2.7.5.

11.2.7.5. Extracts of Particulates from Aqueous Samples

11.2.7.5.1. If the extract is from the particulates from an aqueous sample, it must be concentrated to approximately 2 mL by rotary evaporator, and combined with concentrated extract of the filtrate (Section 11.2.7.4) prior to acid-base washing treatment.

11.2.7.5.2. Concentrate the combined extract to approximately 2 mL (the volume of the toluene) by rotary evaporator.

11.2.7.5.3. Transfer the concentrated combined extract to a 500 mL separatory funnel. Rinse the concentrator with three 5 mL volumes of hexane and add each rinse to the separatory funnel. Proceed with acid-base washing treatment according to Section 11.2.8.

11.3. There are several useful methods to decrease or eliminate emulsion in aqueous samples when extracting with DCM. These methods may include stirring with a pipet 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/H2O 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.

11.3.1. Preparing the solution:

Add 1.0L of reagent grade NaOH solution to an empty 2.0L NaOH container. Then add 1.0L of DI H2O to the container and leave the container in secondary containment with the lid off. ***(The solution will begin to heat so let the solution stand 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.

11.3.2 Using the solution to decrease emulsions:

11.3.2.1 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/H20 into a 1.0L AGB.

11.3.2.2 Drain the sample with emulsion from the 2.0L separatory funnel into the 1:1 NaOH/H2O and let stand. Empty aqueous waste into the LLE waste drum.

11.3.2.3 Pour the solution with DCM back into the same 2.0L separatory funnel and drain the DCM phase through Na2SO4 into a 500mL roundbottom. Empty the aqueous waste into the LLE waste drum.

11.4. Extract Cleanup Procedures (All Matrices)

11.4.1.1.Prior to cleanup, all extracts are spiked with the ^{37}Cl-2, 3,7,8-TCDD cleanup standard. The recovery of this standard is used to monitor the efficiency of the cleanup procedures. Spike 50 µL of the cleanup standard (or a larger volume of diluted solution containing 25 ng of ^{37}Cl-2,3,7,8-TCDD) into each separatory funnel containing an extract, resulting in a concentration of 0.25 ng/µL in the final extract analyzed by GC/MS. Add 150 mL of hexane to dilute the extract in the separatory funnel.

11.4.1.1.1.**For Method 8280A:** The procedures outlined in Sections 11.2.8.2 through 11.2.8.5 need not apply to <u>uncolored</u> extracts, but all the other cleanup procedures should be employed, regardless of the color of the extract.

11.4.1.2. Partition the concentrated extract against 40 mL of concentrated sulfuric acid. Shake for thirty seconds. Remove and discard the acid layer (bottom). Repeat the acid washing until there is no visible color in the acid layer. (Perform acid washings a maximum of four times).

***CAUTION:** Concentrated sulfuric acid is hazardous and should be handled with care. A faceshield shall be used when handling bulk acids and bases.*

11.4.1.3. Partition the concentrated extract against 40 mL of distilled water. Shake for thirty seconds. Remove and discard the aqueous layer (bottom).

11.4.1.4. Partition the concentrated extract against 40 mL of 10N NaOH. Shake for thirty seconds. Remove and discard the base layer (bottom). Repeat the base washes until there is no color visible in the bottom layer (perform base washes a maximum of four times). Strong base, NaOH, is known to degrade certain PCDDs/PCDFs; therefore, contact time should be minimized.

11.4.1.5. Partition the concentrated extract against 40 mL of distilled water. Shake for thirty seconds. Remove and discard the aqueous layer (bottom). Dry the organic layer by pouring it through a funnel containing anhydrous sodium sulfate. Collect the extract in an appropriate size round bottom flask. Wash the separatory funnel with two 15 mL portions of hexane, pour through the funnel and combine the extracts. Concentrate the extracts to 1.0 mL using the procedures described in Section 11.2.7.

11.4.2. Silica Gel and Alumina Column Chromatographic Procedure

11.4.2.1. Column 1: Insert a glass wool plug onto the bottom of a 20 mm disposable glass column. Add 1g silica gel and tap the column gently to settle the silica gel. Add 2g sodium hydroxide-impregnated silica gel, 1g silica gel, 4g sulfuric acid-impregnated silica gel, and 2g silica gel. Top with 1g anhydrous sodium sulfate. Tap the column gently after each addition. A small positive pressure (5 psi) of clean nitrogen may be used if needed.

11.4.2.2. Column 2: Insert a glass wool plug onto the bottom of a 16 mm disposable glass column. Add 6g of the activated acid alumina. Top with 1g anhydrous sodium sulfate. Tap the top of the column gently.

11.4.2.2.1.Check each new batch of silica gel and alumina and maintain the results of the analyses on file. To accomplish this, combine 100 µL of the internal standard solution and 50 µL of matrix spike solution with 850 µL of hexane. Process this solution through both columns in the same manner as a sample extract (Section 11.2.10.3). Concentrate the continuing calibration solution to a final volume of 50 µL. Proceed to analysis (Section 11.3). If the recovery of any of the analytes is less than 80%, this batch of carbon/silica mixture may not be used.

11.4.2.3.Add 20 mL of hexane to each column until the packing is free of air bubbles. A small positive pressure (5 psi) of clean dry nitrogen may be used if needed. Check the columns for nitrogen may be used if needed. Check the columns for channeling. If channeling is present, discard the column.

***CAUTION**: Do not tap a wetted column.*

11.4.2.4.Assemble the two columns such that the eluate from Column 1 (silica gel) drains directly into Column 2 (alumina).

11.4.2.5.Transfer the extract from Section 11.2.8. to the top of the silica gel column. Rinse the flask with enough hexane (1-2 mL) to complete the quantitative transfer of the sample to the surface of the silica.

11.4.2.6.Using 90 mL of hexane, elute the extract from Column 1 directly onto Column 2, which contains the alumina.

***CAUTION:** Do not allow the alumina column to run dry.*

11.4.2.7. Add 20 mL of 20% methylene chloride/80% hexane (v/v) to Column 2, and elute until the solvent level is just below the top of the alumina.

11.4.2.8. Add 26 mL of 80% methylene chloride/20% hexane (v/v) to Column 2, and collect the eluate in a culture tube.

11.4.2.9. Add 200 µL of tetradecane and concentrate the extract to near dryness using a turbo-evaporator apparatus. The extract is now ready to be transferred to the carbon column.

11.4.3. Carbon Column Chromatographic Procedure

11.4.3.1. Thoroughly mix 95g activated silica gel and 5.0g charcoal. Activate the mixture at 190°C for twelve hours and store in a charcoal/silica oven at 190°C.

11.4.3.1.1. Check each new batch of the charcoal/silica and maintain the results from the analyses for examination. To accomplish this, add 100 µL of the internal standard solution and 50 µL of matrix spike solution to 850 µL of hexane. Process the spiked solution in the same manner as a sample extract (Section 11.2.11.1.2 through 11.2.11.5). Concentrate the solution to 50 µL and proceed with Section 11.3. If the recovery of any of the analytes is less than 80%, this batch of carbon/silica mixture may <u>not</u> be used.

11.4.3.2. Prepare an 8-inch glass column by cutting off each end of a 5 mL disposable serological pipet. Insert a glass wool plug at one end of the column and pack it with 0.30 g of the charcoal/silica mixture. Insert an additional glass wool plug in the other end. See Figure 2.

***CAUTION**: It is very important that the column be packed properly to ensure that carbon fines are not carried into the eluate. PCDDs/PCDFs will adhere to the carbon fines and greatly reduce recovery. If carbon fines are carried into the eluate in Section 11.2.10.5, filter the eluate using a 0.45 micron filter (pre-rinsed with toluene), then proceed to Section 11.3.*

11.4.3.3. Pre-rinse with 5 mL hexane in both directions.

11.4.3.3.1. Pre-elute 2 mL of toluene in Direction B 2.

11.4.3.3.2.mL 75:20 methylene chloride:methanol.

11.4.3.3.3.mL 1:1 Cyclohexane: methylene chloride .

11.4.3.3.4.mL Hexane

11.4.3.3.5.Discard all the column rinsates.

11.4.3.4.While the column is still wet, transfer the concentrated eluate from Section 11.2.9.9. to the prepared carbon column. Rinse the eluate container with two 1.0 mL portions of hexane and transfer the rinses to the carbon column. Elute the column with the following sequence of solvents:

11.4.3.4.1.mL of Cyclohexane/Methylene Chloride (50:50 v/v).

11.4.3.4.2.mL of Methylene Chloride/Methanol (75:20 v/v)

***NOTE:** The above two eluates may be collected, combined and used as a check on column efficiency.*

11.4.3.5.Once the solvents have eluted through the column, turn the column over, elute the PCDD/PCDF fraction with 15 mL of toluene, and collect the eluate.

11.4.4. Final Concentration

11.4.4.1.Evaporate the toluene fraction from Section 11.2.10.5 to approximately 1.0 mL with N_2 via turbo-evaporator.

11.4.4.2.Transfer the extract to a 2.0 mL conical vial using a hexane rinse.

***CAUTION:** Do <u>not</u> evaporate the sample extract to dryness.*

11.4.4.3.Add 100 µL tetradecane to the extract and reduce the volume to 100 µL using a gentle stream of clean dry nitrogen. The final extract volume should be 100 µL of tetradecane. Seal the vial and store the sample extract in the dark at ambient temperature until prior to GC/MS analysis.

11.4.4.4.Transfer a 50 µL aliquot of the extract to a 0.3 mL vial and add sufficient recovery standard solution to yield a concentration of 0.5 ng/µL in a 50 µL

volume. Reduce the volume of the extract back down to 50 µL using a gentle stream of dry nitrogen.

11.5. GC/MS Analysis

11.5.1. Inject a 2 µL aliquot of the extract into the GC/MS instrument. Reseal the vial containing the original concentrated extract.

11.5.2. Analyze the extract by GC/MS and monitor all of the ions listed in TABLE 2. The same MS parameters used to analyze the calibration solutions shall be used for the sample extracts.

11.6. Dilutions

11.6.1. If the concentration in the final extract of any analyte exceeds the upper method calibration limit (MCL) for that compound, the linear range of response versus concentration may have been exceeded. In such cases, the following corrective actions will be undertaken:

- If the signal for the analyte has saturated the detector, a single dilution and reanalysis of the extract will be made in an attempt to bring the signal within the range of the detector. The reported concentration for the analyte will be qualified appropriately.
- If the signal for the analyte is above the MCL, but does not saturate the detector, the concentration will be reported and qualified as "E."
- With the approval of the client, samples may be reextracted and/or reanalyzed with the following adjustments in order to provide a concentration that meets client-specific data quality objectives.
- Extract and analyze one tenth of the original aliquot. This option is appropriate only if it will provide analyte concentration within the MCL and if the sample aliquot will be representative.
- Extract an aliquot large enough to be representative, and increase the concentration of internal standard and surrogate spike components added prior to the extraction. The extract is then diluted either prior to or after the clean up procedures.

- Dilute the original extract. Internal standard components are respiked at an appropriate level prior to analysis. In this case, the internal standard recoveries are taken from the original analysis.

11.6.1.1.**For Method 8280A:** A dilution is only necessary if the detector has been saturated.

11.6.2. An appropriate dilution will result in the largest peak in the diluted sample falling between the mid-point and high-point of the calibration range.

11.6.3. Dilutions are performed using an aliquot of the original extract of which approximately 50 µL remains. Remove an appropriately sized aliquot from the vial and add it to a sufficient volume of tetradecane in a clean 0.3 mL conical vial. Add sufficient recovery standard solution to yield a concentration of 0.5 ng/µL. Reduce the volume of the extract back down to 50 µL using a gentle stream of dry nitrogen.

11.6.4. The dilution factor is defined as the total volume of sample aliquot and clean solvent (50 µL) divided by the volume of the sample aliquot that was diluted.

11.6.5. Inject 2 µL of the diluted sample extract into the GC/MS and analyze according to Section 11.3.

11.6.6. Diluted samples in which the MS response of any internal standard is < 10% of the MS response of that internal standard in the most recent continuing calibration standards are quantified using the recovery standards.

11.6.6.1.**For Method 8280A:** The RRF_{rs} method of quantitation is only used when the sample is diluted to the extent that the S/N ratio for the internal standard is less than 10.0.

11.7. Identification Criteria

11.7.1. For a gas chromatographic peak to be unambiguously identified as a PCDD or PCDF, it must meet <u>all</u> of the following criteria:

11.7.1.1.Retention Times

11.7.1.1.1.Retention times are required for all chromatograms; scan numbers are optional. Retention times shall either be printed at the apex of each peak on the chromatogram, or each peak shall be

unambiguously labeled with an identifier that refers to the quantitation report, or combination of both shall contain the retention time of each peak and its area.

11.7.1.1.2.In order to make a positive identification of the 2,3,7,8-substituted isomers for which an isotopically labeled internal or recovery standard is present in the sample extract, the absolute retention time (RT) at the maximum peak height of the analyte must be within -1 to 3 seconds of the retention time of the corresponding labeled standard.

11.7.1.1.3.In order to make a positive identification of the 2,3,7,8-substituted isomers for which a labeled standard is not available, the relative retention time (RRT) of the analyte must be within 0.05 RRT units of the RRT established by the continuing calibration. The RRT is calculated as follows:

$$RRT = \frac{\text{Retention Time of Analyte}}{\text{Retention Time of Corresponding Internal Standard}}$$

11.7.1.1.4.For non-2,3,7,8-substituted compounds (tetra through hepta), the retention time must be within the retention time windows established by the window defining mix for the corresponding homologue (See Section 10.2).

11.7.1.1.5.In order to assure that retention time shifts do not adversely affect the identification of PCDDs/PCDFs, the absolute retention times of the two recovery standards added to every sample extract prior to analysis, may not shift by more than $\pm$ 10 seconds from their retention times in the continuing calibration standard. **For Method 8280A, this section is not applicable.**

11.7.2. Peak Identification

11.7.2.1.All of the specified ions listed in TABLE 2 for each PCDD/PCDF homologue and labeled standards must be present in the SICP. The ion current response for the two quantitation ions and the M- $[COCl]^+$ ions for the analytes must maximize simultaneously ($\pm$ 2 seconds). This requirement

also applies to the internal standards and recovery standards. For the cleanup standard, only one ion is monitored.

11.7.3. Signal-To-Noise Ratio

11.7.3.1. The integrated ion current for each analyte ion listed in TABLE 2 must be at least 2.5 times background noise and must not have saturated the detector. The internal standard ions must be at least 10.0 times background noise and must not have saturated the detector. However, if the M-$[COCl]^+$ ion does not meet the 2.5 times S/N requirement but meets all other criteria listed in Section 11.5 and, in the judgment of the GC/MS Interpretation Specialist, the peak is a PCDD/PCDF, the peak may be reported as positive.

11.7.4. Ion Abundance Ratios

11.7.4.1. The relative ion abundance criteria listed in TABLE 5 for native analytes and internal standards must be met using peak areas to calculate ratios.

11.7.4.2. If interferences are present and ion abundance ratios are not met using peak areas, but all other qualitative identification criteria are met (RT, S/N, presence of all three ions), the chemist may use peak heights to evaluate the ion ratio.

11.7.4.3. If, in the judgment of the analyst, the peak is a PCDD/PCDF, then report the ion abundance ratios determined using peak heights. Quantitate the peaks using peak heights rather than areas for both the target analyte and the internal standard.

11.7.4.4. The identification of a GC peak as a PCDF cannot be made if a signal having S/N greater than 2.5 is detected at the same retention time (± 2 seconds) in the corresponding PCDPE channel (See TABLE 2). If a PCDPE is detected, an EMPC should be calculated for this GC peak regardless of the ion abundance ratio.

12. DATA ANALYSIS AND CALCULATIONS

12.1. For GC peaks that have met all the identification criteria outlined in Section 11.5, calculate the concentration of the individual PCDD or PCDF isomers using the following formula:

12.1.1. All matrices other than water:

$$\text{Conc. } (\mu g/kg) = \frac{Q_{is} \times (A_{n1} + A_{n2})}{W \times (A_{is1} + A_{is2}) \times RRF_n}$$

12.1.2. Water matrices:

$$\text{Conc. } (ng/L) = \frac{Q_{is} \times (A_{n1} + A_{n2})}{V \times (A_{is1} + A_{is2}) \times RRF_n}$$

Where:

A_{n1}, A_{n2} =integrated ion abundances (peak area) of the quantitation ions of the isomer of interest (TABLE 2).

A_{is1}, A_{is2} =integrated ion abundances (peak areas) of the quantitation ions of the appropriate internal standard (TABLE 2).

***NOTE:** In instances where peak heights are used to evaluate ion abundance ratios due to interference (see Section 11.5.4), substitute peak heights for areas in the formula above.*

W =weight of sample extracted, in grams.

V =volume of sample extracted, in liters.

Q_{is} = quantity of the appropriate internal standard added to the sample prior to extraction, ng.

RRF_n=calculated relative response factor from continuing calibration (See Section 10.6).

12.1.3. For solid matrices, the units of ng/g that result from the formula above are equivalent to µg/Kg. Using isotope dilution techniques for quantitation, the concentration data are recovery corrected, and therefore, the volume of the final extract and the injection volume are implicit in the value of Qis.

12.1.3.1.For homologues that contain only one 2,3,7,8-substituted isomer (TCDD, PeCDD, HpCDD, OCDD, TCDF, and OCDF), the RRF of the 2,3,7,8-

substituted isomer from the continuing calibration (See Section 10.6) will be used to quantitate both the 2,3,7,8-substituted isomers and the non-2,3,7,8-substituted isomers.

12.1.3.2. For homologues that contain more than one 2,3,7,8-substituted isomer (HxCDD, PeCDF, HxCDF, and HpCDF), the RRF used to calculate the concentration of each 2,3,7,8-substituted isomers will be the RRF determined for that isomer during the continuing calibration (See Section 10.6)

12.1.3.3. For homologues that contain one or more non-2,3,7,8-substituted isomers, the RRF used to calculate the concentration of these isomers will be the lowest of the RRFs determined during the continuing calibration (See Section 10.6) for the 2,3,7,8-substituted isomers in that homologue. This RRF will yield the highest possible concentration for the non-2,3,7,8-substituted isomers.

NOTE: *The relative response factors of given isomers within any homologue may be different. However, for the purpose of these calculations, it will be assumed that every non-2,3,7,8-substituted isomer for a given homologue will have the same relative response factor. In order to minimize the effect of this assumption on risk assessment, the 2,3,7,8-substituted isomer with the lowest RRF was chosen as representative of each homologue. All relative response factor calculations for the non-2,3,7,8-substituted isomers in a given homologue are based on that isomer.*

12.2. In addition to the concentrations of specific isomers, the total homologue concentrations are also reported. Calculate the total concentration of each homologue of PCDDs/PCDFs as follows:

Total Concentration = sum of the concentrations of every positively identified isomer of each PCDD/PCDF homologue.

12.2.1. The total must include the non-2,3,7,8-substituted isomers as well as the 2,3,7,8-substituted isomers that are also reported separately.

12.3. If the area of any internal standard in a diluted sample is less than 10% of the area of that internal standard in the continuing calibration standard, then the unlabeled PCDD/PCDF concentrations in the sample shall be estimated using the formula below. The purpose is to ensure that there is an adequate MS response for quantitation in a diluted sample. A smaller

aliquot of the sample may require smaller dilutions and therefore yield a larger area for the internal standard in the homogeneity of the sample and the representativeness of the aliquot take for extraction.

12.3.1. All matrices other than water:

$$\text{Conc. } (\mu g/Kg) = \frac{Q_{rs} \times (A_{n1} + A_{n2}) \times D}{W \times (A_{rs1} + A_{rs2}) \times RRF_{rs}}$$

12.3.2. Water matrices:

$$\text{Conc. } (ng/L) = \frac{Q_{rs} \times (A_{n1} + A_{n2}) \times D}{V \times (A_{rs1} + A_{rs2}) \times RRF_{rs}}$$

D = Dilution factor (See Section 11.4).

(See Section 10.5.5 and 12.1 for identification of the rest of the terms.)

12.3.2.1. **For Method 8280A:** The RRF_{rs} method of quantitation is only used when the sample is diluted to the extent that the S/N ratio for the internal standard is less than 10.0.

12.4. Report results for soil/sediment, fly ash, and chemical waste samples in micrograms per kilograms (µg/Kg) or nanograms per gram (ng/g) and water samples in nanograms per liter (ng/L).

12.5. Calculate the percent recovery for each internal standard and the cleanup standard in the sample extract, R_{is}, using the following formula:

$$R_{is} = \frac{(A_{is1} + A_{is2}) \times Q_{rs}}{(A_{rs1} + A_{rs2}) \times RRF_{is} \times Q_{is}} \times 100\%$$

(See Section 10.5.5 and 12.1 for identification of the terms.)

***NOTE:** When calculating the recovery of the ^{37}Cl-2,3,7,8-TCDD cleanup standard, only one m/z is monitored for this standard; therefore only one peak will be used in the numerator of this formula. Use <u>both</u> peak areas if the 13C-1,2,3,4-TCDD recovery standard in the denominator.*

12.6. Sample Specific Estimated Detection Limit

12.6.1. The sample specific Estimated Detection Limit (EDL) is the estimate made by the laboratory of the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. The estimate is specific to a particular analysis of the sample and will be affected by sample size, dilution, etc.

12.6.2. An EDL is calculated for each 2,3,7,8-substituted isomer that is not identified, regardless of whether or not non-2,3,7,8-substituted isomers in that homologue are present. The EDL is also calculated for 2,3,7,8-substituted isomers giving responses for both the quantitation ions that are less than 2.5 times the background level.

12.6.3. Using the formula below to calculate an EDL for each absent 2,3,7,8-substituted PCDD/PCDF. The background level (H_x) is determined by measuring the height of the noise at the expected retention times of both quantitation ions of the particular 2,3,7,8-substituted isomer. The expected retention time is determined from the most recent analysis of the CC3 standard on the same GC/MS system.

12.6.3.1. All matrices other than water:

$$\text{EDL } (\mu g/kg) = \frac{2.5 \times Q_{is} \times (H_{x1} + H_{x2}) \times D}{W \times (H_{is1} + H_{is2}) \times RRF_n}$$

12.6.3.2. Water matrices:

$$\text{EDL } (ng/L) = \frac{2.5 \times Q_{is} \times (H_{x1} + H_{x2}) \times D}{V \times (H_{is1} + H_{is2}) \times RRF_n}$$

Where:

H_{x1}, H_{x2} =Peak heights of the noise for both of the quantitation ions of the 2,3,7,8-substituted isomer of interest.

H_{is1}, H_{is2} =Peak heights of both the quantitation ions of the appropriate internal standards.

D =Dilution factor (See Section 11.4).
(See Section 12.1 for Q_{is}, RRF_n, W, and V)

NOTE: If the congener class is non-detect, the largest relative response factor (RRF) for that class will be used to calculate the congener's estimated detection limit.

12.7. Estimated Maximum Possible Concentration (EMPC)

12.7.1. An estimated maximum possible concentration is calculated for 2,3,7,8-substituted isomers that are characterized by the response with a S/N of at least 2.5 for both the quantitation ions, but that do not meet all the identification criteria in Section 11.5.

12.7.2. Calculate the EMPC according to the following formula:

12.7.2.1. All matrices other than water:

$$\text{EMPC } (\mu g/L) = \frac{(A_{x1} + A_{x2}) \times Q_{is} \times D}{(A_{is1} + A_{is2}) \times RRF_n \times W}$$

12.7.2.2. Water:

$$\text{EMPC(ng/L)} = \frac{(A_{x1} + A_{x2}) \times Q_{is} \times D}{(A_{is1} + A_{is2}) \times RRF \times V}$$

Where:

A_{x1}, A_{x2} = areas of both quantitation ions. (See Section 10.5.5 and 12.1 for identification of the rest of the terms.)

12.8. Toxicity Equivalency Factor (TEF) Calculation

12.8.1. The 2,3,7,8-TCDD toxicity equivalence of PCDDs/PCDFs present in the sample is calculated according to the method recommended by the Chlorinated Dioxins Workgroup (CDWG) of the EPA and the Centers for Disease Control (CDC). This method assigns a 2,3,7,8-TCDD toxicity equivalency factor to each of the seventeen 2,3,7,8-substituted PCDDs/PCDFs shown in TABLE 1. The 2,3,7,8-TCDD toxicity equivalence of the PCDDs/PCDFs present in the sample are calculated by summing the product of the TEF and the concentration for each of the compounds listed in TABLE 1.

12.8.2. The exclusion of homologues such as mono-, di-, tri-, and the non-2,3,7,8-substituted isomers in the higher homologues does not mean that they are not toxic. Their toxicity, as estimated at this time, is much less that the toxicity of the compounds listed in TABLE 1. Hence, only 2,3,7,8-substituted isomers are included in the TEF calculations. The procedure for calculating the 2,3,7,8-TCDD toxic equivalence cited above is not claimed by the CDWG to be based on a thoroughly established scientific foundation. Rather, the procedure represents a "Consensus Recommendation on Science Policy."

12.8.3. When calculating the 2,3,7,8-TCDD toxicity equivalence of a sample, include only those 2,3,7,8-substituted isomers that were detected in the sample and met all of the qualitative identification criteria in Section 11.5. Do not include EMPC or EDL values in the TEF calculations.

12.8.4. The 2,3,7,8-TCDD toxicity equivalence of a sample is used to determine when second column confirmation may be required.

12.9. Due to a variety of situations that may occur during method performance, the laboratory is required to reextract and reanalyze certain samples or groups of samples. Except in the case of dilutions, the term "rerun" shall indicate sample extraction, cleanup, and reanalysis. When dilutions are required, the original extract shall be diluted and reanalyzed.

12.9.1. When the rerun is required due to matrix effects, interferences, or other problems encountered, the client, upon authorization to perform, will pay the laboratory for the reruns. When the rerun is required due to laboratory materials, equipment or instrumentation problems, or lack of laboratory adherence to specified method procedures, then the rerun shall not be billable.

12.9.2. The following sample reruns may be required as defined below:

12.9.2.1. If the original sample has a percent recovery of any internal standard or the cleanup standard outside of the range of 25-150%, then reextraction and reanalysis is required, upon client approval

12.9.2.2. If the internal standards are not present with at least a 10/1 S/N ratio at their respective m/zs (316, 318, 332, 334, 402, 404, 420, 422, 470, and 472), the reextraction and reanalysis are required. If the ^{37}Cl-2,3,7,8-TCDD is not present with at least a 10/1 S/N ratio at m/z 328, then reextraction and reanalysis may be required.

NOTE: If the congener class is non-detect, the largest relative response factor (RRF) for that class will be used to calculate the congener's estimated detection limit.

12.7. Estimated Maximum Possible Concentration (EMPC)

12.7.1. An estimated maximum possible concentration is calculated for 2,3,7,8-substituted isomers that are characterized by the response with a S/N of at least 2.5 for both the quantitation ions, but that do not meet all the identification criteria in Section 11.5.

12.7.2. Calculate the EMPC according to the following formula:

12.7.2.1. All matrices other than water:

$$\text{EMPC } (\mu g/L) = \frac{(A_{x1} + A_{x2}) \times Q_{is} \times D}{(A_{is1} + A_{is2}) \times RRF_n \times W}$$

12.7.2.2. Water:

$$\text{EMPC}(ng/L) = \frac{(A_{x1} + A_{x2}) \times Q_{is} \times D}{(A_{is1} + A_{is2}) \times RRF \times V}$$

Where:

A_{x1}, A_{x2} = areas of both quantitation ions. (See Section 10.5.5 and 12.1 for identification of the rest of the terms.)

12.8. Toxicity Equivalency Factor (TEF) Calculation

12.8.1. The 2,3,7,8-TCDD toxicity equivalence of PCDDs/PCDFs present in the sample is calculated according to the method recommended by the Chlorinated Dioxins Workgroup (CDWG) of the EPA and the Centers for Disease Control (CDC). This method assigns a 2,3,7,8-TCDD toxicity equivalency factor to each of the seventeen 2,3,7,8-substituted PCDDs/PCDFs shown in TABLE 1. The 2,3,7,8-TCDD toxicity equivalence of the PCDDs/PCDFs present in the sample are calculated by summing the product of the TEF and the concentration for each of the compounds listed in TABLE 1.

12.8.2. The exclusion of homologues such as mono-, di-, tri-, and the non-2,3,7,8-substituted isomers in the higher homologues does not mean that they are not toxic. Their toxicity, as estimated at this time, is much less that the toxicity of the compounds listed in TABLE 1. Hence, only 2,3,7,8-substituted isomers are included in the TEF calculations. The procedure for calculating the 2,3,7,8-TCDD toxic equivalence cited above is not claimed by the CDWG to be based on a thoroughly established scientific foundation. Rather, the procedure represents a "Consensus Recommendation on Science Policy."

12.8.3. When calculating the 2,3,7,8-TCDD toxicity equivalence of a sample, include only those 2,3,7,8-substituted isomers that were detected in the sample and met all of the qualitative identification criteria in Section 11.5. Do not include EMPC or EDL values in the TEF calculations.

12.8.4. The 2,3,7,8-TCDD toxicity equivalence of a sample is used to determine when second column confirmation may be required.

12.9. Due to a variety of situations that may occur during method performance, the laboratory is required to reextract and reanalyze certain samples or groups of samples. Except in the case of dilutions, the term "rerun" shall indicate sample extraction, cleanup, and reanalysis. When dilutions are required, the original extract shall be diluted and reanalyzed.

12.9.1. When the rerun is required due to matrix effects, interferences, or other problems encountered, the client, upon authorization to perform, will pay the laboratory for the reruns. When the rerun is required due to laboratory materials, equipment or instrumentation problems, or lack of laboratory adherence to specified method procedures, then the rerun shall not be billable.

12.9.2. The following sample reruns may be required as defined below:

12.9.2.1. If the original sample has a percent recovery of any internal standard or the cleanup standard outside of the range of 25-150%, then reextraction and reanalysis is required, upon client approval

12.9.2.2. If the internal standards are not present with at least a 10/1 S/N ratio at their respective m/zs (316, 318, 332, 334, 402, 404, 420, 422, 470, and 472), the reextraction and reanalysis are required. If the ^{37}Cl-2,3,7,8-TCDD is not present with at least a 10/1 S/N ratio at m/z 328, then reextraction and reanalysis may be required.

12.9.2.3. If any of the internal standard ion abundance ratios as specified in TABLE 5 are outside the method specified control limits, the laboratory must reanalyze the sample extract on a second GC column with different elution characteristics. No reextraction is required for such an analysis. **For Method 8280A, this section is not applicable.**

12.9.2.4. If the absolute retention time of either the 13C-1,2,3,4-TCDD or 13C-1,2,3,7,8,9-HxCDD recovery standard in a sample extract shifts by greater than 10 seconds from the retention time of that standard in the continuing calibration standard, then the sample extract must be reanalyzed after the laboratory has investigated the cause of the retention time shift and taken corrective action. No reextraction is required for such an analysis. **For Method 8280A, this section is not applicable.**

12.9.3. If the calculated concentration of the unlabeled PCDDs/PCDFs exceeded the initial calibration range, the sample shall be diluted and reanalyzed. See Section 11.4 for specific corrective actions.

12.9.4. The following sample reruns shall be performed at the laboratory's expense and shall <u>not</u> be billable under the terms of the contract:

12.9.4.1. All positive samples associated with a contaminated method blank <u>and</u> any samples which contain peaks that do not meet all of the qualitative identification criteria in Section 11.5 associated with a contaminated method blank must be reextracted and reanalyzed. Acceptable laboratory method blanks must not contain any chemical interference or electronic noise at the m/z of the specified unlabeled PCDD/PCDF ions that is greater than five percent of the signal of the appropriate internal standard quantitation ion. A peak that meets identification criteria in the method blank must not exceed two percent of the signal of the appropriate internal standard. **For Method 8280A, this section is not applicable.**

12.9.4.2. If the chromatographic peak separation between 13C-2,3,7,8-TCDD and 13C-1,2,3,4-TCDD is not resolved with a valley of $\leq$ 25% on the DB-5 (or equivalent) column, or 2,3,7,8-TCDD is not resolved from the closest eluting isomer with a valley of $\leq$ 25% on the SP-2331 (or equivalent) column, then the laboratory shall adjust the GC/MS operating conditions and rerun the affected sample. This criterion applies to sample analyses. If this criterion is not met for a <u>calibration standard</u>, all associated samples

must be rerun. **There is no TCDD resolution criteria for method 8280A.**

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 expertise.

14. POLLUTION PREVENTION

14.1. No solvents of any kind or in any amount are to be disposed of in the sinks or evaporated in the hoods.

15. WASTE MANAGEMENT

15.1. Waste management in the procedure must be segregated and disposed of according to the waste streams defined in the facility hazardous waste management procedures, Attachment B, Chemical Hygiene Plan, Section WS002, Table 1, current edition.

15.2. Samples and other solutions containing high concentrations of toxic materials must be disposed of according to the facility hazardous waste management procedures, Attachment B of the Chemical Hygiene Plan, Section WS003, Disposal of Samples After Analysis, current edition.

16. REFERENCES

16.1. Chemical Hygiene Plan, Attachment B, Hazardous Waste Management Procedures, current edition.

16.2. Document Number DFLM 01.0, including Revision DFLM 01.1 (September 1991).

16.3. Update of Toxicity of Equivalency Factors (TEFs) for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-dioxins and Dibenzofurans (CDDs/CDFs), EPA 625/3-89/016 (March 1989).

16.4. SW-846, Method 8280A, Update III, December 1996.

17. MISCELLANEOUS

17.1. Deviations from reference method(s).

17.1.1. The levels of pentachlorinated dioxins and furans are at 0.25, 0.625, 1.25, 2.5 and 5.0 in the calibration solutions as opposed to the method specified levels of 0.1, 0.25, 0.5, 1.0 and 2.0. (See TABLE 4) This adjustment aligns the calibration solutions with the CRQLs.

17.1.2. The levels of the hexa- to heptachlorinated isomers were adjusted from 1.25 ng/µL to 0.5 ng/µL in the window defining mixture. (See TABLE 6)

17.1.3. Tridecane was replaced with tetradecane.

17.1.4. The stock solution concentrations and volumes added to extracts were adjusted for ease of application.

17.1.5. NaCl and KOH were replaced with deionized water and NaOH for the acid-base washing procedure.

17.2. List of other SOPs cross-referenced in SOP.

17.3. Facility-specific information required to implement SOP.

17.4. Record Management and Documentation. (Sample bench sheets, logbook pages, data review checklists, etc.).

TABLE 1

Target Compound List (TCL) and Contract Required Quantitation Limits① (CRQL)

PCDD/PCDF	CAS Number	Water (ng/L)	Soil (µg/Kg)	Fly Ash (µg/Kg)	Chemical Waste② (µg/Kg)
2,3,7,8-TCDD	1746-01-6	10	1.0	1.0	10
2,3,7,8-TCDF	51207-31-9	10	1.0	1.0	10
1,2,3,7,8-PeCDF	57117-41-6	25	2.5	2.5	25
1,2,3,7,8-PeCDD	40321-76-4	25	2.5	2.5	25
2,3,4,7,8-PeCDF	57117-31-4	25	2.5	2.5	25
1,2,3,4,7,8-HxCDF	70648-26-9	25	2.5	2.5	25
1,2,3,6,7,8-HxCDF	57117-44-9	25	2.5	2.5	25
1,2,3,4,7,8-HxCDD	39227-28-6	25	2.5	2.5	25
1,2,3,6,7,8-HxCDD	57653-85-7	25	2.5	2.5	25
1,2,3,7,8,9-HxCDD	19408-74-3	25	2.5	2.5	25
2,3,4,6,7,8-HxCDF	60851-34-5	25	2.5	2.5	25
1,2,3,7,8,9-HxCDF	72918-21-9	25	2.5	2.5	25
1,2,3,4,6,7,8-HpCDF	67562-39-4	25	2.5	2.5	25
1,2,3,4,6,7,8-HpCDD	35822-46-9	25	2.5	2.5	25
1,2,3,4,7,8,9-HpCDF	55673-89-7	25	2.5	2.5	25
OCDD	3268-87-9	50	5.0	5.0	50
OCDF	39001-02-0	50	5.0	5.0	50

① All CRQL values listed here are based on the wet weight of the sample.

② The matrices included are oils, stillbottoms, oily sludge, wet fuel oil, oil-laced soil, and surface water heavily contaminated with the above-mentioned matrices.

TABLE 2

Ions Specified for Selected Ion Monitoring for PCDDs/PCDFs

Analyte	Quantitation Ions		M- [COCl]+
TCDD	320	322	259
PeCDD	356	358	293
HxCDD	390	392	327
HpCDD	424	426	361
OCDD	458	460	395
TCDF	304	306	243
PeCDF	340	342	277
HxCDF	374	376	311
HpCDF	408	410	345
OCDF	442	444	379
Internal Standards			
13C-2,3,7,8-TCDD	332	334	---
13C-1,2,3,6,7,8-HxCDD	402	404	---
13C-OCDD	470	472	---
13C-2,3,7,8-TCDF	316	318	---
13C-1,2,3,4,6,7,8-HpCDF	420	422	---
Recovery Standards			
13C-1,2,3,4-TCDD	332	334	---
13C-1,2,3,7,8,9-HxCDD	402	404	---
Cleanup Standard			
^{37}Cl-2,3,7,8-TCDD	328	③	263
Polychlorinated Diphenyl Ethers			

Analyte	Quantitation Ions		M- [COCl]+
HxCDPE	376	---	---
HpCDPE	410	---	---
OCDPE	446	---	---
NCDPE	480	---	---
DCDPE	514	---	---

③ There is only one quantitation ion monitored for the cleanup standard.

TABLE 3

Relationship of Internal Standards to Analytes and Relationship of Recovery Standards to Analytes, Internal Standards and Cleanup Standard

Internal Standards vs. Analytes

13C-TCDD	13C-HxCDD	13C-OCDD	13C-TCDF	13C-HpCDF
TCDD	HxCDD	OCDD	TCDF	HxCDF
PeCDD	HpCDD	OCDF	PeCDF	HpCDF

Recovery Standards vs. Analytes, Internal Standards, and Cleanup Standard

13C-1,2,3,4-TCDD	13C-1,2,3,7,8,9-HxCDD
TCDD	HxCDD
TCDF	HxCDF
PeCDD	HpCDD
PeCDF	HpCDF
	OCDD
	OCDF
13C-2,3,7,8-TCDD	13C-1,2,3,6,7,8-HxCDD
13C-2,3,7,8-TCDF	13C-1,2,3,4,6,7,8-HpCDF
^{37}Cl-2,3,7,8-TCDD	13C-OCDD

TABLE 4

Concentration Calibration Solutions

Analyte	CC1	CC2	CC3	CC4	CC5
2,3,7,8-TCDD	0.1	0.25	0.5	1.0	2.0
2,3,7,8-TCDF	0.1	0.25	0.5	1.0	2.0
1,2,3,7,8-PeCDF	0.25	0.625	1.25	2.0	5.0
1,2,3,7,8-PeCDD	0.25	0.625	1.25	2.0	5.0
2,3,4,7,8-PeCDF④	---	---	1.25	---	---
1,2,3,4,7,8-HxCDF④	---	---	1.25	---	---
1,2,3,6,7,8-HxCDF	0.25	0.625	1.25	2.5	5.0
1,2,3,4,7,8-HxCDD④	---	---	1.25	---	---
1,2,3,6,7,8-HxCDD	0.25	0.625	1.25	2.5	5.0
13C-1,2,3,4-TCDD	0.5	0.5	0.5	0.5	0.5
13C-1,2,3,7,8,9-HxCDD	0.5	0.5	0.5	0.5	0.5
^{37}Cl-2,3,7,8-TCDD④	---	---	0.25	---	---
1,2,3,4,7,8,9-HpCDF④	---	---	1.25	---	---
1,2,3,4,6,7,8-HpCDF	0.25	0.625	1.25	2.5	5.0
1,2,3,4,6,7,8-HpCDD	0.25	0.625	1.25	2.5	5.0
OCDD	0.5	1.25	2.5	5.0	10.0
OCDF	0.5	1.25	2.5	5.0	10.0
13C-2,3,7,8-TCDD	0.5	0.5	0.5	0.5	0.5
13C-2,3,7,8-TCDF	0.5	0.5	0.5	0.5	0.5
13C-1,2,3,6,7,8-HxCDD	0.5	0.5	0.5	0.5	0.5
13C-1,2,3,4,6,7,8-HpCDF	1.0	1.0	1.0	1.0	1.0

Analyte	CC1	CC2	CC3	CC4	CC5
13C-OCDD	1.0	1.0	1.0	1.0	1.0
13C-1,2,3,4-TCDD	0.5	0.5	0.5	0.5	0.5
13C-1,2,3,7,8,9-HxCDD	0.5	0.5	0.5	0.5	0.5
^{37}Cl-2,3,7,8-TCDD④	---	---	0.25	---	---

④ Do not perform %RSD calculations on these analyses; however, these compounds are added to every calibration solution.

All concentrations are in ng/µL

TABLE 5

Criteria for Isotopic Ratio Measurements for PCDDs/PCDFs

Analyte	Selected Ions	Theoretical Ion Abundance	Control Limits
TCDD	320/322	0.77	0.65-0.89
PeCDD	356/358	1.55	1.32-1.78
HxCDD	390/392	1.24	1.05-1.43
HpCDD	424/426	1.04	0.88-1.20
OCDD	458/460	0.89	0.76-1.02
TCDF	304/306	0.77	0.65-0.89
PeCDF	340/342	1.55	1.32-1.78
HxCDF	374/376	1.24	1.05-1.43
HpCDF	408/410	1.04	0.88-1.20
OCDF	442/444	0.89	0.76-1.02
Internal Standards			
13C-2,3,7,8-TCDD	332/334	0.77	0.65-0.89
13C-1,2,3,6,7,8-HxCDD	402/404	1.24	1.05-1.43
13C-OCDD	470/472	0.89	0.76-1.01
13C-2,3,7,8-TCDF	316/318	0.77	0.65-0.89
13C-1,2,3,4,6,7,8-HpCDF	420/422	1.04	0.88-1.20
Recovery Standards			
13C-1,2,3,4-TCDD	332/334	0.77	0.65-0.89
13C-1,2,3,7,8,9-HxCDD	402/404	1.24	1.05-1.43

TABLE 6

PCDD/PCDF Isomers in the Window Defining Mix for A 60M DB-5 (or equivalent) Column

Homologue	First Eluted	Last Eluted	Approximate Concentration (ng/µL)
TCDD	1,3,6,8-	1,2,8,9-	0.5
TCDF	1,3,6,8-	1,2,8,9-	0.5
PeCDD	1,2,4,7,9-	1,2,3,8,9-	0.5
PeCDF	1,3,4,6,8-	1,2,3,8,9-	0.5
HxCDD	1,2,4,6,7,9-	1,2,3,4,6,7-	0.5
HxCDF	1,2,3,4,6,8-	1,2,3,4,8,9-	0.5
HpCDD	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-	0.5
HpCDF	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-	0.5

TABLE 7

Matrix Spiking Solution

Analyte	Concentration (ng/µL)
2,3,7,8-TCDD	0.5
2,3,7,8-TCDF	0.5
1,2,3,7,8-PeCDF	1.25
1,2,3,7,8-PeCDD	1.25
1,2,3,6,7,8-HxCDF	1.25
1,2,3,6,7,8-HxCDD	1.25
1,2,3,4,6,7,8-HpCDF	1.25
1,2,3,4,6,7,8-HpCDD	1.25
OCDD	2.5
OCDF	2.5

This solution is prepared in isooctane (or nonane) and diluted with acetone prior to use. Only the ten isomers listed above will be used for evaluation. All seventeen 2,3,7,8-substituted isomers are incorporated into the matrix spike solution.

TABLE 8

Internal Standard, Recovery Standard, and Cleanup Standard Solutions

Internal Standards	**Stock Solution Concentration (ng/L)**	**Vol. Added to Sample (µL)**	**Final Amount (ng)**
13C-2,3,7,8-TCDD	0.5	100	50
13C-2,3,7,8-TCDF	0.5	100	50
13C-1,2,3,6,7,8-HxCDD	0.5	100	50
13C-1,2,3,4,6,7,8-HpCDF	1.0	100	100
13C-OCDD	1.0	100	100
Recovery Standards	**Concentration (ng/µL)**	**Vol. Added to Sample (µL)**	**Final Amount (ng)**
13C-1,2,3,4-TCDD	0.5	50	25
13C-1,2,3,7,8,9-HxCDD	0.5	50	25
Cleanup Standard	**Concentration (ng/µL)**	**Vol. Added to Extract (µL)**	**Final Amount (ng)**
^{37}Cl-2,3,7,8-TCDD	0.25	100	25

TABLE 9

Example Analytical Sequences

Time	Analysis
	Window Defining Mix
	Column Performance Solution (SP-2331)
Hour 0	CC3
	CC1 (Initial Calibration)
	CC2
	CC4
	CC5
	Blanks and Samples
Within 12 hour period	CC1
Hour 12	Column Performance Solution (SP-2331)
	CC3
	Blanks and Samples
Within 12 hour period	CC1
Hour 24	Column Performance Solution (SP-2331)
	CC3
	Blanks and Samples
	etc...
End of sequence	CC1

TABLE 10

Operating Conditions Guidelines	
Column Coating	DB-5 (or SP-2331)
Film Thickness	0.25 µm
Column Dimensions	60 m x 0.32 mm
Helium Linear Velocity	35-40 cm/sec at 240°C
Initial Temperature	170°C
Initial Time	5 min.
Temperature Program	increase to 310°C at 4°C/min.
Hold Time	until OCDF elutes

APPENDIX I

List of Analytes and Detection Limits

Analyte	Soil MDL	Water MDL
2,3,7,8-TCDF	See QAMP facility appendix.	
2,3,7,8-TCDD		
1,2,3,7,8-PnCDF		
2,3,4,7,8-PnCDF		
1,2,3,7,8-PnCDD		
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		

APPENDIX II

Operating Instruction for the Finnigan - Mat. 4500

I. System Check-Out and Startup

A. Vacuum

1. High vacuum should be in the 10^{-6} to 10^{-8} range with a capillary column installed and all other gases shut off.

2. Normal column head pressure should be 08-12 psi for 30m narrow bore columns and 18-20 psi for 60m wide bore columns.

B. Temperatures

1. Manifold temperature: 100°C

2. Transfer line temperature: This temperature should be set high enough to allow the last eluting compound to have good peak shape. Approximate temperatures at 10°C above the final column temperature.

3. Ion source temperature: 150°C, LED blinking

C. RF Generator

1. Verify that all lights are on for various power supplies.

2. Depress multiple mass maker button on scope module. Check that these mass markers extend to the full range.

D. Tuning

1. Place the GC/MS in the manual mode by entering SS, type: EM1, Fl1 and CA1 to turn on multiplier, filament, and cal gas.

2. Check to see if the following conditions are met:

a) Filament: ON

b) EM voltage/DS: ON

c) Dynode: ON

d) Helium GC Carrier: ON

e) Cal Gas: ON

f) Vacuum Protect: ON

g) Interface Power: ON

h) MS/MS Control Module: ON

3. Set up the GC/MS with m/z 219 and m/z 502 on the split screen.

4. Tune for the following:

a) Peak shape

b) Resolution

c) Peak intensities

d) Using the Quad offsets, offset programs, lenses and magnet

II. System Shutdown

A. Check to see that the following conditions are met:

1. Filament: OFF

2. EM voltage/DS: STBY

3. Dynode: ON

4. Helium GC Carrier: ON

5. Cal Gas: OFF

6. Vacuum Protect: ON

7. Interface power: ON

8. MS/MS Control Module: ON

APPENDIX III

Basic Maintenance

I. Removal of the Ion Source

A. Venting the Manifold

1. Turn the filament OFF; the dynode and multiplier to STBY

2. Turn the ionizer heater OFF by dialing in 00 on the thumbwheel switches. Allow the ionizer to cool about 0.5 hour.

3. Turn the Vacuum Protect and Ion Gauge OFF

4. Turn OFF the turbos; then the mechanical pumps.

5. Insert the backfill plug assembly into the solid inlet port.

6. Open the solids inlet valve and wait for the pressure to equalize.

B. Loosen the O-ring fitting on the inlet evacuation solenoid and disconnect the ionizer cable and cal gas cables from the front flange assembly.

C. Loosen and remove all but the top one of the flange bolts.

D. Holding the front flange firmly, remove the last flange bolt.

E. Looking through the viewing port, remove the source, being careful not to scrape it against the transfer line.

II. Steps to Cleaning the Source

A. Refer to pages 6-3 through 6-9 in the 4500 series GC/MS operators manual.

III. Installation of the Ion Source

A. Check to see that the copper gasket is in good condition. If not, replace it.

B. Check with an ohmmeter that the lens leads are not touching each other.

C. Slip the O-ring nut and O-ring over the inlet evacuation line.

D. Carefully take the ionizer flange assembly in two hands and insert the ionizer into the vacuum manifold. Looking through the viewing port, guide the flange into place.

E. Put in the bolts and hand-tighten.

F. Wrench-tighten the bolts using the opposite bolt technique.

G. Fasten the inlet evacuation line to the solenoid.

H. Re-evacuating the manifold.

1. Turn on the mechanical pumps and turbomolecular pumps by pressing MECH Pumps and TURBO Pumps.

2. When the manifold fore pressure is reduce to at least 0.04 torr and the turbopump is at least 80%, start the ion gauge.

3. With the ion gauge operating, place the system in the protect mode by pressing the VACUUM PROTECT button.

IV. Removing the Ion Volume

A. Make sure that the filament and electron multiplier are OFF.

B. Make sure that the release knob in the handle of the insertion/removal (I/R) tool is retracted and locked.

C. Insert the tip of the tool into the vacuum seal at the entrance of the solids inlet valve, with the guide pin in the groove of the guide bar.

D. Slide the tool in until the guide pin reaches the first step in the guide bar.

E. Tighten the seal by rotating the black vacuum seal nut clockwise until finger tight.

F. Evacuate the solids inlet valve by depressing the INLET EVAC push button on the vacuum controller.

G. Set the FOREPRESSURE switch to INLET.

H. Monitor the inlet pressure, and when it is reduced to 0.05 torr (after 5 or 10 seconds) disengage the INLET EVAC push button.

I. Open the solids inlet valve by rotating the handle fully counterclockwise.

J. Slowly slide the I/R tool collet all the way into the ion volume adapter.

K. Pull the release knob away from the handle and let it slide forward to expand the collet inside the adapter.

L. Slowly and carefully withdraw the I/R tool, with ion volume assembly attached until the guide pin reaches the offset stop.

M. Close the solids inlet valve by turning the handle fully clockwise.

N. Loosen the vacuum seal nut, rotate the pin past the offset stop, and withdraw the tool.

O. Release the ion volume by pulling back the release knob until it locks in the handle of the tool. Using clean gloves (or tweezers if it is hot), place the ion volume in the storage box provided. Close the lid to keep out dust.

V. Installing the Ion Volume

A. Ensure that the release knob is retracted and insert the collet end of the I/R tool into the adapter of the selected ion volume assembly.

B. Pull the release knob out and let it go forward so as to expand the collet. Be sure that the adapter is fully seated on the collet and that the alignment bracket orientation is correct. The forks on the alignment bracket should be on the spring near the collar of the adapter.

C. Insert the I/R tool with the ion volume assembly through the solids inlet valve as described in Section IV.

D. Carefully slide the tool through the solids inlet valve, stopping about 20 mm short of complete insertion.

E. Look through the window on the top of the manifold and make sure the collector hole is pointing straight up.

F. Slowly slide the I/R tool the rest of the way in and check the proper seating of the ion volume assembly. If it is not properly seated, slide the I/R tool back about 20 mm and make sure that the collector hold is up and the detent flats down, and the ion volume does not seat properly, it usually means there is an alignment problem.

G. Retract and lock the release knob (close the collet) and remove the tool as directed in Section IV.

H. Store the I/R tool in the accessory rack on the side of the instrument.

VI. Column Installation

A. Bring the manifold to atmospheric pressure in Section I.A. and cool the injector and transfer line.

B. Uncoil a few turns of both ends of the column from its cage.

C. Using a diamond pencil, score, and break about 6 inches from each of the sealed ends of the column.

D. Mount the on its cage inside the GC oven, and slide a 1/16 in. Swagelok nut and graphite ferrule onto the front end of the column.

E. Again, using a diamond pencil, score and break about 1 inches from the front end to ensure that no pieces of the ferrule are inside the column.

F. Insert the fused-silica capillary column into the bottom of the injector 55-60 mm.

G. Attach the 1/16 inch Swagelok nut and tighten finger-tight first, then tighten with a 5/16 inch wrench.

H. For a 30m x 0.25 mm ID fused-silica capillary column, set the column head pressure, using the pressure regulator on the front panel, to 8-12 psi. For a 60m x 0.32 mm ID, set the head pressure to 18-20 psi.

I. Using a bubble flow meter, adjust the SWEEP ADJUST valve on the front of the GC to 5 cc/min. and adjust the SPLIT ADJUST valve to 75 cc/min.

J. Slide a 1/16 inch Swagelok nut and a graphite vespel onto the detector end of the column.

K. Using a diamond pencil, score, and break about 1 inch off the end of the column to ensure that no pieces of the ferrule get into the column.

L. Using a flashlight, look through the vacuum view port and thread the column through the transfer-line to the point where it appears out the end of the transfer-line nozzle.

M. Now, thread the column to the entrance of the source block.

CAUTION: If the column is inserted too far into the source block, it will be shaved off by insertion or removal of the ion volume. This piece could end up in the instrument's vacuum system.

N. Attach the 1/16 inch Swagelok, tighten with a 5/16 inch wrench, and bring the system back to high vacuum as in Section III.H.

FIGURE 1

FIGURE 2

STL SACRAMENTO STANDARD OPERATING PROCEDURE
TITLE: METHOD 8290 - POLYCHLORINATED DIOXINS & FURANS BY HRGC/HRMS

(SUPERSEDES: SAC-ID-0005, REVISION 4.0, 9/11/98)

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1. SCOPE AND APPLICATION

1.1. This method provides procedures for the detection and quantitative measurement of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), polychlorinated dibenzo-p-dioxins (tetra- through octachlorinated homologs; PCDDs), and polychlorinated dibenzofurans (tetra- through octachlorinated homologs; PCDFs) in a variety of environmental matrices at part-per-trillion (ppt) concentrations by SW 846 Method 8290. The analytical method calls for the use of high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS) on purified sample extracts. An optional method for reporting the analytical results using a 2,3,7,8-TCDD toxicity equivalency factor (TEF) is also described. Table 1 lists the various sample types covered by this analytical protocol, the 2,3,7,8-TCDD-based method calibration limits and other pertinent information.

1.2. The sensitivity of this method is dependent upon the level of interferences within a given matrix.

1.3. This method is designed for use by analysts who are experienced with residue analysis and skilled in high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS).

1.4. Samples containing concentrations of specific congeners (PCDDs and PCDFs) that are greater than the calibration limit should be analyzed by a protocol designed for such concentrations, such as 8280A.

2. SUMMARY OF METHOD

2.1. This procedure uses matrix-specific extraction, analyte-specific cleanup, and high resolution capillary column gas chromatography/high resolution mass spectrometry (HRGC/HRMS) techniques.

2.2. If interferences are encountered, the method provides selected cleanup procedures to aid the analyst in their elimination. A simplified analysis flow chart is show in Figure 1.

2.3. A specified amount (see Table 1) of soil, sediment, fly ash, water, sludge (including paper pulp), still-bottom, fuel oil, chemical reactor residue, air sample (QFF, PUF or XAD media) or fish tissue, is spiked with a solution containing specified amounts of each of nine isotopically (^{13}C) labeled PCDDs/PCDFs listed in Table 2. The sample is then extracted according to a matrix-specified extraction procedure. The extraction procedures are: a) toluene Soxhlet extraction for soil, sediment, fly ash samples, aqueous sludges, and solid air matrices (XAD, QFF, PUF); b) methylene chloride liquid-liquid extraction for water samples; c) dilution of a

small sample aliquot in solvent for wastes/chemical products; and d) toluene (or hexane/methylene chloride) Soxhlet extraction for fish tissue.

2.4. If interferences are present, extracts may be cleaned as described below. The extracts are submitted to an acid and/or base washing treatment and dried. Following a solvent exchange step, the residue is cleaned up by column chromatography on acid/base silica, acid alumina and carbon on silica. The preparation of the final extract for HRGC/HRMS analysis is accomplished by adding 20 µL (depending on the matrix type) of a tetradecane solution containing 100 pg/µL of each of the two recovery standards 13C-1,2,3,4-TCDD and 13C-1,2,3,7,8,9-HxCDD (Table 2) to the concentrated eluate. The former is used to determine the percent recoveries of tetra- and penta-chlorinated PCDD/PCDF internal standards while the latter is used for the determination of hexa-, hepta- and octa-chlorinated PCDD/PCDF internal standard percent recoveries.

2.5. One to two µL of the concentrated extract are injected into an HRGC/HRMS system capable of performing selected ion monitoring at resolving powers of at least 10,000 (10 percent valley definition).

2.6. The identification of ten of the 2,3,7,8-substituted congeners (Table 3), for which a 13C-labeled standard is included as a spiked compound, is based on their elution at their exact retention time (-1 to +3 seconds from the respective internal or recovery standard signal) and simultaneous detection of the two most abundant ions in the molecular ion region. All other identified PCDD/PCDF congeners are identified by their relative retention times based on the daily CCV standard , and the simultaneous detection of the two most abundant ions in the molecular ion region. Confirmation is based on a comparison of the ratio of the integrated ion abundance of the molecular ion species to their theoretical abundance ratio.

2.7. Quantification of the individual congeners, total PCDDs and total PCDFs is achieved in conjunction with the establishment of a multipoint (five points) calibration curve for each homolog, during which each calibration solution is analyzed once.

3. DEFINITIONS

3.1. Definitions of terms used in this SOP may be found in the glossary of the Laboratory Quality Manual (LQM).

3.2. Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs): compounds (Figure 2) 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 4.

3.3. Homologous series: Defined as a group of chlorinated dibenzodioxins or dibenzofurans having a specific number of chlorine atoms.

3.4. Isomer: Defined by the arrangement of chlorine atoms within an homologous series. For example, 2,3,7,8-TCDD is a TCDD isomer.

3.5. Congener: Any isomer of any homologous series.

3.6. Surrogate Standards: A 13C-labeled analog or mixture of analogs that are added to the sample collection media prior to shipment toe the field.

3.7. Internal Standard: An internal standard is a 13C-labeled analog of a congener chosen from the compounds listed in Table 3. Internal standards 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 internal standards 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 internal standards may be added to act as retention time references, but they are not used for quantitation.

3.8. Recovery Standard: 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.

3.9. High-Resolution Concentration Calibration Solutions (Table 5): Tetradecane solutions containing known amounts of the 17 2,3,7,8-substituted PCDDs and PCDFs, a minimum of nine internal standards (13C-labeled PCDDs/PCDFs), and two carbon-labeled recovery standards; the set of five solutions is used to determine the instrument response of the unlabeled analytes relative to the internal standards and of the internal standards relative to the recovery standards.

3.10. Sample Fortification Solution (Table 2): A solution (isooctane or toluene) containing the nine internal standards, which is used to spike all samples before extraction and cleanup.

3.11. Recovery Standard Solution (Table 2): A tetradecane solution containing the two recovery standards, which is added to the final sample extract before HRGC/HRMS analysis.

3.12. Field Blank: A portion of a sample representative of the matrix under consideration, which is used to assess potential PCDD/F contribution from sampling and transport.

3.13. Rinsate: A portion of solvent used to rinse sampling equipment. The rinsate is analyzed to demonstrate that samples were not contaminated during sampling.

3.14. GC Column Performance Check Mixture: A tetradecane solution containing a mixture of selected PCDD/PCDF standards including the first and last eluters for each homologous series, which is used to demonstrate continued acceptable performance of the capillary column (i.e., ≤ 25 percent valley separation of 2,3,7,8-TCDD from all the other 21 TCDD isomers) and to define the homologous PCDD/PCDF retention time windows.

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. Relative Response Factor: Response of the mass spectrometer to a known amount of a native analyte relative to a known amount of an internal standard, or a known amount of internal standard to a known amount of a recovery standard.

3.17. Sample Re-extraction: Extraction of another portion of the sample followed by extract cleanup and extract analysis.

3.18. Extract Reanalysis: Instrument analysis by HRGC/HRMS of another aliquot of the final extract.

3.19. Tuning (Mass Resolution Check): Standard method used to demonstrate a static resolving power of 10,000 minimum (10 percent valley definition).

3.20. 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.

3.21. Matrix Spike Fortification Solution: Solution used to prepare the laboratory control sample, matrix spike, and matrix spike duplicate samples. It contains all unlabeled analytes listed in Table 5. The solution also contains all internal standards used in the sample fortification solution per the method

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. Re-use 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. PCDDs and PCDFs are often associated with other interfering chlorinated substances such as polychlorinated biphenyls (PCBs), polychlorinated diphenyl ethers (PCDPEs), polychlorinated naphthalenes, and polychlorinated xanthenes 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 (60m DB-5) is used to resolve as many PCDD and PCDF isomers as possible. However, no single column is known to resolve all isomers. The DB-225 column is used for the quantitation of 2,3,7,8-TCDF.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Corporate Safety Manual), laboratory coat, and chemically resistant gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.2.1. N-Dex nitrile gloves provide varying degrees of intermittent splash protection against those chemicals listed. Refer to permeation/degradation charts for the actual data.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

5.3.1. Chemicals that have been classified as **carcinogens**, or **potential carcinogens**, under OSHA include: methylene chloride.

5.3.2. Chemicals known to be **flammable** are: toluene, hexane, acetone. Hexane is also a neurotoxic agent.

5.3.3. The following materials are known to be **corrosive**: H_2SO_4, NaOH, KOH.

5.3.4. 2,3,7,8-TCDD is identified as a carcinogen, teratogen, and mutagen. Other PCDDs and PCDFs containing chlorine atoms in positions 2,3,7,8 are known to have toxicities comparable to that of 2,3,7,8-TCDD.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, 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.

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL Sacramento associate. The situation must be reported **immediately** to a laboratory supervisor.

5.7. The analyst should note that 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. If additional protection (i.e. respirators) are required, associates must notify the Environmental Health and Safety (EH&S) Coordinator. A hazard assessment must be conducted. Only the EH&S Coordinator is able to select and issue respiratory protection.

5.8. Safety practices described in Section 5.9 are adapted from EPA Method 613, Section 4 (July 1982 version).

5.9. Each laboratory must develop a strict safety program for the handling of 2,3,7,8-TCDD. The laboratory practices listed below are recommended.

5.9.1. Contamination of the laboratory will be minimized by conducting the manipulations in a fume hood.

5.9.2. 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 alcohols.

6. EQUIPMENT AND SUPPLIES

6.1. High-Resolution Gas Chromatograph/High-Resolution Mass Spectrometer/Data System (HRGC/HRMS/DS).

6.1.1. The GC must be equipped for temperature programming. All required accessories must be available, such as syringes, gases, and capillary columns. 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. 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.

6.1.2. Gas Chromatograph/Mass Spectrometer (GC/MS) Interface - The GC/MS interface components should withstand 350° C. 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. Cold spots or active surfaces (adsorption sites) in the GC/MS interface can cause peak tailing and peak broadening. It is recommended that the GC column be fitted directly into the mass spectrometer ion source without being exposed to the ionizing electron beam. Graphite ferrules should be avoided in the injection port because they may adsorb the PCDDs and PCDFs. Vespel® or equivalent ferrules are recommended.

6.1.3. Mass Spectrometer - The static resolving power of the instrument must be maintained at a minimum of 10,000 (10 percent valley). 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.

6.1.4. Data System - A dedicated data system is employed to control the rapid multiple ion monitoring process and to acquire the data. 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. Quantifications may be reported based upon computer-generated peak areas or upon measured peak heights (chart recording). The data system must be capable of acquiring data for a minimum of 10 ions in a single scan. It is also recommended to have a data system capable of switching to different sets of ions (descriptors) at specified times during an HRGC/HRMS acquisition. The data system should be able to provide hard copies of individual ion chromatograms for selected gas chromatographic time intervals. It should also be able to acquire mass-spectral peak profiles and provide hard copies of peak profiles to demonstrate the required resolving power. The data system should also permit the measurement of noise on the base line.

6.2. 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. 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. Operating conditions known to produce acceptable results with the recommended column are shown in Table 7.

6.3. Miscellaneous Equipment and Materials

The following list of items does not necessarily constitute an exhaustive compendium of the equipment needed for this analytical method.

6.3.1. Nitrogen evaporation apparatus with variable flow rate.

6.3.2. Balances capable of accurately weighing to 0.01 g and 0.0001 g.

6.3.3. Centrifuge.

6.3.4. Water bath, equipped with concentric ring covers and capable of maintaining temperature control within ± 2°C.

6.3.5. Stainless steel or glass containers large enough to hold contents of one-pint sample containers.

6.3.6. Glove box.

6.3.7. Drying oven.

6.3.8. Stainless steel spoons and spatulas.

6.3.9. Laboratory hoods.

6.3.10. Pipettes, disposable, Pasteur, 150 mm long x 5 mm ID.

6.3.11. Pipettes, disposable, serological, 10 mL, for the preparation of the carbon column specified in Section 7.1.

6.3.12. Reacti-vial, 2 mL, silanized amber glass.

6.3.13. Stainless steel meat grinder with a 3- to 5-mm hole size inner plate.

6.3.14. Separatory funnels, 125 mL.

6.3.15. Kuderna-Danish concentrator, 500 mL, fitted with 10-mL concentrator tube and three-ball Snyder column.

6.3.16. Teflon® boiling chips (or equivalent), washed with DCM before use.

6.3.17. Chromatographic column, glass, 300 mm x 10.5 mm, fitted with Teflon® stopcock.

6.3.18. Adapters for concentrator tubes.

6.3.19. Glass fiber filters.

6.3.20. Dean-Stark trap, 5 or 10 mL, with T-joints, condenser and 125 mL flask.

6.3.21. Continuous liquid-liquid extractor.

6.3.22. All-glass Soxhlet apparatus, 500 mL flask.

6.3.23. Glass funnels, sized to hold 170 mL of liquid.

6.3.24. Desiccator.

6.3.25. Solvent reservoir (125 mL), Kontes; 12.35 cm diameter (special order item), compatible with gravity carbon column.

6.3.26. Rotary evaporator with a temperature controlled water bath.

6.3.27. High speed tissue homogenizer, equipped with an EN-8 probe or equivalent.

6.3.28. 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, applying the following procedure:

6.4. Proper cleaning of glassware is extremely important because glassware may not only contaminate the samples, but may also remove the analytes of interest by adsorption on the glassware surface.

6.4.1. Glassware should be rinsed with solvent and washed with a detergent solution as soon after use as is 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.

6.4.2. After detergent washing, glassware should be immediately rinsed with acetone, toluene, hexane, and then methylene chloride.

6.4.3. Do not kiln reusable glassware in an oven as a routine part of cleaning. Kilning may be warranted after particularly dirty samples are encountered, but should be minimized, as repeated kilning of glassware may cause the formation of active sites

on the glass surface that will irreversibly adsorb PCDDs/ PCDFs.

6.4.4. Immediately prior to use, Soxhlet extraction glassware should be pre-extracted with toluene for a minimum of 3 hours.

7. REAGENTS AND STANDARDS

7.1. Column Chromatography Reagents

7.1.1. Silica Gel - Kieselgel 60 or equivalent, activate for 1 hour at 184°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 3.6 g granular carbon and 16.4 g activated silica gel; (alternatively, prepare AX-21/silica gel (5%/95%); i.e., combine 5 g precleaned AX-21 with 95 g silica gel). Activate mix for >12 hours at 130°C before use. Store at 130°C in covered flask. 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 24 mL conc. H_2SO_4 and 56 g activated silica gel. Stir and shake until free flowing. Store at room temperature.

7.1.6. 33% NaOH/silica gel - Mix 34 mL 1N NaOH and 67 g activated silica gel. Stir and shake until free flowing. Store at room temperature.

7.2. Reagents

7.2.1. Sulfuric acid, concentrated, ACS grade, specific gravity 1.84.

7.2.2. Potassium hydroxide, ACS grade, 20 percent (w/v) in distilled water.

7.2.3. Distilled water demonstrated to be free of interferents

7.2.4. Potassium carbonate, anhydrous, analytical reagent.

7.2.5. Silica gel.

7.2.6. Solution for breaking emulsions: Add 1.0L of reagent grade NaOH solution to an empty 2.0L NaOH container. Then add 1.0L of DI H2O to the container and leave the container in secondary containment with the lid off. ***(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.

7.3. Desiccating Agent

7.3.1. Sodium sulfate, granular, anhydrous.

7.4. Solvents

7.4.1. High-purity, distilled-in-glass or highest available purity: Methylene chloride, hexane, benzene, methanol, tetradecane, isooctane, toluene, cyclohexane, and acetone.

7.5. All calibration, internal standard, clean up recovery standards, and spiking solutions are stable for one year from preparation. After 1 year, solutions may be revalidated. The revalidated solution may be used for an additional year, or until there is evidence of compound degradation or concentration. The revalidation must be performed using an unexpired, not previously validated solution from a second lot or second vendor.

7.5.1. 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 1 year from the date the ampule is opened.

7.6. Calibration Solutions

7.6.1. High-Resolution Concentration Calibration Solutions (Table 5) - Five tetradecane solutions containing unlabeled (totaling 17) and carbon-labeled (totaling 16) PCDDs and PCDFs at known concentrations are used to calibrate the instrument. The concentration ranges are homolog dependent, with the lowest values associated with the tetra chlorinated dioxins and furans (0.5 pg/µL) and the highest for the octachlorinated congeners (2000 pg/µL).

7.6.2. Individual isomers that make up the high-resolution concentration calibration solutions are obtained from commercial sources and prepared in the laboratory.

These standards are traceable back to EPA-supplied standard solutions.

7.6.3. Store the calibration solutions in appropriate containers and at room temperature in the dark.

7.7. GC Column Performance Check Solution

7.7.1. This solution contains the first and last eluting isomers for each homologous series from tetra- through hepta-chlorinated congeners. The solution also contains a series of other TCDD isomers for the purpose of documenting the chromatographic resolution. The 13C-2,3,7,8-TCDD is also present. The laboratory is required to use tetradecane as the solvent and adjust the volume so that the final concentration does not exceed 100 pg/µL per congener. Table 8 summarizes the qualitative composition (minimum requirement) of this performance evaluation solution for the DB-5 column.

7.7.2. For the DB-225 column, the column performance check solution contains a series of TCDF isomers in addition to the 2,3,7,8-TCDF. The solution is injected and evaluated at the start of each analytical sequence on the DB-225 column to ensure that 2,3,7,8-TCDF is resolved from its closest eluting isomers with a baseline-to-valley ratio of ≤ 25%. Table 8 summarizes the qualitative composition (minimum requirement) of this performance evaluation solution on for the DB-225 column.

7.8. Field Surrogate Solution (air matrices)

7.8.1. This solution contains one 13C labeled (for Method TO-9/TO-9A) or five 13C labeled (for Method 0023) analogs at the nominal concentration indicated in Table . It is used to assess sample collection and recovery procedures.

7.9. Sample Fortification Solution (Internal Standard)

7.9.1. This isooctane (or toluene) solution contains the nine internal standards at the nominal concentrations that are listed in Table 2. The solution contains at least one carbon-labeled standard for each homologous series, and it is used to measure the concentrations of the native substances. (Note that 13C-OCDF is not present in the solution.)

7.10. Recovery Standard Solution

7.10.1. This tetradecane solution contains two recovery standards (13C-1,2,3,4-TCDD

and 13C-1,2,3,7,8,HxCDD). An appropriate volume of this solution will be spiked into each sample extract before the final concentration step and HRGC/HRMS analysis.

7.10 Preparation and QC of PUF material

7.10.1 The PUF material is purchased pre-cut.

7.10.2 The PUFs are rinsed by Soxhlet with methylene chloride for a minimum of 16 hours and air dried for a minimum of 2 hours in a contaminant-free area.

7.10.3 One PUF from the rinsed batch is randomly selected to be the QC sample for the batch.

7.10.4 The PUF is loaded into a pre-cleaned Soxhlet extractor charged with toulene.

7.10.5 The 1613/8290 daily internal standard solution is spiked into the PUF and it is extracted for a minimum of 16 hours.

7.10.6 The Soxhlet extract is recovered and processed according to section 11.4.

7.10.7 The batch of PUF is considered acceptable if no target analytes are detected at or above the laboratory or project specific reporting limit.

8. SAMPLE COLLECTION, PRESERVATION 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. Grab and composite samples must be collected in glass containers.

8.3. Ambient air samples are collected on a Quartz Fiber Filter followed by a glass sleeve containing a polyurethane foam plug.

8.4. Samples from stationary sources are collected on glass or quartz fiber filters and XAD-2 Resin. (See SAC-ID-0009 for sample preparation procedures).

8.5. Conventional sampling practices must be followed. Do not rinse the bottle with sample before collection. Sampling equipment must be free of potential sources of contamination.

8.6. Grinding or Blending of Fish Samples.

8.6.1. 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.

8.6.2. Hearing protection **must** be worn when grinding samples.

8.7. With the exception of the fish tissues, which must be stored at - 20°C, all samples should be stored at 4°C ± 2, extracted within 30 days and completely analyzed within 45 days of collection. The 30 day hold time is recommended. PCDDs and PCDFs have demonstrated stability for greater than one year.

8.8. All extracts must be stored capped, in the dark, at room temperature (approximately 21°C to 28°C).

8.9. Soil, Sediment or Paper Sludge (Pulp) Percent Moisture Determination.

The percent moisture of soil or sediment samples showing detectable levels (see note below) of at least one 2,3,7,8-substituted PCDD/PCDF congener is determined according to the following recommended procedure.

Generally, depending on sample availability, a 5-10 g sample, weighed to three significant figures, is used for % solids determination. The sample is then dried to constant weight at 110°C± 10 in an adequately ventilated oven. Weigh the dried solid to three significant figures. Calculate and report the percent moisture on the appropriate form. Do not use this solid portion of the sample for extraction, but instead dispose of it as hazardous waste.

$$\text{Percent Moisture} = \frac{\text{Weight of wet soil - Weight of dry soil}}{\text{Weight of wet soil}} \times 100$$

8.10. Fish Tissue Lipid Content Determination

The percent lipid of fish samples is determined as follows:

Concentrate the extract from Section 11.3.5 on a rotary evaporator until constant weight is attained. The percent lipid is calculated using the following expression:

$$\text{Percent lipid} = \frac{\text{Weight of residue from extraction (in g)}}{\text{Weight of fish tissue portion (in g)}} \times 100$$

9. QUALITY CONTROL

9.1. 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 aliquot of laboratory reagent water 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 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. The method blank contains a PUF plug prepared from the same batch as the field samples whenever possible.

9.1.1. If the accompanying samples are aqueous, use distilled water as a matrix. Take the method blank through all steps detailed in the analytical procedure.

9.1.2. Use sodium sulfate as the method blank laboratory matrix when solids are extracted. Take the MB through all steps detailed in the analytical procedure.

9.1.3. The method blank must be spiked prior to extraction with the same amount of 13C-labeled internal standards as added to samples.

9.1.4. 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.

9.1.4.1. OCDD is a ubiquitous laboratory contaminant. A method blank and the associated samples are deemed acceptable if the OCDD concentration is <5x the specified reporting limit. Flag data

appropriately. The analyst is expected to investigate and eliminate potential sources of systematic contamination.

9.1.4.2. 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.

9.1.4.3. If a target analyte is detected in the blank, but the concentration of the contaminant in the samples >10x the blank concentration, then the data may be reported, unless otherwise directed by the client. Note the action in the narrative.

9.1.5. If new batches of reagents or solvents contain interfering contaminants, purify or discard them.

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, Ottawa sand, sodium sulfate, PUF, XAD, etc.) spiked 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. 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. See QA Policy 003 for specific acceptance criteria. When associated with PUF samples, the LCS should contain a PUF plug prepared from the same batch as the field samples whenever possible.

9.2.1. A LCS is deemed acceptable if control analytes are above control limits and the associated samples are ND, unless otherwise specified by the client. Note any actions in the narrative.

9.3. A Matrix Spike/Matrix Spike Duplicate (MS/MSD or MS/SD) pair are extracted at the client's request only, or per NELAP requirements. An MS/MSD pair are aliquots of a selected field sample spiked with analytes of known identity and concentration. When requested by the client, the MS/MSD pair shall 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 spike analyte is outside control limits provided on the LIMS or by the client. Re-extraction of the blank, an LCS, the selected field sample, the MS/MSD may be required after evaluation and review. Matrix Spike/ Matrix Spike Duplicates are not generally applicable for air samples due to the

difficulty in collecting identical or representative samples. An LCS/LCSD may be extracted to show precision of the extraction and analysis process.

9.3.1. Matrix Spike (MS): A sample, which is spiked with a known amount of the matrix spike fortification solution prior to the extraction step. The recoveries of the matrix spike compounds are determined; they are used to estimate the effect of the sample matrix upon the analytical methodology.

9.3.2. Matrix Spike Duplicate (MSD): A second portion of the same sample as used in the matrix spike analysis and which is treated like the matrix spike sample.

9.3.3. Locate the sample for the MS and MSD analyses (the sample may be labeled "double volume").

9.3.4. Add an appropriate volume of the matrix spike fortification solution, adjusting the fortification level as specified in Table 1, under IS Spiking Levels.

9.3.5. Analyze the MS and MSD samples as described in Section 11.

9.3.6. The results obtained from the MS and MSD samples (percent recovery and concentrations of 2,3,7,8-substituted PCDDs/PCDFs) should agree within 20 percent relative difference. Report all results and flag outliers.

9.3.7. Internal standard recoveries are flagged if they are outside the recovery goals. Re-extraction of affected samples should be performed if signal-to-noise for any internal standard is less than 10:1.

9.4. Duplicates

9.4.1. 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. Duplicate samples are not generally applicable for air samples due to the difficulty in collecting identical or representative samples. A duplicate injection of a sample extract may be performed to display instrument precision.

9.4.1.1. The results of the laboratory duplicates (percent recovery and concentrations of 2,3,7,8-substituted PCDD/PCDF compounds)

should agree within 25 percent relative difference. Report all results and flag outliers.

9.4.2. Internal standard recoveries are flagged if they are outside the recovery goals. Re-extraction of affected samples should be performed if signal-to-noise for any internal standard is less than 10:1.

9.5. Field Blanks

9.5.1. Each batch of samples may contain a field blank sample of nominally uncontaminated soil, sediment or water that is to be processed for analysis.

9.5.1.1. Weigh a 10-g portion or use 1 L (for aqueous samples) of the specified field blank sample and add the appropriate amount of internal standard to yield 100 pg/µL in the final extract.

9.5.1.2. Extract by using the procedures described in Section 11.3. As applicable, add the appropriate amount of recovery standard to yield 100 pg/µL in the final extract. Analyze a 1-2 µL aliquot of the concentrated extract.

9.5.1.3. Calculate the concentration of 2,3,7,8-substituted PCDDs/PCDFs and the percent recovery of the internal standards.

9.6. Rinsate Samples

9.6.1. 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.

9.6.2. The rinsate sample must be processed like a regular sample.

9.6.2.1. 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.

9.6.3. Using appropriate methods, concentrate to approximately 10 mL.

9.6.4. Just 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.

9.6.5. Analyze an aliquot following the same procedures used to analyze samples.

9.6.6. Report percent recovery of the internal standard and the presence of any PCDD/PCDF compounds in pg/mL of rinsate solvent.

9.7. Surrogate/Clean Up Recovery Standard

9.7.1. A surrogate compound may be spiked into all air media samples prior to collection. For all other matrices, a clean up recovery standard is spiked following extraction and just prior to cleanup, in order to monitor relative loss of internal standard during both extraction and cleanup.

9.8. Internal Standards

9.8.1. Internal standards must be spiked into all samples, QC samples, and included in all calibrations.

9.8.2. For each sample and QC aliquot, calculate the percent recovery. The percent recovery should be between 40 percent and 135 percent for tetra-hexa 2,3,7,8-substituted internal standards, and 25 – 135 percent for hepta and octa 2,3,7,8-substituted internal standards.

9.8.3. A low or high percent recovery for a blank does not require discarding the analytical data but it may indicate a potential problem with future analytical data. Internal standard recoveries are flagged if they are outside the recovery goals. Re-extraction of affected samples should be performed if signal-to-noise for any internal standard is less than 10:1.

9.9. Recommended Corrective Actions and Troubleshooting Steps

- Verify satisfactory instrument performance.
- If possible, verify that no error was made while weighing the sample portions.
- Review the analytical procedures with the performing laboratory personnel.

9.10. Identification Criteria

9.10.1. If either one of the identification criteria appearing in Sections 11.5.4.1 is not met for an homologous series, it is reported that the sample does not contain unlabeled 2,3,7,8-substituted PCDD/PCDF isomers for that homologous series at the calculated detection limit.

9.10.2. If the criteria specified in sections 11.5.4.1 and 11.5.4.2 are not met (i.e. retention time and ion abundance ratios), that sample is presumed to contain interfering contaminants. This must be noted on the analytical report form. The sample may be rerun or the extract reanalyzed as directed by the client.

10. CALIBRATION AND STANDARDIZATION

Calibration and Standardization requires a check of mass resolution (tuning), a check of chromatographic resolution, a verification of switching times (i.e. descriptors), and a calibration curve verification.

10.1. Tuning (Mass Resolution Check)

10.1.1. The mass spectrometer must be operated in the electron ionization mode. A static resolving power of at least 10,000 (10 percent valley definition) must be demonstrated at appropriate masses before any analysis is performed. Corrective actions must be implemented whenever the resolving power does not meet the requirement.

10.1.2. Chromatography time for PCDDs and PCDFs exceeds the long-term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm (e.g., 5 ppm in mass) can have serious adverse effects on instrument performance. Therefore, a mass-drift correction is mandatory. To that effect, it is recommended to select a lock-mass ion from the reference compound (PFK is recommended) used for tuning the mass spectrometer. The selection of the lock-mass ion is dependent on the masses of the ions monitored within each descriptor. Table 6 offers some suggestions for the lock-mass ions. However, an acceptable lock-mass ion at any mass between the lightest and heaviest ion in each descriptor can be used to monitor and correct mass drifts. The level of the reference compound (PFK) metered into the ion chamber during HRGC/HRMS analyses should be adjusted so that the amplitude of the most intense selected lock-mass ion signal (regardless of the descriptor number) does not exceed 10 percent of the full-scale deflection for a given set of detector parameters. Under those conditions, sensitivity changes that might occur

during the analysis can be more effectively monitored.

NOTE: Excessive PFK (or any other reference substance) may cause noise problems and contamination of the ion source resulting in downtime for source cleaning.

10.1.3. By using a PFK molecular leak, tune the instrument to meet minimum required resolving power of 10,000 (10 percent valley) at m/z 304.9824 (PFK) or any other reference signal close to m/z 303.9016 (from TCDF). Verify that the exact mass of m/z 380.9760 (PFK) is within 5 ppm of the required value. Note that the selection of the low- and high-mass ions must be such that they provide the largest voltage jump performed in any of the five mass descriptors (Table 6).

10.1.4. Documentation of the instrument resolving power must then be accomplished by recording the peak profile of the high-mass reference signal (m/z 380.9760). The minimum resolving power of 10,000 must be demonstrated on the high-mass ion while it is transmitted at a lower accelerating voltage than the low-mass reference ion, which is transmitted at full sensitivity. The format of the peak profile representation (Figure 6) must allow manual determination of the resolution, i.e., the horizontal axis must be a calibrated mass scale (amu or ppm per division). The result of the peak width measurement (performed at 5 percent of the maximum, which corresponds to the 10-percent valley definition) must appear on the hard copy and cannot exceed 100 ppm at m/z 380.9760 (or 0.038 amu at that particular mass).

10.2. Performance Checks

10.2.1. At the beginning of each 12-hour period during which samples are to be analyzed, aliquots of the 1) GC column performance check solution and 2) high-resolution concentration calibration solution No. 3 (HRCC-3) shall be analyzed to demonstrate adequate GC resolution and sensitivity, response factor reproducibility, and mass range calibration, and to establish the PCDD/PCDF retention time windows. A mass resolution check shall also be performed to demonstrate adequate mass resolution using an appropriate reference compound (PFK is recommended). If the required criteria not met, remedial action must be taken before any samples are analyzed. The mass resolution check will be taken at the beginning and completion of an analytical sequence. An analytical sequence may contain one or more 12 hour period.

10.2.1.1. Method blanks or solvent blanks are used to demonstrate that the analytical system is free of contamination after the analysis of calibration standards or high level samples. The blank must demonstrate that the system has returned to appropriate background levels prior to continued analysis.

10.2.2. At a minimum, the ions listed in Table 6 for each of the five SIM descriptors must be monitored. Note that the PeCDF masses (M+2 & M+4) are also monitored in the first descriptor. This is because the first PeCDF isomer elutes closely to the final tetra isomer. The selection (Table 6) of the molecular ions M and M+2 for 13C-HxCDF and 13C-HpCDF rather than M+2 and M+4 (for consistency) is to eliminate, even under high-resolution mass spectrometric conditions, interferences occurring in these two ion channels for samples containing high levels of native HxCDDs and HpCDDs. It is important to maintain the same set of ions for both calibration and sample extract analyses. The recommended mass spectrometer tuning conditions are based on the groups of monitored ions shown in Table 6.

10.2.2.1. The GC column performance check mixture, high-resolution concentration calibration solutions, and the sample fortification solutions may be obtained from the EMSL-CIN. However, if not available from the EMSL-CIN, standards can be obtained from other sources, and solutions can be prepared in the laboratory. Concentrations of all solutions containing 2,3,7,8-substituted native PCDDs/PCDFs, must be verified by comparison with second-source standard solutions.

10.3. Initial Calibration

Initial calibration is required before any samples are analyzed for PCDDs and PCDFs. Initial calibration is also required if any routine calibration (Section 10.5) does not meet the required criteria listed in Section 10.6.

10.3.1. Five high-resolution concentration calibration solutions, listed in Table 5, must be used for the initial calibration.

10.3.2. Tune the instrument with PFK.

10.3.3. Inject 1 or 2 µL of the GC column performance check solution and acquire SIM mass spectral data as described earlier in Section 6.1.3. The total cycle time must be ≤ 1 second. The laboratory must not analyze samples until it is demonstrated and documented that the criterion listed in Section 13.1 is met.

10.3.3.1. Select the injection volume based upon the expected target analyte concentration, or expected matrix interferences.

10.3.3.2. The same injection volume must be used for all samples, QC, and standards.

10.3.4. By using the same GC and mass spectrometer conditions that produced acceptable results with the column performance check solution, analyze a 1 or 2-µL portion of each of the five concentration calibration solutions once with the following mass spectrometer operating parameter.

10.3.4.1. The total cycle time for data acquisition must be < 1 second. The total cycle time includes the sum of all dwell times and voltage reset times.

10.3.4.2. Acquire SIM data for all the ions listed in the five descriptors of Table 6.

10.3.4.3. The ratio of integrated ion current for the ions appearing in Table 9 (homologous series quantification ions) must be within the indicated control limits (set for each homologous series).

10.3.4.4. The ratio of integrated ion current for the ions belonging to the 13C labeled internal and recovery standards must be within the control limits stipulated in Table 9.

NOTE: Section 10.4.3 requires that ion ratios be within the specified control limits simultaneously in one run. It is the laboratory's responsibility to take corrective action if the ion abundance ratios are outside the limits.

10.3.5. For each SICP and for each GC signal corresponding to the elution of a target analyte and of its labeled standards, the signal-to-noise ratio (S/N) must be better than or equal to 10. This measurement is suggested for any GC peak that has an apparent S/N of less than 5:1. The result of the calculation must appear on the SICP above the GC peak in question.

10.3.5.1. Referring to Table 10, calculate the 17 relative response factors (RRF) for unlabeled target analytes [RRF(n); n=1 to 17] relative to their appropriate internal standards (Table 5) and the nine RRFs for

the labeled 13C internal standards [RRF(m); m=18 to 26] relative to the two recovery standards according to the following formulae:

$$RRF(n) = \frac{A_x \times Q_{is}}{Q_x \times A_{is}}$$

$$RRF(m) = \frac{A_{is} \times Q_{rs}}{Q_{is} \times A_{rs}}$$

Where:

A_x = sum of the integrated ion abundances of the quantitation ions (Tables 6 and 10) for unlabeled PCDDs/PCDFs,

A_{is} = sum of the integrated ion abundances of the quantitation ions (Tables 6 and 10) for the labeled internal standards,

A_{rs} = sum of the integrated ion abundances of the quantitation ions (Tables 6 and 10) for the labeled recovery standards,

Q_{is} = quantity of the internal standard injected (pg),

Q_{rs} = quantity of the recovery standard injected (pg), and

Q_x = quantity of the unlabeled PCDD/PCDF analyte injected (pg).

The RRF(n) and RRF(m) are dimensionless quantities; the units used to express Qis, Qrs, and Qx must be the same.

10.3.5.2. Calculate the RRF(n)s and their respective percent relative standard deviations (%RSD) for the five calibration solutions:

$$\overline{RRF}(n) = (1/5)\sum_{j=1}^{5} RRF_j(n)$$

Where n represents a particular PCDD/PCDF (2,3,7,8-substituted) congener (n = 1 to 17; Table 10), and j is the injection number (or calibration solution number; j = 1 to 5).

10.3.5.3. The relative response factors to be used for the determination of the concentration of total isomers in a homologous series (Table 10) are calculated as follows:

10.3.5.3.1. For congeners that belong to a homologous series containing only one isomer (e.g., OCDD and OCDF) or only one 2,3,7,8-substituted isomer (Table 4; TCDD, PeCDD, HpCDD, and TCDF), the mean RRF used will be the same as the mean RRF determined in Section 10.3.5.2.

NOTE: The calibration solutions do not contain 13C-OCDF as an internal standard. This is because a minimum resolving power of 12,000 is required to resolve the [M+6]+ ion of 13C-OCDF from the [M+2]+ ion of OCDD (and [M+4]+ from 13C-OCDF with [M]+ of OCDD). Therefore, the RRF for OCDF is calculated relative to 13C-OCDD.

10.3.5.3.2. For congeners that belong to a homologous series containing more than one 2,3,7,8-substituted isomer (Table 4), the mean RRF used for those homologous series will be the mean of the RRFs calculated for all individual 2,3,7,8-substituted congeners using the equation below:

$$\overline{RRF}(k) = (1/t)\sum_{n=1}^{t} RRF_n$$

Where:

k = 27 to 30 (Table 10), with 27 = PeCDF;
28 = HxCDF; 29 = HxCDD; and 30 = HpCDF,
t = total number of 2,3,7,8-substituted isomers present in the calibration solutions (Table 5) for each homologous series (e.g., two for PeCDF, four for HxCDF, three for HxCDD, two for HpCDF).

NOTE: Presumably, the HRGC/HRMS response factors of different isomers within a homologous series are different. However, this analytical protocol will make the assumption that the HRGC/HRMS responses of all isomers in a homologous series that do not have the 2,3,7,8-substitution patterns are the same as the responses of one or more of the 2,3,7,8-substituted isomer(s) in that homologous series.

10.3.5.4. Relative response factors [RRF(m)] to be used for the determination of the percent recoveries for the nine internal standards are calculated as follows:

$$RRF(m) = \frac{A_{is}^{m} \times Q_{rs}}{Q_{is}^{m} \times A_{rs}}$$

$$\overline{RRF}(m) = (1/5)\sum_{j=1}^{5} RRF_j(m)$$

Where:

m =	18 to 26 (congener type)
j =	1 to 5 (injection number),
A_{is}^{m} =	sum of the integrated ion abundances of the quantitation ions (Tables 6 and 10) for a given internal standard (m = 18 to 26),
A_{rs} =	sum of the integrated ion abundances of the quantitation ions (Tables 6 and 10) for a given internal standard (m = 18 to 26),
Q_{rs} & Q_{is}^{m} =	quantities of, respectively, the recovery standard (rs) and a particular internal standard (m) injected (pg),
RRF(m) =	relative response factor of a particular internal standard (m) relative to an appropriate recovery standard, as determined from one injection, and
$\overline{RRF(m)}$ =	calculated mean relative response factor of a particular internal standard, as determined from the five initial calibration injections (j).

10.4. Criteria for acceptable calibration

The criteria listed below for acceptable calibration must be met before sample analysis is performed.

10.4.1. The percent relative standard deviations for the mean response factors [RRF(n) and RRF(m)] from the 17 unlabeled standards must be ≤ 20 percent, and those for the nine labeled reference compounds must be ≤ 30 percent.

10.4.2. The signal/noise ratio (S/N) for the GC signals present in every SICP (including the ones for the labeled standards) must be ≥ 10.

10.4.3. The isotopic ratios (Table 9) must be within the specified control limits.

NOTE: If the criterion for acceptable calibration listed in Section 10.4.1 is met, the analyte-specific RRF can then be considered independent of the analyte quantity for the calibration concentration range. The mean RRFs will be used for all calculations until the routine calibration criteria (Section 10.6) are no longer met. At such time, new mean RRFs will be calculated from a new set of injections of the calibration solutions.

10.5. Routine Calibration (continuing calibration check)

Routine calibrations must be performed at the beginning of (following a successful tune and GC column performance check) and after a 12 hour period. The routine calibration initiates the 12 hour clock during which samples may be subsequently analyzed. The last sample in the sequence must be injected within 12 hours of the routine calibration, followed by the analysis of a closing calibration check. An acceptable closing calibration check standard may be used to initiate the next 12 hour analysis sequence when consecutive acquisition sequences occur. The ending mass resolution check shall be performed after the closing calibration check of an analysis acquisition sequence or after the final bracketing standard when consecutive 12 hour acquisition sequences are run.

10.5.1. Inject 1 or 2 µL of the concentration calibration solution HRCC-3 containing 10 pg/µL of tetrachlorinated congeners, 50 pg/µL of penta-, hexa-, and heptachlorinated congeners, 100 pg/µL of octachlorinated congeners, and the respective internal and recovery standards (Table 5). By using the same HRGC/HRMS conditions as used in Sections 6.1.3 through 6.2, determine and document an acceptable calibration as provided in Section 10.6.

10.6. Criteria for Acceptable Routine Calibration

The following criteria must be met before further analysis is performed. If these criteria are not met, corrective action must be taken, including recalibration if needed.

10.6.1. The measured RRFs [RRF(n) for the unlabeled standards] obtained during the opening continuing calibration must be ± 20 percent of the mean values established during the initial calibration (Section 10.3.5.)

10.6.1.1. The bracketing continuing calibration must be ± 25% of the average RRF calculated from the initial calibration.

10.6.2. The measured RRFs [RRF(m) for the labeled standards] obtained during the opening continuing calibration must be ± 30 percent of the mean values established during the initial calibration (Section 10.1.5).

10.6.2.1. The bracketing continuing calibration must be + 35% of the average RRF calculated from the initial calibration.

10.6.3. The ion-abundance ratios (Table 9) must be within the allowed control limits.

10.6.4. If either one of the above criteria (Sections 10.6.1 and 10.6.2) is not satisfied, the entire initial calibration process (Section 10.3) must be repeated. If either criteria in Sections 10.6.1.1 or 10.6.2.1 are not met, additional samples may not be analyzed. Sample data collected must be evaluated for usability. Narrate any reported data from the analytical sequence. If the ion-abundance ratio criterion is not satisfied, refer to the note in Section 10.3.4.4 for resolution.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Extraction

11.3.1. Internal Standard Addition. A 2000 pg aliquot of the internal standard mixture is added to all samples, regardless of sample size. As an example, for 13C-2,3,7,8-TCDD, a 10-g soil sample requires the addition of 2000 pg of 13C-2,3,7,8-TCDD to give the requisite fortification level.

11.3.2. Sludges. Paper Pulp Sludges are generally air-dried and ground. Because of the drying procedure, a Dean-Stark water separator is optional for extraction.

Extraction is generally done by Soxhlet with 200-300 mL of toluene.

11.3.2.1. Non-Paper Pulp Sludges are extracted with 200-300 mL of toluene.

11.3.2.2. Extract the sample for a minimum of 16 hours. Cool the sample, 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 50°C. Use of an inert gas to concentrate the extract is also permitted. Proceed with Section 11.6 as necessary.

11.3.3. 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 dissolved in 1-2 mL of an appropriate solvent; then diluted with 5-10 mL of Hexane if no acid wash is required. Spike with appropriate Internal Standards and proceed with Section 11.6 as necessary.

11.3.4. Fly Ash. Extract fly ash samples by jar shake with hydrochloric acid before Soxhlet extraction. Weigh 2-10g of sample aliquot into a clean glass jar. Add 1.0mL of the internal standard mixture with 2 mL of acetone. Add 150 mL of 1N hydrochloric acid and shake for 4 hours. If the sample reacts violently with acid, then allow the sample to equilibrate for 4 hours with no shaking. The contents of the jar are then filtered. The solids are Soxhlet extracted for 16 hours. The aqueous filtrate is extracted with 100 mL of toluene and twice with 100 mL of hexane. Concentrate the combined toluene solutions to near dryness on a rotary evaporator at 50°C. Proceed with Section 11.6 as necessary.

Note: As an option, a Soxhlet/Dean Stark extractor system may be used, with toluene as the solvent. No sodium sulfate is added when using this option.

11.3.5. Solids/Tissues. Add anhydrous sodium sulfate to the soil sample portion in a ratio of 2 to 1 (e.g. 20 g sodium sulfate to 10 g of sample) and mix thoroughly with a stainless steel spatula. After breaking up any lumps, place the soil/sodium sulfate mixture in the Soxhlet apparatus on top of a glass-wool plug (the use of an extraction thimble is optional). Add 200 to 250 mL toluene to the Soxhlet apparatus and reflux for 16 hours. The solvent must cycle completely through the system at least five times per hour. Proceed with Section 11.6.

11.3.6. Preparation of stationary source samples. See SOP SAC-ID-0009.

11.4. Preparation of Crawfish Samples

11.4.1. Prior to dissecting the crawfish, rinse the animal with reagent water.

11.4.2. Isolate the crawfish abdomen by manually pulling the abdomen away from the cephalothorax.

11.4.3. Using forceps, hold the abdomen down and make a ventral incision of the cuticle along the full length of the abdomen midline using either dissection scissors or a scalpel blade. If using a scalpel blade, cut from the hand toward the tail.

11.4.4. Hold open the abdomen midline incision and remove the abdominal flexor muscle (tail meat) with forceps and place in a weighing boat.

11.4.5. If any of the anterior portion of the abdominal flexor muscle remained in the cephalothorax, remove it with forceps and combine with the muscle portion from 11.4.4. The combined portion should yield 3-6 grams of meat.

11.4.6. With a spatula, remove a portion of the hepatopancreous from the cephalothorax. An attempt should be made to recover as much of the hepatopancreous as possible. This should yield a few hundred milligrams of tissue. (Test yielded approximately 0.5-0.8 g wet weight of hepatopancreous from medium sized crawfish.)

11.4.7. Combine the hepatopancreous with the abdominal flexor muscle tissue. (Tests yielded approximately 5 g total wet weight of combined tissue per crawfish specimen using 12-18 g animals.)

11.4.8. Repeat steps 11.4.1 through 11.4.6 with additional crawfish specimens and composite the tissue until sufficient tissue mass is acquired for sample preparation and analysis as specified in the appropriate laboratory SOPs. (The composited tissue may be required for more than just the Dioxin analysis described in this SOP).

11.4.9. Record the composited tissue mass collected.

Note: The laboratory may elect to perform a combination of Dioxin/Furans and PCBs, in which case a 20 gram aliquot of the sample will be extracted and split prior to extract cleanup.

11.4.10. Homogenize the composited tissue and proceed with removal of a sample aliquot for extraction and analysis as directed in Section 11.4.11.

11.4.11. Weigh approximately a 10 gram aliquot into an extraction thimble and record the sample weight on the extraction sheet.

11.4.12. Place the extraction thimble containing the sample in a pre-cleaned Soxhlet extractor charged with 200-220 mL of fresh toluene and boiling chips.

11.4.13. Proceed with the extraction according to section 11.3.5.

Note: If a % lipid determination is required a tared round bottom flask is used. There is no solvent keeper added prior to extract concentration by rotary evaporation and the sample is reduced to dryness and reweighed according to section 8.11. The sample is then redissolved in hexane and process to section 11.6.2.

11.4.14. Aqueous Samples. Mark the water meniscus on the side of the 1-L sample bottle for later determination of the exact sample volume. Pour the entire sample (approximately 1-L) into a 2-L separatory funnel.

11.4.14.1. 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. The internal standard mixture is first mixed in 2 mL of acetone then it is added to the sample 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 methylene chloride.

11.4.14.2. Determine the original sample volume by filling the sample bottle to the mark with water and transferring the water to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11.4.14.3. 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.

11.4.14.4. Transfer the extract to a 500-mL round-bottom, add approximately 100 µL of tetradecane and concentrate on a rotary evaporator or TurboVap.

11.4.15. A continuous liquid-liquid extractor may be used in place of a separatory funnel when experience with a sample from a given source indicates that a serious emulsion problem will result or an emulsion is encountered when using a separatory funnel.

11.4.15.1. Add 60 mL methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface.

11.4.15.2. Transfer the solvent to the extractor.

11.4.15.3. Repeat the sample bottle rinse with an additional 50- to 100-mL portion of methylene chloride and add the rinsate to the extractor.

11.4.15.4. Add 200 to 500 mL methylene chloride to the distilling flask, add sufficient reagent water to ensure proper operation, and extract for 24 hours.

11.4.15.5. Allow to cool, then detach the distilling flask.

11.4.16. Filter/PUF Samples

11.4.16.1. Place the glass sleeve containing the PUF and the Quartz Fiber Filter into the pre-cleaned Soxhlet extractor charged with toluene.

11.4.16.2. Add 2 mL (4000 pg) of 1613/8290 Internal Standard solution to all samples and QC.

11.4.16.3. Add 50 mL of 1613/8290 Native Spike to the LCS.

11.4.16.4. Extract the samples and QC for a minimum of 16 hours.

11.4.16.5. Concentrate the extract from the round bottom flask with hexane and adjust the volume.

11.4.16.6. Transfer the extract from the round bottom flask with hexane and adjust the volume.

11.4.16.7. Split the extract 50:50 for analysis and archive.

11.4.16.8. Proceed to Section 11.6.

11.5. There are several useful methods to decrease or eliminate emulsion in aqueous samples when extracting with DCM. These methods may include stirring with a pipet 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/H2O solution to change the pH enough to disrupt the emulsion phase, which works 90% of the time. See section 7.2 for reagent preparation.

11.5.1. Breaking Emulsions:

11.5.1.1. Check the pH of the sample to verify that the pH is between 3 and 7. If the pH is greater than 7, consult the supervisor and client for instructions.

11.5.1.2. Pour approximately 100 mL of the 1:1 NaOH:H_2O into a 1.0L AGB.

11.5.1.3. Drain the sample with the emulsion from the 2.0L separatory funnel into the 1L AGB and let it stand.

11.5.1.4. Empty the aqueous waste into the LLE waste drum.

11.5.1.5. Pour the solution with DCM back into the same 2.0L separatory funnel and drain the DCM phase through Na2SO4 into a 500mL roundbottom flask.

11.5.1.6. Empty the aqueous waste into the LLE waste drum.

11.5.1.7. Proceed with section 11.6.

11.6. Optional Extract Clean-Ups

11.6.1. Acid/Base Partitioning

11.6.1.1. 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).

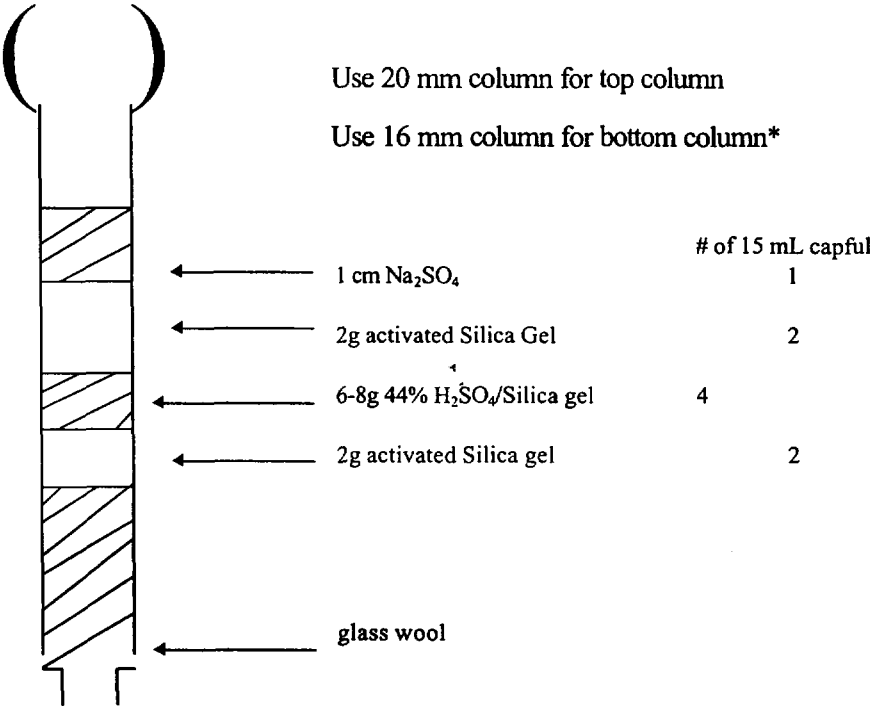
11.6.1.2. Partition the extract against 50 mL distilled H_2O. Shake for two minutes. Remove and discard the aqueous layer (bottom). If further cleanup is required, proceed to section 11.6.1.3

11.6.1.3. Partition the extract using 50 mL of 10 N NaOH. Shake for two minutes. Remove and discard the aqueous layer (bottom). Repeat the base washing until no color is visible in the bottom layer (perform a maximum of four base washings). Strong base is known to degrade certain PCDDs/PCDFs, so contact time must be minimized. The NaOH partition is applied only as samples warrant it at the discretion of the analyst.

11.6.1.4. Partition the extract against 50 mL of distilled H_2O. Shake for two minutes. Remove and discard the aqueous layer (bottom). Dry the extract by pouring it through a funnel containing anhydrous sodium sulfate and collect it in a round-bottom flask. Rinse the sodium sulfate with two 15-mL portions of hexane, add the rinsates to the flask, and concentrate the hexane solution to near dryness on a rotary evaporator (35°C water bath), making sure all traces of toluene (when applicable) are removed. (Use of blow-down with an inert gas to concentrate the extract is also permitted.) The DI H_20 partition is applied only as samples warrant it at the discretion of the analyst.

11.6.2. Silica Column Clean-Up "Exhibit A"

EXHIBIT A
IFB Column Clean-up



*Upper and lower columns are piggy backed

11.6.2.1. Pre-rinse both columns with hexane - 20 mL Top and 20 mL Bottom.

11.6.2.2. Put one column above the other.

11.6.2.3. Add extract to the top column. Rinse extract vessel 2 times with 1 mL each of hexane and add to column.

11.6.2.4. Elute 60 mL hexane directly onto acid silica column (upper piggy backed columns).

11.6.2.5. Discard upper column.

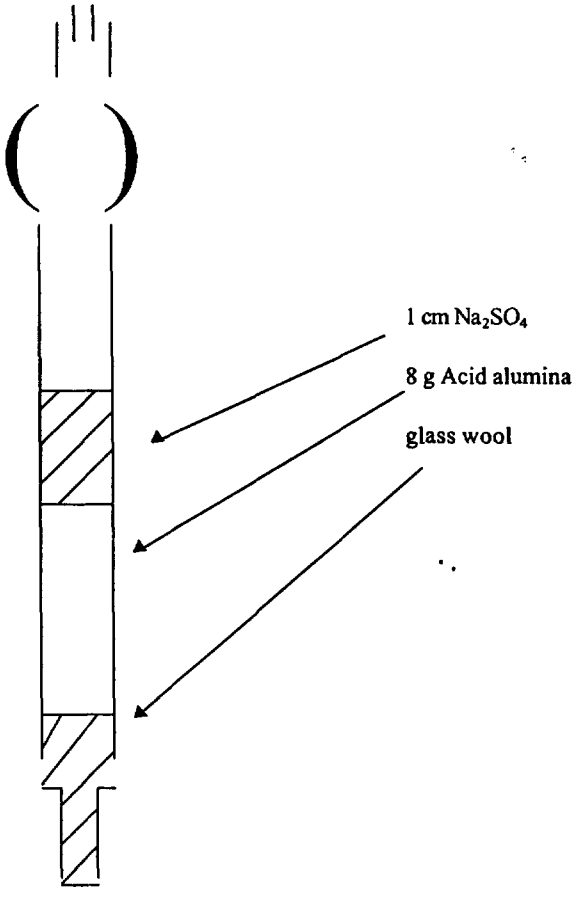
11.6.2.6. Elute lower column with 10 mL of 20% methylene chloride/hexane. Discard in proper waste stream.

11.6.2.7. Elute lower column with 30 mL of 65% methylene chloride/hexane. Save and collect in culture tube.

11.6.2.8. Proceed with additional cleanups as necessary.

11.6.3. Acid Alumina Column Clean-Up "Exhibit B"

Exhibit B
Acid Alumina Column Clean-up



11.6.3.1. Alumina activity may vary with the matrix or environmental conditions. Monitor internal standard and cleanup recovery standard recoveries in extract analysis. Low recoveries of cleanup recovery standard (CRS) may indicate loss of alumina activity. Assess stability of alumina activity and apply corrective action as appropriate (reactivate and reprofile).

11.6.3.2. Profile each vendor lot of activated alumina as corrective actions to low internal standard and CRS. recoveries dictate. If necessary, proceed as follows:

11.6.3.2.1. Set up and label 3 acid alumina columns.

11.6.3.2.2. Pre-rinse with 20 mL hexane.

11.6.3.2.3. Add 2 mL hexane spiked with internal standards and natives (spike amounts equivalent to those for LCS) with 2X2 mL hexane rinse of fractions.

11.6.3.2.4. Elute each column with 20 mL hexane. Collect and label these fractions.

11.6.3.2.5. Elute each column with 5 x10 mL methylene chloride/hexane at the appropriate v/v percent. Collect and label these fractions separately.

11.6.3.2.6. Elute each column with 10 mL of 100% methylene chloride. Collect and label these fractions. Reduce all fractions to final volume and add recovery standard.

11.6.3.3. Review data and select and elution scheme. Group the fraction from each solvent system as follows:

- Pre-analyte fraction - consists of all eluent prior to elution of first target analytes..
- Analyte fraction - consists of all which contain detectable levels of target analytes.
- Post-analyte fraction - consists of all eluents after elution of the last target analyte.

11.6.3.4. Select the solvent system which best meets the following two conditions:

- Pre-analyte fraction consists of 20 mL hexane and no more than 20 mL mixed solvent.
- Analyte fraction consists of no more than 20 mL of mixed solvent and contains greater than 90% of all target analytes and greater than 80% of all internal standards.

11.6.3.5. After selection of the appropriate solvent system and fractionation pattern, perform triplicate acid alumina cleanups on spiked hexane to ensure reproducibility of the fractionation pattern. Document each elution scheme and append to this SOP.

11.6.3.6. Each subsequent batch of acid alumina used in the lab (from the same vendor lot) must be checked for stable activity.

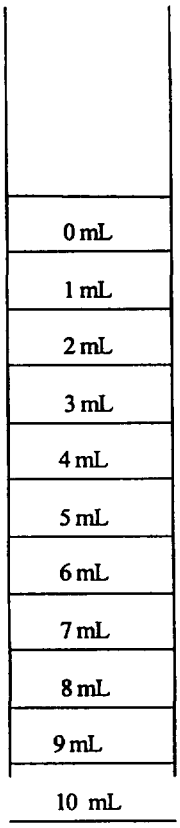
11.6.4. Carbon Column Clean-up "Exhibit C"

11.6.4.1. Prepare an activated Carbon & Silica Gel column as described in EXHIBIT C, below.

Exhibit C

Carbon Column Clean-up
Special D2

"A"



"B"

- Cut off both ends of a 10 mL pipette, or use pre-cut column.

- Push a glasswool plug down to the mark.

- Add 1g of 5% activated carbon/silica and top with another glasswool plug.

- Pre-elute with 5 mL 1:1 MeCl2:cyclohexane. Direction "A"
- Turn over and pre-elute with 5 mL 1:1 MeCl2:cyclohexane in direction "B".

- Discard pre-eluates.

- Dilute extract to 1 mL with hexane and transfer to the column.

- Rinse sample vial onto the column with 2 X 2 mL 1:1 MeCl2:cyclohexane.

- Elute with 6mL 1:1 MeCl2:cyclohexane
  5mL 75:20:5 MeCl2:MeOH:Benzene

- Discard Evaluates

-After flipping column back to the "A" direction, the column is eluted with 30 mL of toluene and collected

- N2 or roto-vap to NEAR dryness and proceed to 11.8.

11.7. Sample Dilution Procedure

11.7.1. Simple dilutions: Dilutions from 2X to 50X can be achieved without respiking the final extract. The calculation to determine the final extract concentration is as follows:

(Concentration of the original extract) x (amount of aliquot taken) x (volume of diluted extract) = final concentration of dilution.

Ex: 50X dilution of original 10 g/20 uL sample
(10 g/20 uL) x (2 ul aliquot + 98 uL keeper) = 1 g/100 uL FV

Record the final sample concentration on the extract label.

11.7.2. Complex dilution requiring respiking of IS and RS: Dilutions greater than 50x must be done by diluting and respiking the extract with IS and RS. This procedure may require serial dilution to be performed. If this procedure is done, then the sample size must be adjusted to reflect the aliquot taken.

Ex. 100X dilution (original sample with 10 g/20 uL final volume)

Take a 2 uL aliquot (1/10 of original sample) and add 18 uL of solvent keeper. Take a 2 uL aliquot of the dilution (1/100 of the original sample), respike with 1 mL IS and 20 uL RS, reduced to 20 uL FV.

Record the final sample concentration of the extract label.

11.8. Analytical Procedures

11.8.1. With a stream of dry, purified nitrogen, reduce the extract volume to 10 µL. Add 20 µL of the recovery standard solution (Table 2). With a stream of dry, purified nitrogen, reduce the extract to volume to 20 µL.

11.8.1.1. Transfer the extract to an autoinjection vial and store in the dark at room temperature.

11.8.2. Inject a 1 or 2 µL aliquot of the extract into the GC, operated under the conditions previously used (Section 6.2) to produce acceptable results with the performance check solution.

11.8.3. Acquire SIM data according to Section 6.1.3. Use the same acquisition and mass spectrometer operating conditions previously used to determine the relative response factors (Section 10). Ions characteristic for polychlorinated diphenyl ethers are included in the descriptors listed in Table 6. Their presence is used to monitor their interference during the characterization of PCDFs.

11.8.4. Identification Criteria

For a gas chromatographic peak to be identified as a PCDD or PCDF, it must meet all of the following criteria:

11.8.4.1. Retention Times

11.8.4.1.1. For 2,3,7,8-substituted congeners, which have an isotopically labeled internal or recovery standard present in the sample extract, the retention time (at maximum peak height) of the sample components (i.e., the two ions used for quantitation purposes listed in Table 6) must be within -1 and +3 seconds of the retention time of the peak for the isotopically labeled internal or recovery standard at m/z corresponding to the first characteristic ion (of the set of two; Table 6) to obtain a positive identification of these nine 2,3,7,8-substituted PCDDs/PCDFs and OCDD.

11.8.4.1.2. For 2,3,7,8-substituted compounds that do not have an isotopically labeled internal standard present in the sample extract, the relative retention time (relative to the appropriate internal standard) must fall within 0.005 relative retention time units of the relative retention times measured in the daily routine calibration. Identification of OCDF is based on its retention time relative to 13C-OCDD as determined from the daily routine calibration results.

11.8.4.1.3. For non-2,3,7,8-substituted compounds (tetra through octa; totaling 119 congeners), the retention time must be within the corresponding homologous retention time windows established by analyzing the column performance check solution.

11.8.4.1.4. The ion current responses for both ions used for quantitative purposes (e.g., for TCDDs: m/z 319.8965 and 321.8936) must reach a maximum simultaneously (± 2 seconds).

11.8.4.1.5. The ion current responses for both ions used for the labeled standards (e.g., for 13C-TCDD: m/z 331.9368 and m/z 333.9339) must reach a maximum simultaneously (± 2 seconds).

11.8.4.2. Ion Abundance Ratios

11.8.4.2.1. The integrated ion current for the two ions used for quantitation purposes must have a ratio between the lower and upper limits established for the homologous series to which the peak is assigned. See Table 9.

11.8.4.3. Signal-To-Noise Ratio

11.8.4.3.1. All ion current intensities must be >2.5 times noise level for positive identification of the PCDD/PCDF compound or a group of coeluting isomers. Figure 7 describes the procedure to be followed for the determination of the S/N.

11.8.4.4. Polychlorinated Diphenyl Ether Interferences

11.8.4.4.1. In addition to the above criteria, the identification of a GC peak as a PCDF can only be made if no signal having a S/N >2.5 is detected, at the same retention time (± 2 seconds), in the corresponding polychlorinated diphenyl ether (PCDPE, Table 6) channel.

12. DATA ANALYSIS AND CALCULATIONS

12.1. For gas chromatographic peaks that have met the criteria outlined in Section 11.5.4 calculate the concentration of the PCDD or PCDF compounds using the formula:

$$C_x = \frac{A_x \times Q_{is}}{A_{is} \times W \times RRF(n)}$$

Where:

C_x = concentration of unlabeled PCDD/PCDF congeners (or group of coeluting isomers within an homologous series) usually in pg/g or pg/L,

Ax = sum of the integrated ion abundances of the quantitation ions (Table 6) for the unlabeled PCDD/PCDFs,

Ais = sum of the integrated ion abundances of the quantitation ions (Table 6) for the labeled internal standards,

Qis = quantity, in pg, of the internal standard added to the sample before extraction,

W = sample size in g (if solid) or L (if liquid).

RRF(n) = Calculated mean relative response factor for the analyte

[RRF(n) with n = 1 to 17; Section 10.3.5].

If the analyte is identified as one of the 2,3,7,8-substituted PCDDs or PCDFs, RRF(n) is the value calculated using the equation in Section 10.3.5.1. However, if it is a non-2,3,7,8-substituted congener, the RRF(k) value is the one calculated using the equation in Section 10.3.5.3.2 [RRF(k) with k = 27 to 30].

12.2. Calculate the percent recovery of the nine internal standards measured in the sample extract, using the formula:

$$\text{Internal Standard Percent Recovery} = \frac{A_{is} \times Q_{rs}}{Q_{is} \times A_{rs} \times RRF(m)} \times 100$$

Where:

Ais = sum of the integrated ion abundances of the quantitation ions (Table 6) for the labeled internal standard,

Ars = sum of the integrated ion abundances of the quantitation ions (Table 6) for the labeled recovery standard; the selection of the recovery standard depends on the type of congeners (see Table 5, footnotes),

Qis = Quantity, in pg, of the internal standard added to the sample before extraction,

Qrs = Quantity, in pg, of the recovery standard added to the cleaned-up sample residue before HRGC/HRMS analysis, and

RRF(m) = calculated mean relative response factor for the labeled internal standard relative to the appropriate (see Table 5, footnotes) recovery standard. This represents the mean obtained in Section 10.3.5.4 [RRF(m) with m = 18 to 26].

12.3. If the concentration in the final extract of any of the fifteen 2,3,7,8-substituted PCDD/PCDF compounds (Table 3) exceeds the upper method calibration limit (MCL) for that compound listed in Table 1, the linear range of response versus concentration may have been exceeded. In such cases, the following corrective actions will be undertaken:

- If the signal for the analyte has saturated the detector, a single dilution and reanalysis of the extract will be made in an attempt to bring the signal within the range of the detector. If the measured concentration of the analyte is still above the MCL, the reported concentration for the analyte will be qualified appropriately.

- If the signal for the analyte is above the MCL but does not saturate the detector, the concentration will be reported and qualified appropriately.

In either case, **with the approval of the client**, the sample may be re-extracted and/or re-analyzed with one or more of the following adjustments made to the analytical procedure in order to provide a concentration which meets client-specific data quality objectives.

- Extraction and analysis of a one tenth aliquot. This is appropriate if it will provide analyte concentration within the MCL and will also provide a representative sample aliquot.
- Extraction of an aliquot large enough to be representative with an increased concentration of internal standard and surrogate spike components added prior to the extraction. The extract is then diluted either prior to or after the cleanup procedures.
- Dilution of the original extract. Internal standard components are re-spiked at an appropriate level prior to analysis. In this case, the internal standard recoveries are taken from the original analysis.

For the other congeners (including OCDD and OCDF), however, report the measured concentration and indicate that the value exceeds the upper calibration standard.

12.4. The total concentration for each homologous series of PCDD and PCDF is calculated by summing up the concentrations of all positively identified isomers of each homologous series. Therefore, the total should also include the 2,3,7,8-substituted congeners. The total number of GC signals included in the homologous total concentration value may be specified in the report.

12.5. Sample-Specific Estimated Detection Limit

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 signal level. An EDL is calculated for each 2,3,7,8-substituted congener that is not identified, regardless of whether or not other non-2,3,7,8-substituted isomers are present. Two methods of calculation can be used, as follows, depending on the type of response produced during the analysis of a particular sample.

12.5.1. Samples giving a response for both quantitation ions (Tables 6 and 9) that is less than 2.5 times the background level.

12.5.1.1. Use the expression for EDL (specific 2,3,7,8-substituted PCDD/PCDF) below to calculate an EDL for each absent 2,3,7,8-substituted PCDD/PCDF (i.e., S/N <2.5). The background level is determined by measuring the range of the noise (peak to peak) for the two quantitation ions (Table 6) of a particular 2,3,7,8-substituted isomer within an homologous series, in the region of the SICP trace corresponding to the elution of the internal standard (if the congener possesses an internal standard) or in the region of the SICP where the congener is expected to elute by comparison with the routine calibration data (for those congeners that do not have a 13C-labeled standard), multiplying that noise height by 2.5, and relating the product to an estimated concentration that would produce that product height.

NOTE: The quantitation ions for both the unlabeled PCDDs/PCDFs and their internal standard must be consistently paired (using either both lighter mass ions or both heavier mass ions).

Use the formula:

$$EDL_{Specific2,3,7,8-subst.PCDD\,/\,PCDF} = \frac{2.5 \times H_x \times Q_{is}}{H_{is} \times W \times RRF(n)}$$

$$\text{EDL(specific 2,3,7,8-subst. PCDD/PCDF)} = \frac{2.5 \text{ x } H_x \text{ x } Q_{is}}{H_{is} \text{ x W x RRF(n)}}$$

Where:

EDL = estimated detection limit for homologous 2,3,7,8-substituted PCDDs/PCDFs.

H_x = height of the average noise for one of the quantitation ions (Table 6) for the unlabeled PCDDs/PCDFs.

H_{is} = height of one of the quantitation ions (Table 6) for the labeled internal standards.

W, RRF (n), and Qis retain the same meanings as defined in Section 12.1

12.5.2. Samples characterized by a response above the background level with a S/N of at least 2.5 for at least one of the quantitation ions (Tables 6 and 9).

12.5.2.1. When the response of a signal having the same retention times as a 2,3,7,8-substituted congener has a S/N in excess of 2.5 and does not meet any of the other qualitative identification criteria listed in Section 11.5.4, calculate the "Estimated Maximum Possible Concentration" (EMPC) according to the expression shown in Section 12.1, except that Ax in Section 12.1 should represent the sum of the area under the smaller peak and of the other peak area calculated using the theoretical chlorine isotope ratio. Alternatively, an EDL can be calculated using the above formula and the height of one of the ions as appropriate.

12.6. The relative percent difference (RPD) is calculated as follows:

$$RPD = \frac{|S_1 - S_2|}{(S_1 + S_2)/2} \times 100$$

S_1 and S_2 represent sample and duplicate sample results.

12.7. The 2,3,7,8-TCDD toxic equivalents (TEQ) of PCDDs and PCDFs present in the sample are calculated at the data user's request. This method assigns a 2,3,7,8-TCDD toxicity equivalency factor (TEF) to each of the seventeen 2,3,7,8-substituted PCDDs and PCDFs (Table 11). The 2,3,7,8-TCDD equivalent of the PCDDs and PCDFs present in the sample is calculated by summing the TEF times their concentration for each of the compounds or groups of compounds listed in Table 11.

12.7.1. Two-GC Column TEF Determination

12.7.1.1. The concentration of 2,3,7,8-TCDD (see note below), is calculated from the analysis of the sample extract on the 60m DB-5 fused silica capillary column. The chromatographic separation of this isomer must be < 25% valley.

12.7.1.2. For samples that have a presumptive positive result for 2,3,7,8-TCDF on the DB-5 column, the extract is reanalyzed on a 30m DB-225 fused silica column. The GC/MS conditions are altered so that only the first descriptor (Table 6) is used. The reported concentration for 2,3,7,8-TCDF is then the result calculated from the DB-225 analysis. The chromatographic separation between 2,3,7,8-TCDF and any other unlabeled TCDF isomers must be < 25% valley using the column performance check solution for the DB-225 column. Concentration calculations are performed as in Section 12.1 through 12.6.

12.7.1.3. A DB-225 column can be used in the quantitative analysis of 2,3,7,8-TCDF and 2,3,7,8-TCDD analytes. Since the DB-225 cannot resolve 2,3,7,8-TCDD any positively identified 2,3,7,8-TCDD which exceeds the reporting limit shall be confirmed on a DB-5 column.

12.7.1.4. For a gas chromatographic peak to be identified as a 2,3,7,8-substituted PCDD/PCDF congener, it must meet the ion abundance (Section 11.5.4) and signal-to-noise ratio criteria. In addition, the retention time identification criterion described in Section 11.5.4 applies here for congeners for which a carbon-labeled analog is available in the sample extract. However, the relative retention time (RRT) of the 2,3,7,8-substituted congeners for which no carbon-labeled analogs are available must fall within 0.006 units of the carbon-labeled standard RRT. Experimentally, this is accomplished by using the attributions described in Table 12 and the results from the routine calibration run on the DB-5 column.

13. METHOD PERFORMANCE

It must be documented that all applicable system performance criteria specified were met before analysis of any sample is performed. Table 7 provides recommended GC conditions that can be used to satisfy the required criteria. Figure 4 provides a typical 12-hour analysis sequence. A GC column

performance check is only required at the beginning of each 12-hour period during which samples are analyzed.

13.1. GC Column Performance

13.1.1. Inject 1 or 2 µL of the column performance check solution and acquire selected ion monitoring (SIM) data as described in Section 6.1.3 within a total cycle time of < 1 second.

13.1.2. The chromatographic separation between 2,3,7,8-TCDD and the peaks representing any other TCDD isomers must be resolved with a valley of ≤ 25 percent (Figure 5),

Where:

$$\text{Valley Percent} = (x/y) \times 100$$

x = measured as in Figure 5 from the 2,3,7,8-closest TCDD eluting isomer,

y = the peak height of 2,3,7,8-TCDD

13.1.3. It is the responsibility of the laboratory to verify the conditions suitable for the appropriate resolution of 2,3,7,8-TCDD from all other TCDD isomers. The GC column performance check solution also contains the known first and last PCDD/PCDF eluters under the conditions specified in this protocol. Their retention times are used for qualitative and quantitative purposes. The peak for 2,3,7,8-TCDD must be labeled on the chromatograms. The chromatograms showing the first and last eluters of a homologous series must be included.

13.1.4. The retention times for the switching of SIM ions characteristic of one homologous series to the next higher homologous series must be indicated in the SICP. Accurate switching at the appropriate times is absolutely necessary for accurate monitoring of these compounds.

14. POLLUTION PREVENTION

14.1. No solvents/wastes of any kind or in any amount are to be disposed of in the sinks or evaporated in the hoods.

15. WASTE MANAGEMENT

15.1. Waste management in the procedure must be segregated and disposed according to the waste streams identified in the Corporate Safety Manual

15.2. Samples and other solutions containing high concentrations of toxic materials must be disposed of according to the Corporate Safety Manual.

16. REFERENCES

16.1. SW846, Test Methods for Evaluating Solid Waste, Third edition, Update III. Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by high-Resolution Mass Spectrometry September 1994.

16.2. Method 0023A, December 1996.

16.3. Protocol for the Analysis of 2,3,7,8-TCDD by HRGC/HRMS". J. S. Stanley and T. M. Sack, EPA 600/4-86-004.

16.4. "Safety in Academic Chemistry Laboratories", American Chemical Society Publication, Committee on Chemical Safety (3rd Edition, 1979.)

16.5. "Carcinogens - Working with Carcinogens". Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control. National Institute for Occupational Safety and Health. Publication No. 77-206, August 1977.

16.6. "OSHA Safety and Health Standards, General Industry", (29 CFR 1910) Occupational Safety and Health Administration, OSHA 2206 (revised January 1976).

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Deviations from reference method.

17.1.1. The method specifies that 2 µL injections are used throughout the analysis. If an instrument demonstrates adequate sensitivity and chromatographic resolution, then the analyst may use 1 µL injections for all performance checks, standards, QC samples, and samples.

17.1.2. In Section 2.7 of Method 8290, a retention time window of 0.005 RT units is used to tentatively identify unlabeled PCDD/PCDFs for which there are no

corresponding labeled internal standards. All available labeled internal standards are used; therefore, a retention time window of -1 to +3 seconds is used to identify all compounds. See Section 7.8.4.1 of Method 8290.

17.1.3. 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.

17.1.4. Extract clean-ups are performed at the discretion of the analyst when interferences are observed. Then, the analyst should select the clean-up procedure appropriate to the interferent.

17.1.5. Section 7.4.6.4 of Method 8290 indicates that extracts should be transferred with hexane, then toluene. Toluene is used to transfer extracts to maintain compound solubility and minimize analyte loss.

17.1.6. Section 7.5.1.2 of Method 8290 specifies that a NaCl solution should be used for partitioning. Instead the laboratory uses laboratory water only. NaCl is used to break up emulsions that may form. An analyst may use NaCl, NaOH, or any other mechanical means to break up an emulsion.

17.1.7. Section 7.5.3 of Method 8290 specifies that hexane is used as a column elution solvent. The laboratory uses cyclohexane to achieve better and more reproducible separation of the target analyte from the interferent.

17.1.8. Carbon columns are packed with silica gel in place of celite. Elution solvents are changed accordingly. (SOP Section 11.4; Method 8290 Section 7.5.3.2).

17.1.9. Modifications from TO-9A method

17.1.9.1. Quartz Fiber Filters are cleaned by Soxhlet extraction with methylene chloride, not baked at 400 degrees C for 5 hours.

17.1.9.2. The PUF material is pre-cleaned with methlyene chloride not acetone. The PUFs are not reused.

17.1.9.3. Samples are extracted with toluene not benzene.

17.1.9.4. Concentration is performed by rotary evaporation not Kuderna-Danish.

17.1.9.5. All cleanup procedures are optional and applied based on the analyst's discretion.

17.1.9.6. The final volume is adjusted to 20 uL in tetradecane.

17.1.9.7. Calibration and quantitation are performed in accordance to this SOP.

17.2. Summary of modifications to SOP from previous revisions

17.2.1. The SOP format was updated.

17.2.2. Modified to include extraction and analysis of ambient air samples collected in filter/PUF material.

17.2.3. Added sample dilution procedure.

17.2.4. Added extraction procedure for crawfish.

17.2.5. Added procedure to eliminate emulsions.

17.3. Tables or figures referenced in body of SOP.

17.3.1. Table 1 - Types of Matrices

17.3.2. Table 2 - Composition of The Sample Fortification and Recovery Standard Solutions.

17.3.3. Table 3 - The Fifteen 2,3,7,8-Substituted PCDD and PCDF Congeners

17.3.4. Table 4 - Isomers of Chlorinated Dioxins and Furans

17.3.5. Table 5 - Concentrations of Calibration Solutions

17.3.6. Table 6 - Ions Monitored for PCDDs/PCDFs

17.3.7. Table 7 - Recommended GC Operating Conditions

17.3.8. Table 8 - Congeners in the GC Performance Evaluation Solution (DB-5)

17.3.9. Table 9 - Theoretical Ion Abundance Ratios and Control Limits

17.3.10. Table 10 - Relative Response Factor Attributes

17.3.11. Table 11 - 2,3,7,8-TCDD Equivalent Factors

17.3.12. Table 12 - TEF: Analyte Relative Retention Time Reference Attributes

17.3.13. Figure 1 - Analysis Flowchart

17.3.14. Figure 2 - Compound Structure

17.3.15. Figure 3 - PFK Resolution Example

17.3.16. Figure 4 - Analysis Scheme

17.3.17. Figure 5 - GC Performance Check Chromatogram on the DB-5 Column

17.3.18. Figure 6 - PFK Peak Profile

17.3.19. Figure 7 - Manual Determination of Signal-to-Noise

17.3.20. Appendix A - Periodic Wipe Test Performance

TABLE 1

Types of Matrices, Sample Sizes and 2,3,7,8-TCDD-Based Method Calibration Limits (Parts per Trillion)

	Water	Soil Sediment Paper Pulp	Fly Ash	Human/ Fish Tissue	Adipose Tissue	Sludges, Fuel Oil	Still-Bottom	Ambient or Source Samples
Lower MCL(a)	0.02	2.0	2.0	2.0	2.0	10	20	40
Upper MCL(a)	4.0	400	400	400	400	2000	4000	8000
Weight (g)	1000	10	10	10	10	2.0	1.0	1 sample
IS Spiking Levels (ng)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	4.0
Final Extract Volume (µL)	20	20	20	20	20	20	20	20

(a) For other congeners, multiply the values by 1 for TCDF, by 2.5 for PeCDD/PeCDF/HxCDD/HxCDF/HpCDD/HpCDF, and by 5 for OCDD/OCDF.

TABLE 2

Composition of the Sample Fortification and Recovery Standard Solutions

Analyte	Sample Fortification Solution Concentration pg/µL; Solvent: Isooctane	Sample Fortification Solution Concentration pg/µL; Solvent: Tetradecane
13C-2,3,7,8-TCDD	10	--
13C-2,3,7,8-TCDF	10	--
13C-1,2,3,4-TCDD	--	100
13C-1,2,3,7,8-PeCDD	10	--
13C-1,2,3,7,8-PeCDF	10	--
13C-1,2,3,6,7,8-HxCDD	25	--
13C-1,2,3,4,7,8-HxCDF	25	--
13C-1,2,3,7,8,9-HxCDD	--	100
13C-1,2,3,4,6,7,8-HpCDD	25	--
13C-1,2,3,4,6,7,8-HpCDF	25	--
13C-OCDD	50	--

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-PeCDD(*)
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

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 5

High Resolution Concentration Calibration Solutions

Compound	Concentration (ng/mL)				
	CS1	CS2	CS3 (VER(6))	CS4	CS5
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
Cleanup Standard/ FS					
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	2	10	40	200
Recovery 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*

Ions Monitored for HRGC/HRMS Analysis of PCDDs/PCDFs

Descriptor	Accurate[a] Mass	Ion ID	Elemental Composition	Analyte
1	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 (S)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	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
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9338	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD (S)
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
	[354.9792]	LOCK	C_9F_{13}	PFK
2	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
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	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
	367.8949	M+2	$^{13}C_{12}H3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M+4	$^{13}C_{12}H3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD (S)
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCDPE
	[354.9792]	LOCK	C_9F_{13}	PFK
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
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8156	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
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD (S)

TABLE 6 (cont.)*

Ions Monitored for HRGC/HRMS Analysis of PCDDs/PCDFs

Descriptor	Accurate[a] Mass	Ion ID	Elemental Composition	Analyte
4	407.7818	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7788	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8250	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF (S)
	419.8220	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	423.7767	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
	435.8169	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M+4	$^{13}C_{12}H^{35}Cl_5{}^{37}CL_2O_2$	HpCDD (S)
	479.7165	M+4	$C_{12}H^{35}CL_7{}^{37}Cl_2O$	NCDPE
	[430.9728]	LOCK	C_9F_{17}	PFK
5	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	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
	469.7780	M+2	$^{13}C1_2{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M+4	$^{13}C1_2{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)
	513.6775	M+4	$^{13}C1_2{}^{35}Cl_8{}^{37}Cl_2O$	DCDPE
	[442.9728]	LOCK	$C_{10}F_{17}$	PFK

[a] The following nuclidic masses were used:

H =	1.007825	O =	15.994915
C =	12.000000	^{35}Cl =	34.968853
^{13}C =	13.003355	^{37}Cl =	36.965903
F =	18.9984		

S = Internal/recovery standard

*The homologous groups for functions 1-3 do not use the same lockmass as described in Table 6. They use masses 316.9824, 366.9792, and 380.9760, respectively.

TABLE 7

Recommended GC Operating Conditions

The GC Operating Conditions (Temperatures (°C), and Times (minutes))
Are as Follows:

Injector Temperature: 280°C

Interface Temperature: 280°C

Initial Temperature and Time: 190°C / 1 Minute

Temperature Program: 190°C, increasing at a rate of 4°C per minute up to 240°C, and maintaining at this temperature until the last of the tetra- group has eluted from the column. (The total time required for this is approximately 25 minutes, depending on the length of the column). The maintained temperature of 240°C is then increased to 320°C at the rate of 20°C per minute and held at this level until the last compound (octa-group) has eluted from the column.

TABLE 8

PCDD and PCDF Congeners Present in the GC Performance Evaluation Solution and Used for Defining the Homologous GC Retention Time Windows on a 60-M DB-5 Column[(b)]

# of Chlorine Atoms	PCDD Positional Isomer		PCDF Positional Isomer	
	Early Eluter	Late Eluter	Early Eluter	Late Eluter
4[(a)]	1,3,6,8	1,2,8,9	1,3,6,8	1,2,8,9
5	1,2,4,6,8/1,2,4,7,9	1,2,3,8,9	1,3,4,6,8	1,2,3,8,9
6	1,2,3,4,6,8	1,2,3,4,6,7	1,2,3,4,6,8	1,2,3,4.8,9
7	1,2,3,4,6,7,8	1,2,3,4,6,7,9	1,2,3,4,6,7,8	1,2,3,4,6,7,9
8	1,2,3,4,6,7,8,9		1,2,3,4,6,7,8,9	

[(a)] In addition to these two PCDD isomers, the 1,2,3,4-, 1,2,3,7-, 1,2,3,8-, 2,3,7,8-, $^{13}C_{12}$-2,3,7,8-, and 1,2,3,9-TCDD isomers must also be present.

(b) The PCDF Congeners present in GC the Performance Evaluation Solution for the 30 m DB-225 column include:

- 1,2,3,9-TCDF
- 2,3,7,8-TCDF
- 2,3,4,7-TCDF
- $^{13}C_{12}$-2,3,7,8-TCDF

Column performance criteria is met when the percent valleys between the 2,3,7,8-TCDF analyte and the closest eluting isomers are $\leq$ 25%.

TABLE 9

Theoretical Ion Abundance Ratios and Their Control Limits for PCDDs and PCDFs

# of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits	
			Lower	Upper
4	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[a]	M / M+2	0.51	0.43	0.59
7[b]	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

[a] Used only for ^{13}C-HxCDF (IS)
[b] Used only for ^{13}C-HpCDF (IS)

TABLE 10

Relative Response Factor [RRF (number)] Attributes

Number	Specific Congener Name
1	2,3,7,8-TCDD (and total TCDDs)
2	2,3,7,8-TCDF (and total TCDFs)
3	1,2,3,7,8-PeCDD (and total PeCDDs)
4	1,2,3,7,8-PeCDF
5	2,3,4,7,8-PeCDF
6	1,2,3,4,7,8-HxCDD
7	1,2,3,6,7,8-HxCDD
8	1,2,3,7,8,9-HxCDD
9	1,2,3,4,7,8-HxCDF
10	1,2,3,6,7,8-HxCDF
11	1,2,3,7,8,9-HxCDF
12	2,3,4,6,7,8-HxCDF
13	1,2,3,4,6,7,8-HpCDD (and total HpCDDs)
14	1,2,3,4,6,7,8-HpCDF
15	1,2,3,4,7,8,9-HpCDF
16	OCDD
17	OCDF
18	$^{13}C_{12}$-2,3,7,8-TCDD
19	$^{13}C_{12}$-2,3,7,8-TCDF
20	$^{13}C_{12}$-1,2,3,7,8-PeCDD
21	$^{13}C_{12}$-1,2,3,7,8-PeCDF
22	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
23	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF
24	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
25	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
26	$^{13}C_{12}$-OCDD
27	Total PeCDFs
28	Total HxCDFs
29	Total HxCDDs
30	Total HpCDFs

TABLE 11

2,3,7,8-TCDD Equivalent Factors (TEFs) for the Polychlorinated Dibenzodioxins and Dibenzofurans

Number	Compound(s)	TEF
1	2,3,7,8-TCDD	1.00
2	1,2,3,7,8-PeCDD	0.50
3	1,2,3,6,7,8-HxCDD	0.10
4	1,2,3,7,8,9-HxCDD	0.10
5	1,2,3,4,7,8-HxCDD	0.10
6	1,2,3,4,6,7,8-HpCDD	0.01
7	1,2,3,4,6,7,8,9-OCDD	0.001
8	2,3,7,8-TCDF	0.1
9	1,2,3,7,8-PeCDF	0.05
10	2,3,4,7,8-PeCDF	0.5
11	1,2,3,6,7,8-HxCDF	0.1
12	1,2,3,7,8,9-HxCDF	0.1
13	1,2,3,4,7,8-HxCDF	0.1
14	2,3,4,6,7,8-HxCDF	0.1
15	1,2,3,4,6,7,8-HpCDF	0.01
16	1,2,3,4,7,8,9-HpCDF	0.01
17	1,2,3,4,6,7,8,9-OCDF	0.001

TABLE 12

Toxicity Equivalency Factor:
Analyte Relative Retention Time Reference Attributes

Analyte	Analyte RRT Reference[a]
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF

(a) The retention time of 2,3,4,7,8-PeCDF on the DB-5 column is measured relative to $^{13}C_{12}$-1,3,7,8-PeCDF and the retention time of 1,2,3,4,7,8,9-HpCDF relative to $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF.

FIGURE 1

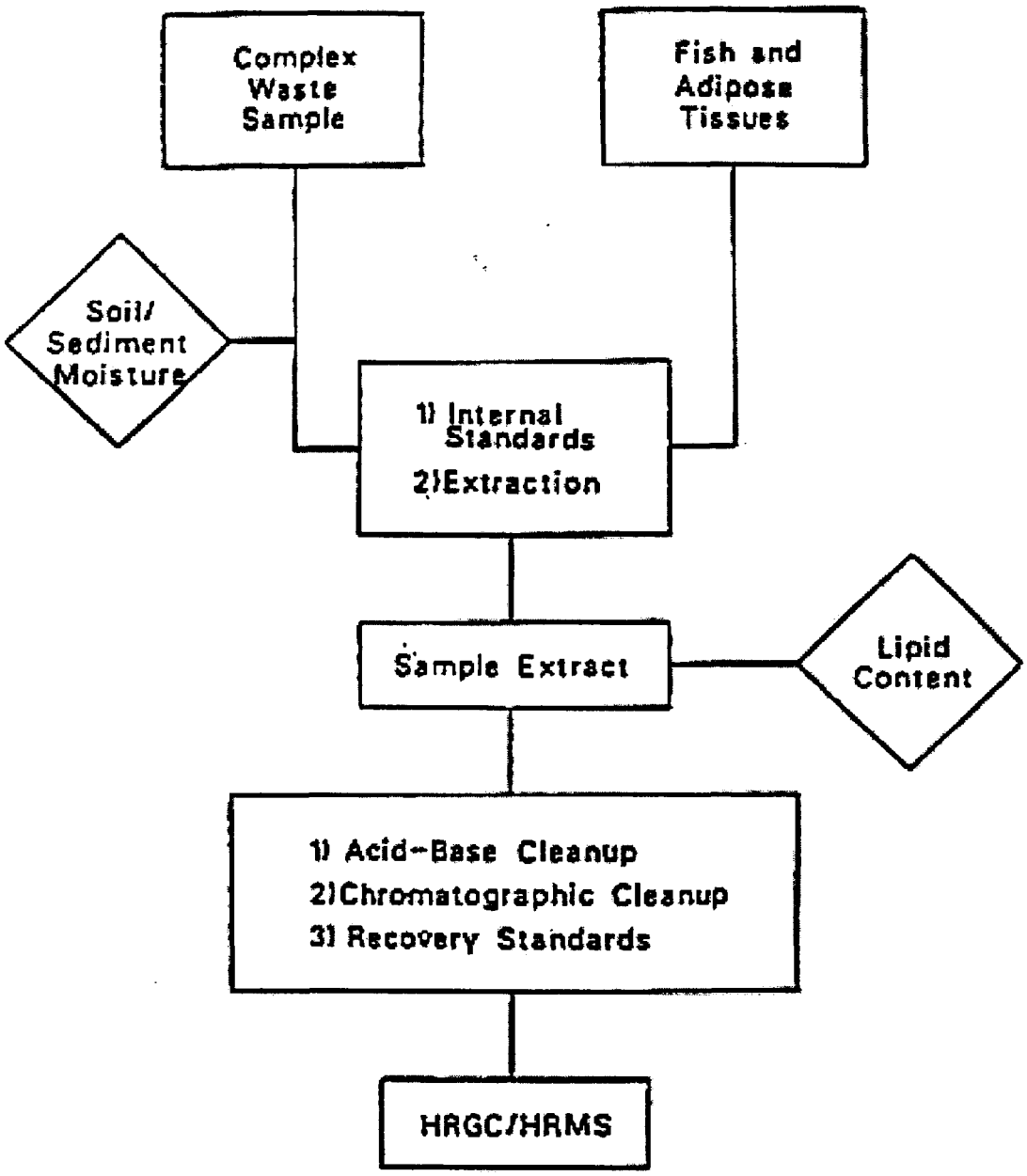
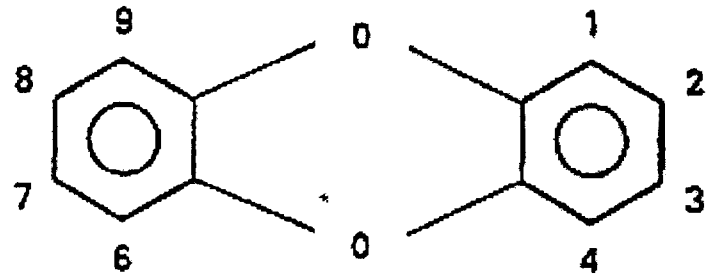
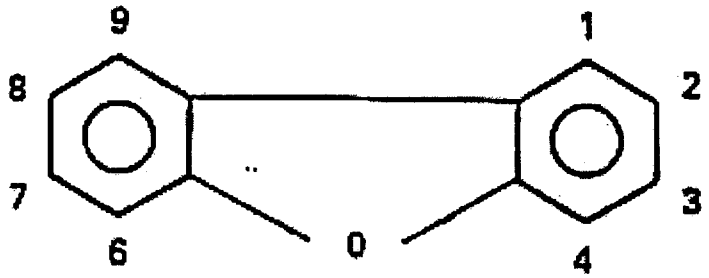

Complex Waste Sample
Fish and Adipose Tissues
Soil/ Sediment Moisture
1) Internal Standards
2) Extraction
Sample Extract
Lipid Content
1) Acid-Base Cleanup
2) Chromatographic Cleanup
3) Recovery Standards
HRGC/HRMS

FIGURE 2



Dibenzodioxin



Dibenzofuran

FIGURE 3

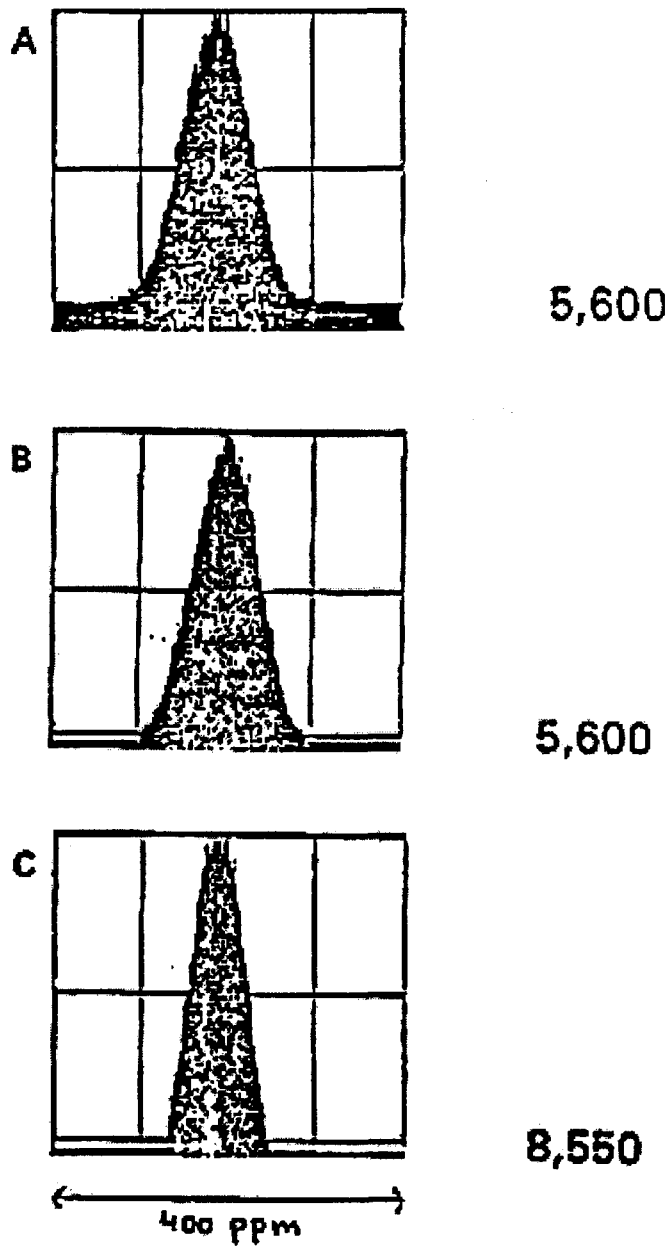


FIGURE 4
Analytical Procedure

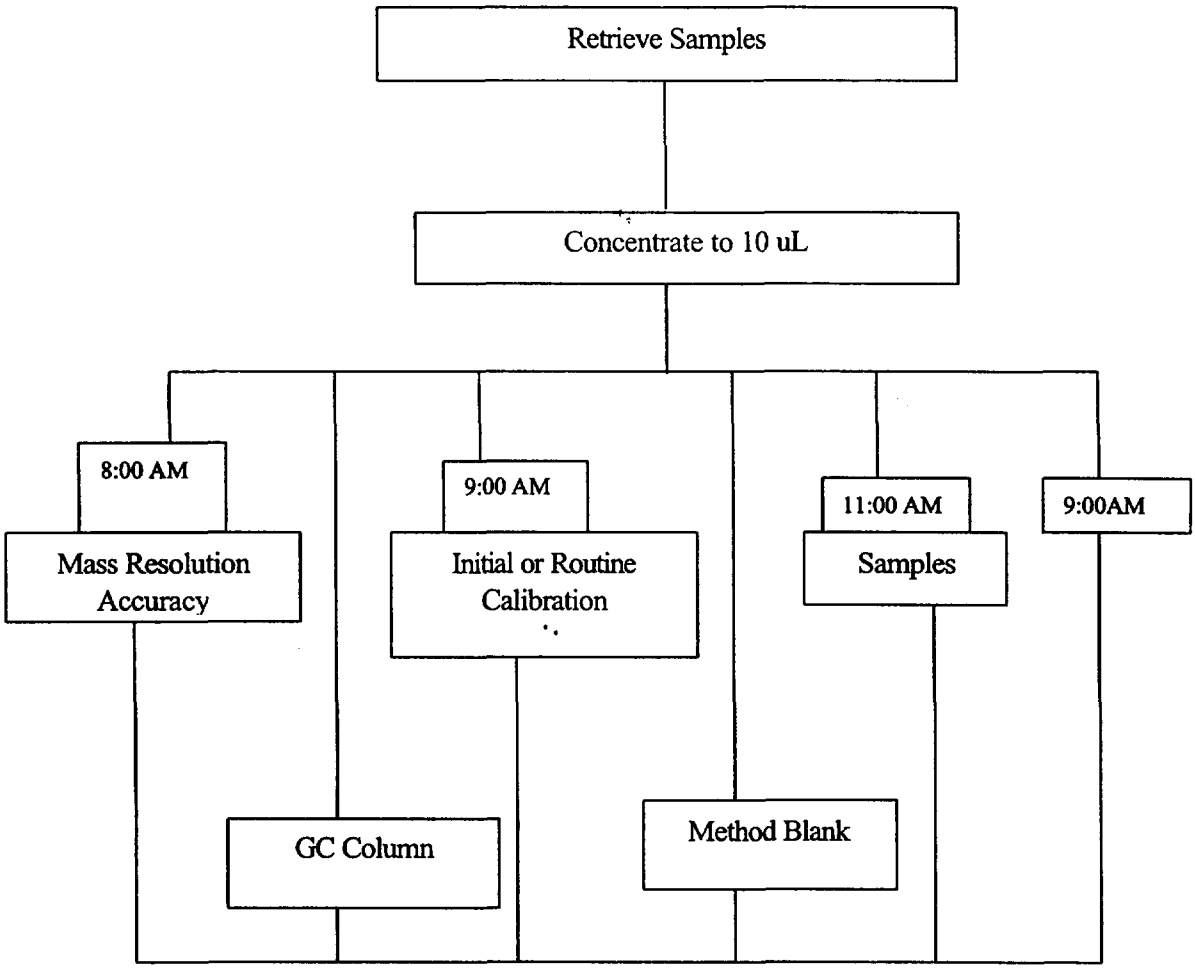
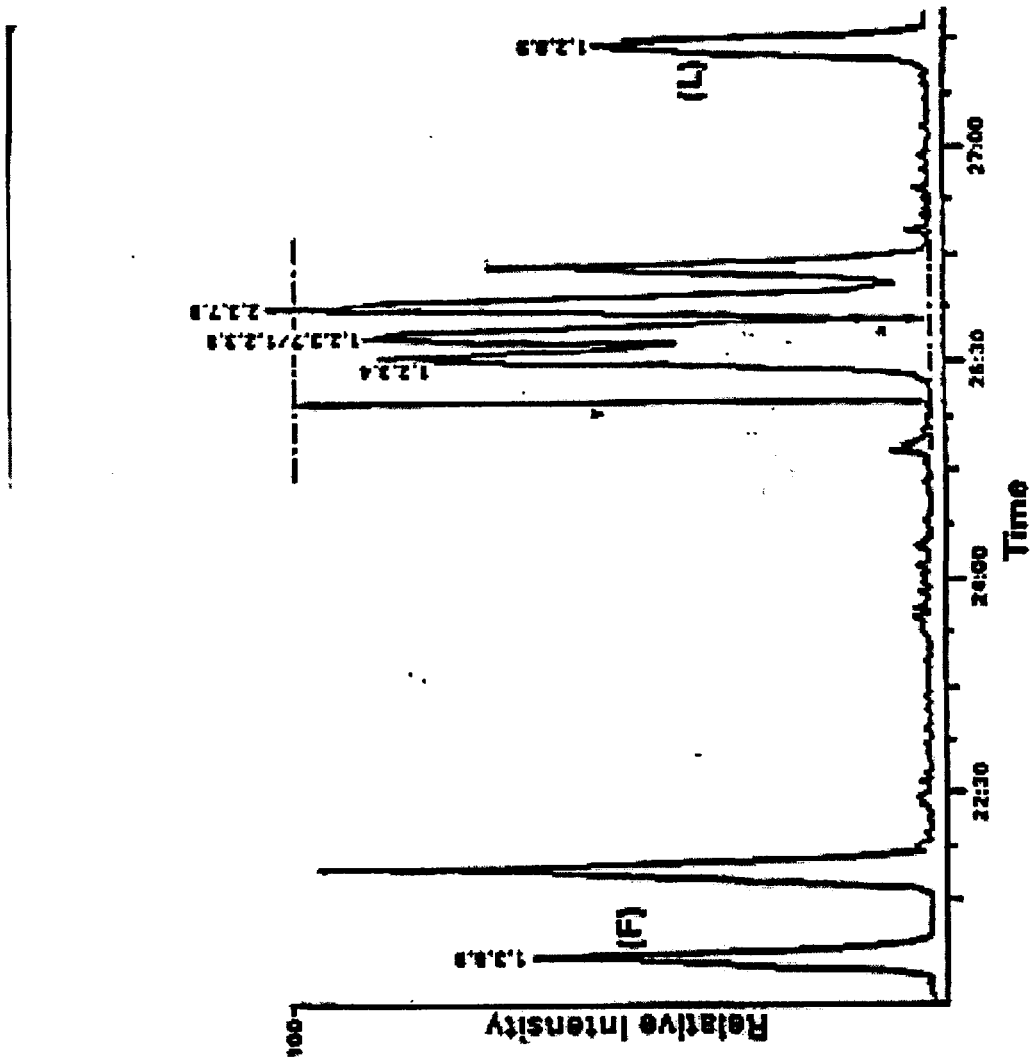
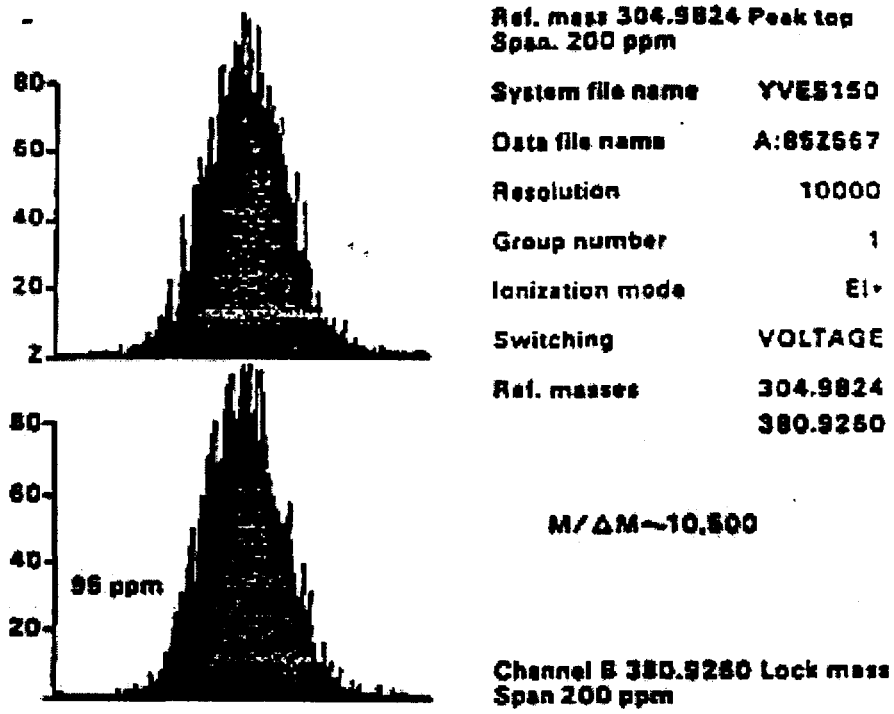


FIGURE 5



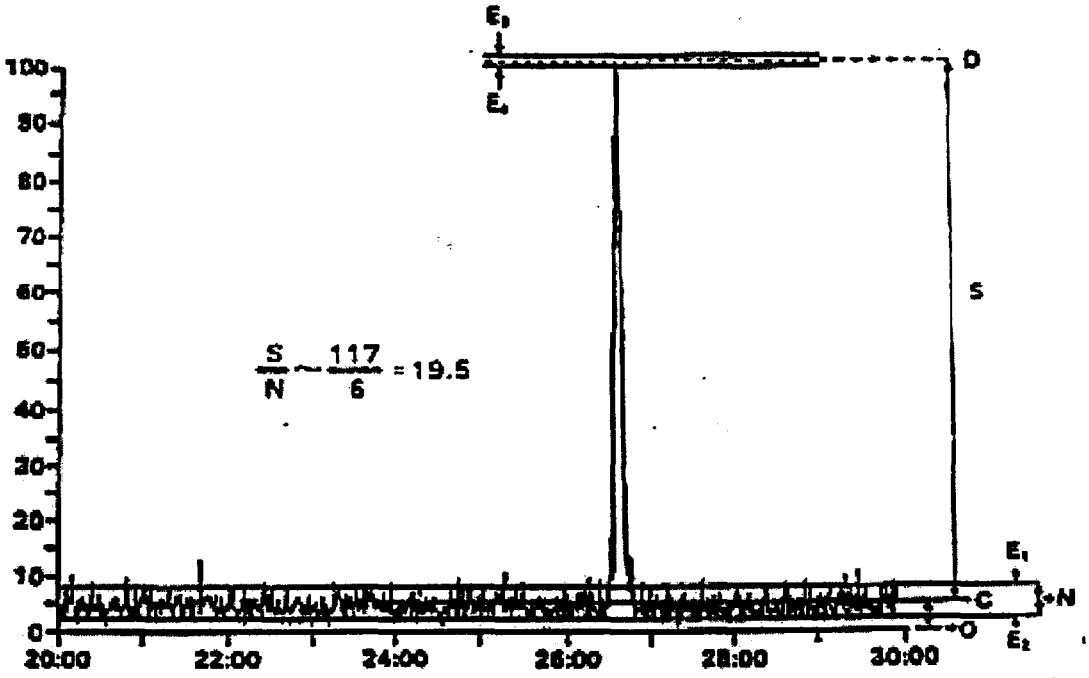
Selected ion current profile for m/z 322 (TCDDs) produced by MS analysis of the GC performance check solution on a 60 m DB-5 fused silica capillary column under the conditions listed in Section 7.6.

FIGURE 6



Peak profiles representing two PFK reference ions at m/z 305 and 381. The resolution of the high-mass signal is 95 ppm at 5 percent of the peak height; this corresponds to a resolving power M/ΔM of 10,500 (10 percent valley definition).

FIGURE 7



Manual determination of S/N.

The peak height (S) is measured between the mean noise (lines C and D). These mean signal values are obtained by tracing the line between the baseline average noise extremes, E1 and E2, and between the apex average noise extremes, E3 and E4, at the apex of the signal.

NOTE: It is imperative that the instrument interface amplifier electronic zero offset be set high enough so that negative going baseline noise is recorded.

APPENDIX A

This procedure is designed for the periodic evaluation of potential contamination by 2,3,7,8-substituted PCDD/PCDF congeners of the working areas inside the laboratory.

PERFORMING WIPE TEST

Perform the wipe tests on surface areas of two inches by one foot with laboratory wipers saturated with distilled-in-glass acetone using a pair of clean stainless steel forceps. Use one wiper for each of the designated areas. Combine the wipers to one composite sample in an extraction jar containing 200 mL distilled-in-glass hexane. Place an equal number of unused wipers in 200 mL hexane and use this as a control.

SAMPLE PREPARATION

Close the jar containing the wipers and 200 mL hexane and extract for 20 minutes using a wrist-action shaker. Use an appropriate means to reduce the volume to approximately 1.0 mL. Put through an alumina column to clean up potential interfering compounds. Add appropriate amount of recovery standard.

EXTRACT ANALYSIS

Concentrate the contents of the vial to a final volume of 20 µL (either in a minivial or in a capillary tube). Inject 2 µL of each extract (wipe and control) onto a capillary column and analyze for 2,3,7,8-substituted PCDDs/PCDFs as specified in the analytical method Section 11 (this exhibit).
Perform calculations according to Section 12 (this exhibit).

REPORTING FORMAT

Report the presence of 2,3,7,8-substituted PCDDs and PCDFs as a quantity (pg or ng) per wipe test experiment (WTE). Under the conditions outlined in this analytical protocol, a lower limit of calibration of 25 pg/WTE is expected for 2,3,7,8-TCDD. A positive response for the blank (control) is defined as a signal in the TCDD retention time window at any of the masses monitored which is equivalent to or above 8 pg of 2,3,7,8-TCDD per WTE. For other congeners, use the multiplication factors listed in Table 1, footnote (a) (e.g., for OCDD, the lower MCL is 25 x 5 = 125 pg/WTE and the positive response for the blank would be 8 x 5 = 40 pg). Also, report the recoveries of the internal standards during the simplified cleanup procedure.

FREQUENCY OF WIPE TESTS

Wipe tests should be performed when there is evidence of contamination in the method blanks.

CORRECTIVE ACTION

An upper limit of 25 pg per TCDD isomer and per wipe test experiment is allowed. (Use multiplication factors listed in footnote (a) from Table 1 for other congeners.) This value corresponds to the lower calibration limit of the analytical method. Steps to correct the contamination must be taken whenever these levels are exceeded. To that effect, first vacuum the working places (hoods, benches, sink) using a vacuum cleaner equipped with a high-efficiency particulate absorbent (HEPA) filter and then wash with a detergent. A new set of wipes should be analyzed before anyone is allowed to work in the dioxin area of the laboratory.

The test results and the decontamination procedure must be reviewed with EH&S.

Soil Gas Sampling Procedures

The following is a detailed description of the field related activities and the procedures involved in active soil gas extraction.

1. The probe borings will be advanced into the unconsolidated sediments utilizing three (3) foot probe rods, retractable point holder, and the hydraulic percussion hammer mounted on the main cylinder of the direct-push technology rig (DPT).

2. Once the desired depth has been achieved, the probe rods are pulled back a minimum of six (6) inches to insure that the retractable point or expendable point has disengaged so that a soil gas sample can be collected.

3. Connect the adapter thread coupler to a section of 0.125-inch polyethylene tubing that is lowered into the probe rods until the bottom is encountered. The tubing should extend approximately two (2) foot above the probe rods.

4. Turn the tubing in a counter-clock wise direction (left-handed threads) to engage the coupler adapter threads into the retractable point holder.

5. Connect the upper end of the polyethylene tubing to a four (4) inch section of silicone tubing, then attach to a section of polyethylene tubing coming from the active vacuum system valve on the operator control panel.

6. A vacuum will be placed in the tubing and the vacuum gauge observed to determine if a vacuum is present at the sample interval.

7. When the vacuum gauge indicates that a return to ambient pressure has been reached between the soil and the inside of the tubing, a soil gas sample can be collected.

8. Using a 60cc disposable syringe with a stainless steel needle, insert the needle into the silicone tubing section and withdraw a 60cc sample of soil gas. Make sure that the vacuum gauge returns to ambient pressure before the needle is removed from the tubing. The sample is now ready for direct injection into the on-site Gas Chromatograph (GC).

9. Remove the sample tubing from the probe rods and dispose.

10. Remove probing rods and sampling equipment from the probe boring.

11. Fill probe boring with bentonite to just below surface, charge bentonite with potable water, and restore the surface to its original condition (i.e. topsoil, asphalt, or concrete).

Hydro-LOGIC, Inc.
STANDARD OPERATING PROCEDURE
SOP No: HLI-SOP-A-015-R1
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TITLE: Method 8021

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REVISION DATE: November 6, 1998

APPROVED By: Date: 11/11/98
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President

OBJECTIVE

This Standard Operating Procedure (SOP) is intended to provide guidance for the EPA Method 8021 at the facilities of Hydro-LOGIC, Inc. (HLI). The method is used to determine the halogenated and non-halogenated volatile organics benzene, bromobenzene, bomochloromethane, bromodichloromethane, bromoform, bromomethane, *n*-butylbenzene, *sec*-butylbenzene, *tert*-butylbenzene, carbon tetrachloride, chlorobenzene, chloroethane, chloroform, chloromethane, 2-chlorotoluene, 4-chlorotoluene, 1,2-dibromo-3-chloropropane, dibromochloromethane, 1,2-dibromoethane, dibromomethane, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, dichlorodifluoromethane, 1,1-dichloroethane, 1,2-dichloroethane, 1,1-dichloroethene, cis-1,2-dichloroethene, trans-1,2-dichloroethene, 1,2-dichloropropane, 1,3-dichloropropane, 2,2-dichloropropane, 1,1-dichloropropene, ethylbenzene, hexachlorobutadiene, isopropylbenzene, 4-isopropyltoluene, methylene chloride, naphthalene, *n*-propylbenzene, styrene, 1,1,1,2-tetrachloroethane, tetrachloroethene, 1,1,2,2-tetrachloroethane, toluene, 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, 1,1,1-trichloroethane, 1,1,2-trichloroethane, trichloroethene, trichlorofluoromethane, 1,2,3-trichloropropane, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, vinyl chloride, and xylenes (o,m,p). Hydro-LOGIC, Inc. uses a fused silica capillary column for EPA Method 8021.

INTRODUCTION TO PURGE AND TRAP OPERATIONS

A. An inert gas (helium) is bubbled through 10 ml of a water sample or 2 grams of a well-blended soil sample (mixed with 10 ml of reagent water) from a 2-ounce soil jar, in a specially designed purging chamber at ambient temperature. Soil-gas samples can be directly injected onto the traps through the front of the purge port of the autosampler. The purging efficiently transfers all volatile organics to two sorbent traps where the organics are concentrated. The HLI purge and trap apparatus is an OI Analytical 4560 Purge and Trap, and the method requires two traps loaded with Carbopak B and Carbosieve II respectively. After purging is complete (40 ml/min for 5 min.), the traps are rapidly heated and backflushed with the inert gas to desorb the volatile organics onto a gas chromatographic column. The gas chromatograph is

INTRODUCTION TO PURGE AND TRAP OPERATIONS (continued)

temperature programmed to separate the volatile organics, which are then detected with a Photo Ionization Detector (PID) run in series with a Dry Electrolytic Conductivity Detector (DELCD). HLI quantifies all volatile halogenated organics with the DELCD, while the PID is used for non-halogenated volatile organics.

B. There are possible interference problems identified by the USEPA when operating this purge and trap method. These problems are as follows. (1) Impurities in the purge gas, and organic compounds outgassing from the plumbing ahead of the trap, account for the majority of contamination problems. The analytical system will be demonstrated to be free from contamination under analysis conditions by running laboratory reagent blanks. (2) Samples can be contaminated by diffusion of volatile organics through the septum seal into the sample during shipment and storage. Trip blanks carried through the sampling and handling protocol can serve as a check on such contamination. (3) Contamination by carry-over can occur when a sample with unusually high levels of halogenated organics is encountered. To reduce carry-over, the purging device and sample syringe will be rinsed with GC grade methanol, followed by reagent grade water. This is followed by an analysis of a blank, to check for carry-over, and possible bakeout of the entire purge and trap and chromatographic system at 250 °C.

C. Each standard, reagent, and/or solvent involved with this method should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by all means available. All employees qualified to perform this method will review the chemical properties and hazards associated with each standard and reagent. Material Safety Data Sheets (MSDS) are located at the offices of Hydro-LOGIC, Inc. (HLI), and have open access to all analysts and technicians involved in gas chromatographic preparations and analysis. The HLI safety manager will explain any special safety precautions involved in the method and before the analyst can perform any of the steps in the 8021 method.

EQUIPMENT AND MATERIALS

A. The HLI purge and trap system consists of three operable units: a purging device, a trap, and a desorber. The commercial purge and trap device HLI employs is an OI Analytical 4560 Purge and Trap, and the method requires two traps loaded with Carbopak B and Carbosieve II respectively. The purging device accepts samples at least 10-ml or 2-g in size for water and soils respectively. Up to 30-cc of a soil-gas (or air) sample can also be injected through the front of the purging ports. The purging device strips volatile organics from samples using ultra-high purity helium. The desorber is capable of rapidly heating to 225 °C to thoroughly desorb all volatile organics to the chromatographic column.

EQUIPMENT AND MATERIALS (continued)

B. HLI uses SRI model 8610 B & C type gas chromatographic (GC) systems for the analysis of volatile organics. These systems are capable of performing purge and trap, direct injection (split/splitless), and thermal desorption type analyses. Each GC is equipped with a FID, PID, and DELCD (dry electrolytic conductivity detector) detector. The FID and DELCD detectors are made by SRI, while the PID is a HNU-type 10.2 electron volt PID lamp supplied by Scientific Services Company. The SRI GC is temperature programmable between 0 °C and 350 °C at rates between 0.1 °C and 30 °C per minute. Additionally, all pressures are flow controlled to within 0.1 psi of the method settings.

C. HLI uses capillary columns supplied by RESTEK. The two columns commonly employed are: (1) A MXT-1 30-meter long x 0.53 mm ID Silcosteel® capillary column coated with 100% dimethyl polysiloxane; or, (2) a MXT-624 75-meter long x 0.53 mm ID Silcosteel® capillary column coated with 6% cyanopropylphenyl – 94% dimethyl polysiloxane.

D. Hamilton supplies all HLI syringes. HLI uses a 10-ml glass hypodermic syringe with Luerlok tip, and 10-ml (± 0.1-ml) boroscilicate glass pipets for sample preparation. HLI also uses 0.5, 1.0, 2.0, and 10.0-µl micro syringes for spiking samples, and introduction of standards to the GC. The vendor standardizes all HLI syringes. All syringes are rinsed with methanol and reagent water between uses. Each syringe is periodically checked for cross contamination and leakage.

E. HLI uses analytical balances capable of accurately weighing soil samples to ± 0.01-grams. Fisher Scientific supplies the HLI analytical balances.

F. Fisher Scientific supplies all pipets, volumetric flasks, beakers, and bottles used in the preparation of samples and standard stock solutions for this method.

SAMPLING AND PRESERVATION REQUIREMENTS

A. There are two main requirements for sample preservation:

1. There will be at least two 40-mL amber vials, or one 2-ounce soil jar, for each sample to be tested for volatiles.

2. All samples should be kept at 4 degrees C with ice or by refrigerator, and all samples will be analyzed within 14 days.

B. There are two main requirements for each sampling trip:

1. Each trip should contain at least one trip blank. A trip blank consists of distilled water that is contained in the sample jars and sealed.

SAMPLING AND PRESERVATION REQUIREMENTS (continued)

2. Each trip should contain at least one field blank. A field blank is a blank of water that is subjected to the same conditions as the sample.

QUALIFICATIONS OF PERSONNEL

A. The operator must demonstrate the ability to generate reliable data using check standards, both internal and external.

B. The sample must be prepared by a technician with experience in sample preparation and must be able to demonstrate that cross-contamination from each sample preparation has not occurred. At Hydro-LOGIC the analyst prepares all volatile samples.

C. Key personnel at Hydro-LOGIC, Inc. who operate the GC systems are:

Peter T. Guy, MS
Laboratory Manager

Don Dulaney
Vice President

Steven Knapp
Analytical Chemist

REAGENTS

A. Reagent grade distilled water, supplied by Hinkley & Schmitt®, is used in all analyses performed by HLI. HLI bubbles contaminant-fee inert gas through the water for one hour to ensure the water is free of all volatile organics.

B. HLI uses either pesticide or GC grade methanol for preparation of all standards and samples, and for cleaning or rinsing equipment and glassware.

C. HLI purchases certified stock standard solutions from one of four vendors: Ultra Scientific, SUPELCO, RESTEK, and Alltech. Standard stock solution certificates are kept on file at the offices of HLI, along with log books containing information on how each standard was handled, labeled with a corresponding HLI standard number, diluted (if applicable), and expected expiration date.

CALIBRATION

A. <u>External Standard Calibration.</u> Prepare a calibration range, with a minimum of five calibration points, using a certified stock standard of USEPA Method 8021 purgeable halocarbons kit. Use either a one or two microliter Hamilton Series 7000 syringe to inject each standard calibration point into the 16 X 150mm borosilicate glass purge vessel containing 10-ml of reagent grade water. One standard should be at a level at, or near, the state, USEPA, or project specified

CALIBRATION (continued)

minimum detection level (MDL). The other concentrations should correspond to a range that should define the working range of the detector.

B. Analyze each calibration standard and tabulate peak area responses, for each component of the method, versus the concentration in the standard. Generating the calibration curve can be done using either Excel® spreadsheets, or programming internal to the Peaksimple® software that operates the GC. The calibration curve is a linear algebraic function of the form Y = mX + B. Each compound of interest in the method should have its own calibration curve that has a correlation coefficient (r-value) of not less than r = 0.99.

C. Internal Standard Calibration. The analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. These internal standards must also not be affected by method or matrix interferences. The compounds bromochloromethane, 1-chloro-2-bromopropane, and 1,4-dichlorobutane can be used successfully as an internal standard.

D. Prepare a calibration range, with a minimum of five calibration points, using a certified stock standard solution containing any or all of the compounds bromochloromethane, 1-chloro-2-bromopropane, or 1,4-dichlorobutane. Use either a one or two microliter Hamilton Series 7000 syringe to inject each internal calibration point into the 16 X 150mm borosilicate glass purge vessel containing 10-ml of reagent grade water, and a purgeable halocarbons calibration standard. Each internal calibration standard point should be at a level at, or near, the state, USEPA, or project specified minimum detection level (MDL). The other concentrations should correspond to a range that should define the working range of the detector.

E. Analyze each calibration standard, and tabulate area responses against concentration for each compound and internal standard, using either Excel® spreadsheets, or programming internal to the Peaksimple® software that operates the GC. Calculate response factors (RF) for each compound of interest in the method, using:

$$RF = \frac{(A_p)(C_{is})}{(A_{is})(C_p)}$$

Where:

A_p = Response for the parameter to be measured.
C_{is} = Concentration of the internal standard.
A_{is} = Response for the internal standard.
C_p = Concentration of the parameter to be measured.

CALIBRATION (continued)

F. If the RF value over the range of standards has a relative standard deviation of less than 10%, then the results can be used to plot a calibration curve of response ratios versus response factor (A_x/A_{is} vs. RF).

QUALITY CONTROL

A. These quality control guidelines will apply to all volatile halogenated organic compounds analyzed by the laboratory at HLI. Each analyst will maintain records to document the quality of data that is generated, and ongoing data quality reviews will be performed to show that quality checks are within established performance criteria for the method.

B. For the full suite of quality control checks the analyst will, at a minimum, perform the following QA/QC checks at a rate equivalent to 10% of all samples analyzed for each project. The frequency of certain QA/QC checks can be reduced if spike recoveries from samples meet all specified quality control criteria.

1. A method blank, which is a blank that is prepared in the lab in the same manner as the samples using reagent grade water. Method blanks will include surrogate spikes.

2. A laboratory control spike, which is a sample prepared by the analyst, containing method specific compounds of interest, to determine if the instrument is performing correctly. The analyst should spike 1-µl of a second source, certified standard stock solution of purgeable halogenated organics to 10-ml of reagent grade water. Analyze the laboratory control sample by purge and trap, and calculate the percent recovery for each compound of interest. Each compound of interest should have a recovery within ±30% of the expected concentration spiked. If one or more compounds of interest fail the acceptance criteria, then repeat the laboratory control spike procedure. If one or more of the parameters still fail, then locate and correct the source of the error, and retest all samples since the last acceptable performance evaluation, as determined by the analyst. Laboratory control samples will include surrogate spikes.

3. A matrix spike, which is a true sample the analyst assumes to be of low to non-detectable concentration, and is spiked with 50 µg/l of a second source, certified standard stock solution of purgeable halogenated organics. The matrix spike sample is handled and analyzed as every other sample in the method, and the percent recovery of each compound of interest is calculated by:

$$\%R = \frac{SSR - SR}{SA} \times 100$$

QUALITY CONTROL (continued)

Where: SSR is the spiked sample result,
SR is the unspiked sample result, and
SA is the spike amount (50 µg/l).

Each compound of interest should have a recovery within approximately 35% of the expected concentration spiked (65-140%). If one or more parameters of the matrix spike fail expected recovery limits, check quality control parameters of the laboratory control spike and surrogate spike. If these values are within limits, matrix interferences are assumed to exist and values associated with this sample are flagged. If other quality control parameters are outside acceptable limits, a system performance error is assumed to exist and the analyst must locate and correct all errors, and retest all samples since the last acceptable performance evaluation, as determined by the analyst. All matrix spike samples will include surrogate spikes.

4. A matrix spike duplicate, which is a sample identical to and analyzed sequentially to the matrix spike sample. A matrix spike duplicate will be spiked in the same manner, and with the same concentration, corresponding to the associated matrix spike sample, and will be analyzed subsequently to the matrix spike sample. The analyst will determine the percent recovery by the same manner as the matrix spike sample, and will calculate the precision (RPD) between the two samples as follows:

$$RPD = \frac{2[MSR-MSRD]}{MSR+MSRD} \times 100$$

Where: MSR is the matrix spike percent recovery, and
MSRD is the matrix spike duplicate percent recovery.

Each compound of interest, as in the matrix spike sample, should have a recovery within approximately 30% of the expected concentration spiked (65-140%). Additionally, the RPD between the matrix spike and its duplicate should be within 30% of each other. However, the results on the matrix spike and matrix spike duplicate are not by and of themselves used to qualify data. In a strict sense, the matrix spike and duplicate recoveries are applicable to only the sample that was spiked. High or low compound recoveries can be related to the behavior of compounds of similar chemical structure or volatility, or the recoveries may be indicative of problems with the results obtained for all target analytes in the sample. In any case high or low recoveries are appropriately flagged and analysis continues. Only in the presence of other qualifying data (i.e. LCS, blank, etc...), or the repeated inability to generate acceptable matrix spike results over a period of time, will the analyst take action to correct system performance and rerun samples.

QUALITY CONTROL (continued)

5. A continuing calibration check, which is a sample prepared by the analyst in the same manner as an initial calibration point, and is used to monitor system performance. A continuing calibration check containing all target analytes and system monitoring compounds (i.e. surrogates) is required to be performed at the beginning of each day, after each set of 10 samples, and at the end of a data set. The analyst should spike a concentration of the primary certified standard stock solution, equivalent to the concentration of the mid-point of the initial calibration curve, into 10-ml of reagent grade water, and analyze by purge and trap as if it were a regular sample. The analyst will then compare the concentration returned in the calibration check sample, for each target analyte, with the concentration of the corresponding initial calibration point, and calculate the percent difference (%D) between the two. The %D for all calibrated compounds of interest should be less than 15% between the initial calibration point and the continuing calibration check. If any calibrated target analyte falls outside the acceptance criteria, another calibration check must be run and compared to the initial calibration point. If the second calibration check also fails acceptance criteria, the analyst will generate a new initial calibration curve, and rerun or flag samples at his/her discretion, before continuing with additional sample analysis.

6. Internal standards, also known as surrogates, will be added to all samples, blanks, spikes, and calibration checks to monitor the system performance. The analyst will spike a final concentration of 50 parts per billion (ppb) of surrogate to all samples, and calculate a percent recovery that should fall within the 65-140% acceptance criteria. The primary surrogate that HLI will use for this method is bromochloromethane. The recoveries of the compounds are used to assess the matrix effects of the sample upon the analysis and to assess the performance of the analytical system for each sample analysis. Poor recoveries may indicate matrix effect, poor purging efficiency, poor spiking efficiency, or non-quantitative transfer of the analytes from the purging system to the GC. When analysis of a sample results in an unacceptable surrogate recovery, the sample should be reanalyzed to verify that the unacceptable recovery is a matrix-derived problem, rather than a laboratory problem. If the reanalyzed sample generates acceptable recoveries, then the reanalyzed sample is reported and the original is omitted. If the reanalysis of the sample again yields unacceptable surrogate recoveries, both samples may be reported, with appropriate estimate flags, at the discretion of the analyst. Only when samples continuously yield low surrogate recoveries, or in the presence of other unacceptable quality control data, will the analyst check system performance and rerun samples as deemed necessary. When a system monitoring compound on a blank does not pass acceptance criteria, system performance will be checked, and a blank rerun to demonstrate acceptable surrogate recovery.

PROCEDURE

A. The appropriate operating conditions for this method are tabulated for each GC, and are located with the laboratory log book corresponding to each GC. Appropriate operating conditions are also programmed within the PeakSimple® operating software associated with each GC, and will not be listed again within this method. Each analyst must become familiar with each GC's operating system, programming, and operating conditions for each method.

B. Each GC system will be calibrated at the beginning of each individual project, as described under the Calibration Section. While continuing with a project, each GC system will be checked for accuracy and consistency each morning, as described in the Quality Control Section, before any samples are analyzed.

C. Before a sample can be analyzed the analyst must allow it to reach ambient temperature. For soils the analyst will:

1. Weigh 2-g (± 0.01g) of blended soil, from the soil sample jar, and add it to the purge vessel, along with 10-ml of reagent grade water. Under conditions where the soil sample has obviously high levels of target analytes (i.e. through olfactory and visual senses), the analyst will appropriately reduce the volume of actual sample (dilute). After the sample weight is recorded, cap the purge vessel and mix the sample with the vortex-mixing machine.

2. Add appropriate matrix, standard, or surrogate spiking solutions, if applicable, through the top of the purge vessel, using a 1-µl Hamilton Series 7000 syringe. The syringe tip should penetrate the surface of the solution to ensure proper transfer of spiking solution.

3. Attach the purge vessel, containing sample and appropriate spiking solutions, to the purging unit, and screw tightly into place. Take caution that overtightening will crack the purge vessel, and not enough tightness will cause the purge unit to literally blast the vessel and sample off of the unit.

4. Prompt the start command for the GC through the PeakSimple® software, and wait for analysis to complete. At this point the only thing the analyst need do is occasionally monitor the system to ensure proper purging, temperature ramping, and injector valve switching. If a system is visibly malfunctioning, the analyst will stop analysis and take appropriate action to correct system performance.

PROCEDURE (continued)

5. Upon completion of the analysis, identify the parameters in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in the standard chromatograms. (The computer library of retention times should be able to accomplish this for the analyst, but the analyst should review each chromatogram for accuracy.) The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a project. Three times the standard deviation of a retention time for a compound can be used to calculate a window size; however, the experience of the analyst should weigh heavily in the interpretation of the chromatogram.

6. If the response for a peak exceeds the working range of the system, prepare a dilution of the sample and reanalyze.

D. For waters the analyst will:

1. Use the Hamilton 10-ml syringe to pierce the septa of the sample VOA, and transfer 10-ml of sample to the purge vessel. Under conditions where the water sample has obviously high levels of target analytes (i.e. through olfactory and visual senses), the analyst will appropriately reduce the volume of actual sample (dilute). However, the total volume of liquid within the purge vessel should always result in a 10-ml volume. Add reagent grade water equivalent to the amount of sample taken under 10-ml, so that the final volume in the purge vessel is 10-ml (i.e. 5-ml sample + 5-ml water).

2. Add appropriate matrix, standard, or surrogate spiking solutions, if applicable, through the top of the purge vessel, using a 1-µl Hamilton Series 7000 syringe. The syringe tip should penetrate the surface of the solution to ensure proper transfer of spiking solution.

3. Attach the purge vessel, containing sample and appropriate spiking solutions, to the purging unit, and screw tightly into place. Take caution that overtightening will crack the purge vessel, and not enough tightness will cause the purge unit to literally blast the vessel and sample off of the unit.

4. Prompt the start command for the GC through the PeakSimple® software, and wait for analysis to complete. At this point the only thing the analyst need do is occasionally monitor the system to ensure proper purging, temperature ramping, and injector valve switching. If a system is visibly malfunctioning, the analyst will stop analysis and take appropriate action to correct system performance.

PROCEDURE (continued)

5. Upon completion of the analysis, identify the parameters in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in the standard chromatograms. (The computer library of retention times should be able to accomplish this for the analyst, but the analyst should review each chromatogram for accuracy.) The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a project. Three times the standard deviation of a retention time for a compound can be used to calculate a window size; however, the experience of the analyst should weigh heavily in the interpretation of the chromatogram.

6. If the response for a peak exceeds the working range of the system, prepare a dilution of the sample and reanalyze.

CALCULATIONS

A. Determine the concentration of individual target analytes in each sample. The target analyte list will be project specific, and it is the responsibility of the analyst to know the project specific target list before any analysis begins. The project specific, target analyte list can be obtained from the project files and contract administrators.

B. If the external standard calibration procedure is used, calculate the concentration of the parameter being measured from the peak response using the calibration curve determined in the Calibration Section A.

C. If the internal standard calibration procedure is used, calculate the concentration in the sample using the response factor (RF) determined in the Calibration Section C.

$$\text{Concentration} = \frac{(A_u)(C_{is})}{(A_{is})(\overline{RF})}$$

Where:

A_u = Response for the parameter to be measured.
C_{is} = Concentration of the internal standard.
A_{is} = Response for the internal standard.

D. Report the results in mg/kg for soil, and µg/l for water, without correction for recovery data. All quality control data obtained will be reported with the final sample report, within 7 business days of the completion of the project. Only actual sample results need be reported in the field, because the nature of the mobile laboratory is to provide real time results. Any analytical delays should be dealt with at the completion of the field day, or during any down time do to field delayed activities.

AUDITS

A. **Internal** - Internal audits shall be conducted at least biannually and more often if the QA/QC supervisor deems necessary. These audits shall follow the format laid down in the audit section of the Hydro-LOGIC, Inc. quality manual.

B. **External** - External audits shall be performed by inspectors for certified states, as well as clients. These audits may be unannounced. However, Hydro-LOGIC, Inc. reserves the right to accompany the auditors throughout the audit.

Hydro-LOGIC, Inc. (HLI)
SOP No: HLI-SOP-A-015-R1

Comments on HLI SOP

A OBJECTIVE

Before analyzing samples, **HLI** should provide MDLs and PQLs for the volatile organics determined by this method. Specify how results will be reported, such as, **ug/m^3** or, maybe, **ng/L Air**, or **ng/g Air**. Some compounds listed in QAPP Table 5N, namely, 2-Butanone, 2-Hexanone, 4-Methyl-2-pentanone, Acetone, Carbon Disulfide, and cis- and trans-1,3-Dichloropropene are not included in this method. Verify if these compounds will be required for determining Total VOCs.

RESPONSE

MDL for these compounds is 1.0 ppb. Results will be reported in ppbv. If the compounds listed above are present in the sample, they will be included in the total VOC calculation. Please keep in mind that the compounds listed in QAPP Table 5N are for samples analyzed by EPA Method 8260 and will be used for human health risk assessment purposes. The analytical method being used for the soil gas survey is EPA Method 601 and is being used for screening purposes.

B SAMPLING AND PRESERVATION REQUIREMENTS

Specify any preservation and holding time requirements for the 60 cc syringes.

REPONSE

There are no preservation requirements, other than keeping samples at <4 degrees C in a laboratory refrigerator. All samples will be run within 48 hours, although the working goal will be to run all samples the same day they are collected.

C CALIBRATION

Specify concentration of the 3 to 5 calibration standards.

RESPONSE

Ultra HCM-601 Lot #P-1270. Standard solution is 100 ng. Low 0.1 ul, mid 0.5 ul, mid 1.0 ul, high 2.0 ul.

D QUALITY CONTROL

QAPP Section 3.7 specifies QC requirements for the field GC. Method blank must be analyzed at the start of each day, and every 10 samples.

RESPONSE

This will be done.

E CALCULATIONS

Describe the calculations to determine concentration of Total VOCs.

RESPONSE

Average slope of the curve = 1531. Y intercept: 0.00, Linearity: 1.00, # of levels: 3, SD/relative SD of CF's 4.4/28.7. R^2: 0.9980. Formula: Y=15.3063X

Calculation: (total area of peaks x slope + intercept) / volume injected

F Soil Gas Sampling Procedures

Are any field blanks, or background samples, going to be collected?

RESPONSE

No. Table 2 of Volume 2A (the Field Sampling Plan) of the SSP specifically indicates that no field blanks will be collected for the soil gas screening survey. Section 5.6 and Tables 10, 11a, and 11b of this same document discuss the background sampling program, which includes only groundwater, surface soils, and subsurface soils.

URS

October 19, 2001

Mr. Mike Ribordy
U.S. EPA – Region 5
77 West Jackson Boulevard (SR-6J)
Chicago, IL 60604-3590

RE: Sauget Area 2 Sites Deliver by Overnight Mail

Dear Mike,

Enclosed please find one additional Standard Operating Procedure (SOP) for your review in accordance with our discussions via conference call last week (10/9/01) on this topic. The SOP that has been attached includes the following:

Severn Trent Laboratories, On-Site Technologies Division (mobile laboratory for soil screening)

- SOP OSMM1012.R1 Heavy Metals by XRF

Severn Trent (the On-Site Technologies Division) has modified the SOP for metals by X-Ray refraction (XRF) to account for site-specific calibration procedures, based on the discussions held during the conference call on this topic.

Please do not hesitate to call Steve Smith if you have any questions on this information.

Sincerely,

Robert B. Veenstra
Senior Program Manager

Cc: Steve Smith, SA2SG Project Manager

URS Corporation
2318 Millpark Drive
Maryland Heights, MO 63043
Tel: 314.429.0100
Fax: 314.429.0462

K:\Environs\23-20010024.00(SA2)\SA2ST XRF Cvr Ltr

Effective Date: 08/31/01

STL On-Site Technologies
STANDARD OPERATING PROCEDURE

TITLE : Heavy Metals in Soil by Energy Dispersive X-Ray Fluorescence Spectroscopy

SUPERSEDES : (NONE)

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Approvals and Signatures

Division Manager:	Peter A. Law	8/30/01 Date
QA Manager:	Robert S. DeGaetano	8/22/01 Date
Technical Director:	John V. Hawkins	8/29/01 Date

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1.0 SCOPE AND APPLICATION

1.1 The purpose of this SOP is to outline the techniques for determining the concentration of certain metals in soil or sediment samples. Typical reporting levels are as follows:

Table 1 - Reporting Limits for Select Elements by EDXRF

Element	Spectrace 6000 (ppm)
Antimony	10
Arsenic	10*
Barium	10
Cadmium	10
Chromium	20*
Copper	10
Lead	10
Mercury	10
Nickel	10
Selenium	10
Silver	10
Thallium	10
Zinc	10

* Subject to interferences – see section 4

1.2 This method is a screening technique and is based on EPA method 6200. Off-site confirmation using approved techniques is suggested to compliment any investigation.

1.3 It is the policy of STL and of the On-Site Technologies Division to ensure that we administer contracts and orders for goods and services in a manner that is fully compliant with governmental laws and regulations, as well as the STL Policy Statement on Business Ethics and Conduct.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared by a combination of techniques including drying, sieving and pulverizing prior to analysis. Once prepared, approximately five grams of the sample is placed into a X-ray sample cup and covered with Prolene® X-ray film. The sample is analyzed under preset energy conditions for the elements of concern. The software is programmed to calculate final concentrations by "Fundamental Parameters" or by a least squares fit to 'site-specific' calibration data. The software algorithms correct for matrix effects, and calculate final concentrations by an iterative process.

2.2 Background - The Field Portable X-Ray Fluorescence (FPXRF) technologies described in this method use sealed radioisotope sources to irradiate samples with x-rays. When a sample is irradiated with x-rays, the source x-rays may undergo either scattering or absorption by sample atoms. As a result, a rearrangement of electrons occurs resulting in emission of x-rays characteristic of the given atom. It is this emission of x-rays, or fluorescence, that is measured for both reference standards and samples to obtain metals concentrations.

2.3 Analysts must be appropriately trained by an experienced operator and demonstrate acceptable proficiency prior to conducting this analysis without direct supervision.

3.0 DEFINITIONS

3.1 There are many definitions used within the laboratory that may be generic to all laboratory analyses or more specific for certain methods. For the most recent terms and definitions used within the laboratory, refer to the STL-OST Laboratory Quality Manual.

4.0 INTERFERENCES

4.1 The heterogeneity of the sample has a large impact on comparability of results with confirmatory analysis by other spectroscopic techniques such as ICP and GFAA. Consequently, it is imperative to homogenize the sample as best as possible.

4.2 Moisture content may affect the accuracy of analysis of soil and sediment samples. This effect may be minimized by drying the samples in a convection oven prior to analysis. However, if mercury is to be tested, the sample should be dried at ambient temperature.

4.3 Inconsistent positioning of samples in front of the probe window is a potential source of error because the x-ray signal decreases as the distance from the radioactive source increases. This error is minimized by maintaining the sample distance between the window and each sample. For best results, the window of the probe should be in direct contact with the sample, which means that the sample should be flat and smooth to provide a good contact surface.

4.4 Chemical matrix effects result from differences in the concentrations of interfering elements. The effects can be corrected mathematically through the use of fundamental parameter (FP) coefficients or by using a site-specific calibration standard (SSCS). Examples of interfering elements are as follows:

- Iron (Fe) tends to absorb Copper (Cu) x-rays and enhance Chromium (Cr)
- High concentrations of Lead (Pb) may result in no Arsenic (As) being reported

Effective Date: 08/21/01

5.0 SAFETY

5.1 It is strongly recommended that analysts treat all samples as if they are hazardous and take all appropriate safety precautions. Analysts shall wear appropriate personal protective equipment including lab coats, safety glasses with side shields and impervious gloves (Nitrile, eg. Sol-Vex).

5.2 Proper precautions should be taken when formulating new standards, or handling suspected high concentration samples.

5.3 For long term projects, radiation monitoring equipment should be used.

5.4 Material Safety Data Sheets for all chemicals used in the operation are present in the laboratory for immediate access.

6.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

6.1 Samples should be collected in glass jars and stored at 4 ± 2 °C until analysis.

6.2 Sample can be tested up to 6 months after collection for all metals except mercury which must be analyzed within 28 days of collection.

7.0 EQUIPMENT AND MATERIALS

7.1 Spectrace Instruments Model 6000 Field Transportable EDXRF Analyzer with software

7.2 Spectrace Instruments Model 9000 Field Portable EDXRF Analyzer with software.

7.3 Prolene®X-ray film, Chemplex Industries 1/6mil or equivalent.

7.4 Chemplex polyethylene X-ray sample cups.

7.5 Mortar and Pestle suitable for grinding environmental soils.

7.6 Spex Model 8000 Roller mill with tungsten carbide vial set and balls.

7.7 Drying trays: polyethylene or paper.

7.8 Drying oven: microwave oven or temperature controllable convection oven.

7.9 Stainless steel spatulas.

7.10 Scintillation vials: 20ml with plastic caps.

7.11 Manufacturer's Operations Manual

8.0 REAGENTS AND STANDARDS

8.1 NIST Certified Soil Reference Material (SRM): purchased directly from NIST, Gaithersburg, Maryland. For Fundamental Parameters, STL-OST calibrates with NIST SRM 2704, 2709, 2711. Specific sites may require purchase of a SRM with a particular elemental composition. Consult the NIST catalog for possible SRM.

9.0 PROCEDURES

9.1 Set-Up

9.1.1 The Spectrace 6000 must have power to the ion pump at all times. This pump maintains a vacuum on the X-ray source. While connected to shore power, the onboard Nicad battery is constantly charged and will supply approximately tree days of power to the ion pump. If longer transport time is required, connect a full-charged 12V external battery to the ion pump leads.

9.1.2 Arrange the components with the printer and computer to the left and the card cage to the right of the head unit. Turn all components on. If the instrument begins to beeps, perform trouble-shooting activities and refer to operator's manual to correct the problem.

9.1.3 If applicable, turn the defrost switch off, and the cooler switch on to initiate detector cooling. Wait at least on hour for detector to reach operating temperature.

9.2 Energy Calibration

9.2.1 Prior to calibration and sample analysis, the analyst must run an energy calibration. This procedure resets the instrument gain, resolution, and peak offset relative to a pure copper standard, which compensates for drift due to changing temperature conditions.

9.2.2 Be sure that the computer is set to the correct directory. Place the copper disk in the sample chamber and press F7 to initiate the energy calibration. The calibration takes approximately seven minutes. Print out a copy of the instrument setting listed on the PHA status page.

9.2.3 Perform an energy calibration at the beginning of each day, once every twenty samples, and after significant changes in ambient environmental conditions.

9.2.4 Instrument gain settings should not change appreciably between consecutive energy calibrations. If the gain changes by more than +/- 15%, check instrument hardware (especially filter solenoids) and software for problems and repeat energy calibration.

9.3 Initial Calibration

9.3.1 Setup instrument conditions that will allow for 50% dead time in all energy levels (low, mid, high). It is possible to customize the method for a particular analyte by varying energy level livetimes, tube voltage and current. Varying the livetime will affect the sample throughput. Once the instrument conditions have been set for a particular method, they must remain the same for all subsequent calibration and sample analysis events. An example of instrument settings for each of the three energy levels is shown in Appendix A.

9.3.2 Initial calibration is prepared at a minimum of three levels. Use three NIST SRM's that contain the elements of interest. Calibration is performed using a fundamental parameters algorithm with NIST SRM's 2704, 2709, 2711. A project-specific linear calibration may be performed for single elements using site-specific standards. These standards are analyzed by ICP or graphite furnace prior to the start of the project and the values obtained are used in the XRF calibration table.

9.3.3 Set up the calibration table for all elements of interest. Enter the certified values from the NIST standard documentation. enter non-certified values in parenthesis. If a site-specific calibration is used, enter the values provided by the ICAP or AA analysis as certified values into the calibration table.

9.3.4 Change directories using the F5 soft key into the appropriate method directory. Highlight the calibration option line for the current method. Press F1 soft key to begin calibration. Follow screen instructions and insert appropriate SRM into the sample chamber. Repeat for all three SRM's.

9.3.5 After the initial calibration is completed, insert an appropriate SRM to be used as the laboratory control standard (LCS). The SRM should contain the analytes of interest, however it may not be possible to obtain a SRM with all analytes of interest at appropriate concentrations.

9.4 Continuing calibration is done at a sample frequency of 20% or when malfunction of the instrument is suspected. Calibration check is done by analyzing one of the three SRM standards used for calibration. If the result varies from the true value by more than 30% for the analytes of interest, a new calibration must be prepared. The variation is calculated as a Percent Difference (PD):

$$\text{Percent Difference} = \frac{R1 - R2}{R1} \times 100$$

where:

R1= true value

R2= the measured value.

9.4.1 If the certified value of the SRM is within five times the reporting limit, the PD criteria will not apply. If the continuing calibration fails for the compounds of interest, check the hardware and software settings for the instruments, especially the filter solenoids. Be sure that the correct method directory is in use.

9.5 Soil Preparation

9.5.1 Remove foreign debris such as sticks and leaves, if present and screen samples through a 10 mesh sieve.

9.5.2 Dry all samples prior to quantitative analysis. Drying technique may include drying by air, microwave oven, or convection oven. If mercury is an analyte of interest, excessive drying temperature can cause it to volatilize. It is recommended to not exceed 40^0C when drying samples containing mercury or other volatile metals.

9.5.3 Pulverize approximately 10g of the sieved ample by grinding with a mortar and pestle, or equivalent. The sample should be ground to a rock flour consistency (attempt to grind to same consistency as SRM standards).

9.5.4 Place approximately 5g of dried and pulverized ample into an XRF sample cup. Cover the cup with a square piece of Prolene® X-ray film, and secure in place with the plastic rings. Inspect the X-ray film to see that it is free of wrinkles. Wrinkles must be removed prior to analysis.

9.6 Sample Analysis

9.6.1 Sample analysis may begin following successful energy calibration, calibration check, and laboratory control standard analysis.

9.6.2 Analyze samples under same energy conditions as calibration standards.

9.6.3 Place sample in XRF sample chamber. Using the cursor, highlight the appropriate analysis method and press the F1 soft key. Enter sample ID at the prompt and press spacebar to start analysis. The instrument will analyze all energy levels programmed into the method and print out a hard copy at the end of the analysis. Report calculated values from printout for elements of interest.

9.6.4 The analyst must determine whether low level hits for elements of interest are valid. The following test may be used to determine whether a peak is above background signal noise:

peak counts > 3*background check counts

10.0 QUALITY CONTROL

10.1 **Energy Calibration:** See Section 9.2

10.2 **Laboratory Control Standard (LCS):** An NIST SRM may be run as an LCS. The acceptance criteria is +/- 30% of the certified value. Consult the NIST catalog for available SRMs. The SRM should contain the element of interest at an appropriate level. For multiple elements, it may not be possible to find a LCS with all elements of interest.

10.3 **A sample duplicate** is to be analyzed with each batch of twenty samples. The relative percent difference between the initial and duplicate result must be $\leq$ 35%. Calculate the RPD according to the following formula:

$$RPD = \frac{ABS\ (C_1 - C_2)}{(C_1 + C_2)/2)} \times 100$$

where:

C_1 = Concentration from initial sample
C_2 = Concentration from duplicate sample

10.3.1 If the compound of interest is at a concentration within five times the reporting limit, the RPD criteria will not apply.

10.4 **Corrective Action:** Corrective action must be performed when quality control data exceeds acceptance criteria. Activities performed, verification of successful corrective actions and affected samples should be recorded on the Quality Assessment Deviation Form provided as Appendix B to this document.

10.5 **A detection limit study** must be performed initially and after any significant changes to the methodology or when significant instrument maintenance is required. To perform the MDL, obtain an SRM containing the elements of interest at the appropriate levels and generate a minimum of seven sequential measurements conducted over three non-consecutive days.

11.0 CALCULATIONS

11.1 Results are calculated by the manufacturer's software.

12.0 DATA REDUCTION and REVIEW

12.1 Hardcopies of all instrument calibration, calibration verification and daily analytical sequence raw data shall be assembled into "packages" for review.

12.2 Analysts are responsible for reviewing the packages to evaluate the accuracy of transcriptions, the instrument's performance, and the calculated results. Section 10 details the acceptance criteria and corrective actions for instrument and batch QA/QC.

12.3 All necessary documentation to support corrective actions performed shall be included with the packages and available for review.

12.4 Preliminary results may be reported to the client at this time.

13.0 REPORTING OF RESULTS

13.1 Prior to generating a final report of results, the data is reviewed a second time. In addition to the method review performed by the first chemist, the second review includes a verification of any project/client specific criteria and a sensibility check.

13.2 If for any reason there is a question regarding the technical soundness of the data, it is brought directly to the attention of the Technical Director and/or Quality Assurance Manager.

13.3 After completing the secondary review, the final results are reported to the client in hardcopy form and/or electronic deliverable, if requested.

14.0 POLLUTION PREVENTION

14.1 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N.W. Washington D.C. 20036, (202) 872-4477.

15.0 WASTE MANAGEMENT

15.1 No solvents or acid waste is generated.

15.2 Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.3 Refer to the Laboratory Sample and Waste Disposal plan.

15.4 Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

16.0 SUPPLEMENTAL DOCUMENTS – N/A

17.0 REFERENCES

17.1 EPA Method 6200, January 1998

18.0 SUBSTANTIVE REVISIONS

18.1 Original issue – 05/15/01

18.2 Revision #1 – 08/21/01

Effective Date: 08/21/01

Appendix A

Parameters for Low, Mid, High Energy Conditions: Spectrace 6000

Parameter	Low	Mid	High
Tube Voltage	13KV	23KV	50KV
Tube Current	0.35mA	0.35mA	0.35mA
Filter	Aluminum	Thin Palladium	Copper
Livetime*	50-200sec	50-200sec	50-100sec
Preset Count	0 K	0 K	0 K
Max Energy	10 KeV	20 KeV	40 KeV
Atmosphere	Air	Air	Air
Warmup	0 sec	0 sec	0 sec
Elements of Interest K_α	K, Ca, Ti, V, Cr, Mn	Fe, Co, Ni, Cu, Zn, As, Se	Ag, Cd, Sb, Ba
Elements of Interest L_α		Pb, Hg	
Elements of Interest *FP	Fe	Mn, Br, Rb, Sr, Y, Zr, W	Sn

Effective Date: 08/21/01

Appendix B
Quality Assessment Deviation Form

DATE: _____ DATE OF ANALYSIS: _____

TIME: _____ PROJECT #: _____

ANALYST: _____ SDG #: _____

SAMPLES AFFECTED BY THIS DEVIATION

LAB SAMPLE ID	LAB SAMPLE ID	LAB SAMPLE ID	LAB SAMPLE ID

QC SAMPLE	QC DEVIATION	LIMITS	CORR. ACTION

COMMENTS: _____

Effective Date: 10/21/01

SEVERN TRENT LABORATORIES
ON-SITE TECHNOLOGIES (OST) DIVISION

APPENDIX TO STANDARD OPERATING PROCEDURE OSMM1012

TITLE: Heavy Metals in Soil by Energy Dispersive X-Ray Fluorescence Spectroscopy

Approvals and Signatures

Division Manager: _____
Peter A. Law Date

QA Manager: _____
Robert S. DeGaetano Date

Technical Director: _____
John V. Hawkins Date

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1.0 SCOPE AND APPLICATION

1.1 This appendix to SOP OSMM1012 presents the additional procedures and modifications of original procedures for the determination of site-specific calibration standards (SSCS) for XRF analysis. All aspects of the analysis not discussed here are performed as described in the main body of referenced SOP.

2.0 SUMMARY OF THE METHOD

2.1 Soil samples are collected from the site under investigation and analyzed by Inductively Coupled Plasma Spectroscopy (ICP) and/or Graphite Furnace Atomic Absorption (GFAA). The metals concentrations obtained are then compared to the values generated using X-Ray Fluorescence (XRF) for the same samples. Calibration curves for each element of concern are then prepared using the concentrations as determined by ICP and/or GFAA and the associated responses from the XRF analysis. These calibration curves are then used to calculate metals concentrations for samples taken from the site.

3.0 SAMPLE COLLECTION AND PRESERVATION

3.1 Samples should be collected in glass jars and stored at 4 ± 2 °C until analysis.

3.2 Samples can be tested up to 6 months after collection for all metals except mercury, which must be analyzed within 28 days of collection.

3.3 Sufficient quantity and sources must be collected from the site to yield multiple concentration levels for each element of concern as well as the associated interfering element(s).

4.0 PROCEDURES

4.1 Site Specific Calibration Standard Preparation

4.1.1 The SSCS samples collected in the field must be oven-dried at < 150 °C for 2 to 4 hours to remove moisture.

4.1.2 The entire sample should be spread out in a drying pan and clumps broken up with a stainless steel spoon.

4.1.2.1 If mercury is to be analyzed, a separate sample must be air dried until the moisture content is < 20 %, as heating may volatilize the mercury.

4.1.3 After drying, all large organic debris and non-representative material (sticks, twigs, leaves, roots insects, asphalt, rocks, etc.) are removed and the sample is transferred to a mortar and ground with a pestle to a uniform consistency.

4.1.4 The dried and ground sample is then sieved through a No. 60 (250 μm) mesh stainless steel sieve. At no time should the material be forced through the sieve. Pebbles and organic matter remaining on the sieve should be discarded.

4.1.5 The under-sieve fraction of the material constitutes the sample.

4.1.6 Homogenize the sieved sample and fill an XRF sample cup. Transfer the remainder of the sample back into the original container and return it to storage until analysis by ICP and/or GFAA.

4.1.7 Analyze the sample according to procedures found in SOP OSMM1012 and record the intensities of the elements of concern.

4.1.8 Repeat for all SSCS soil samples.

4.1.9 For each SSCS sample, analyze the ICP/GFAA portion in triplicate and average the concentration values to obtain a "certified" value.

4.1.10 Generate calibration curves for each element of concern using the intensity values from the XFR analysis and the "certified" concentration results from the ICP/GFAA analyses.

Note – these calibration procedures are used in place of for the ones identified in Section 9.3 of SOP OSMM1012

4.1.11 **If all elements of concern are not represented in the samples collected from the site, substitute values generated from the XRF and ICP/GFAA analyses of certified reference material soil samples.**

4.2 Sample analysis

4.2.1 Dry, sieve and homogenize the field sample as described above.

4.2.2 Analyze the sample by XRF according to procedures outlined in SOP OSMM1012.

4.2.3 Calculate the elemental concentrations using the intensity values from the XRF and the calibration curves generated above (see calculation section in this SOP).

5.0 QUALITY CONTROL

5.1 The Quality Control is essentially the same as discussed in SOP OSMM1012. Modifications to the acceptance criteria may be made at the time of project inception due to matrix interferences and or data quality objectives for the project. These modifications, however, must be made in writing and communicated to the client for approval.

6.0 CALCULATIONS

1. **Linear Regression** – plot intensity of SSCS as determined by XRF analysis (y) versus "certified" concentrations as determined by ICP/GFAA (x)

   - $Y = M * X + B$ (where M = slope)
   - Determine correlation coefficient (r) – result for r must be > 0.990
   - To obtain sample concentration, enter intensity for elements and solve for x.

2. **Weighted Linear Least Squares Regression**– plot intensity of SSCS as determined by XRF analysis (y) versus "certified" concentrations as determined by ICP/GFAA (x)

   - $Y = M * 1/X + B$ **or** $Y = M * 1/X^2 = B$
   - Determine correlation coefficient (r) – result for r must be > 0.990
   - To obtain sample concentration, enter intensity for elements and solve for x.

APPENDIX B

Quality Assurance/Quality Control (QA/QC) SOP

APPENDIX B Quality Assurance/Quality Control (QA/QC) SOP

QA/QC samples will consist of:

- One duplicate per ten, or fraction of ten, environmental samples collected
- One MS/MSD per twenty, or fraction of twenty, environmental samples collected
- One field blank (or equipment blank) per ten, or fraction of ten, environmental samples collected
- One trip blank for each sample cooler containing samples for VOC analysis.

Duplicate samples are collected to measure consistency of field sampling technique. MS/MSD (matrix spike/matrix spike duplicates) are collected to measure laboratory quality control procedures. The field blank will be submitted to the laboratory with the investigative samples and analyzed for the same parameters as the investigative samples. The minimum required is one per ten, or fraction of ten, environmental samples collected, unless dedicated or disposable sampling equipment is used to collect samples.

APPENDIX C

Waste and Soil Sampling SOP

APPENDIXC

Waste and Soil Sampling SOP

Waste Sample Collection

The following method will be used to collect waste samples:

1. Remove appropriate sample containers from the transport container, and prepare the sample containers for receiving samples. Sample containers will have a Teflon® septa.
2. Fill out a self-adhesive label with the appropriate information and affix it to the appropriate sample container. Place clear polyethylene tape over the completed label to protect it from dirt and water. Sample labels can be prepared prior to sample collection except for time and date. Labels can be filled in on the date of sample collection and just prior to collecting the sample. Sample containers will be kept cool with their caps on until they are ready to receive samples.
3. Place labeled sample containers near the sampling location.
4. Place clean plastic sheeting on the ground surface at the sampling area.
5. Put on a pair of nitrile gloves.
6. The 4-foot long MacroCore® sampler will be driven into the ground. Collect continuous samples from grade to 2 feet below the bottom of waste material. Retrieve the sampler to the surface after each sample collection. Remove the sample from the sampler. For instance, the Geoprobe® will drive the sampler 4 feet into the ground. It will collect a sample from 0 to 4 feet. Retrieve the sampler and empty the soil from it. The Geoprobe® will then drive the sampler 4 feet further into the ground and collect soil from a 4- to 8-foot depth. Retrieve the sampler to the surface and empty it again. Continue this process until continuous samples have been collected from ground surface to 2 feet below the bottom of the waste material.
7. VOC samples cannot be composited without losing volatiles. Thus, use the waste sample with the highest PID readings for VOC analysis. Collect the VOC sample with a 5-gram EnCore® sampler. After pressing the sampler into the soil at the desired location within the split spoon, cap the coring body while it is still in the EnCore® sampler T-handle. Place the remainder of the split spoon sample into a stainless steel bowl and homogenize it. Fill the remaining sample containers from the steel bowl.
8. Use the sample with the highest PID reading for dioxin analysis.
9. Place the sample containers on ice in a cooler.

10. Begin chain-of-custody procedures. A sample chain-of-custody form is included as Appendix F.

11. Decontaminate the sample equipment as described below.

Surface Soil Sample Collection

Use the following procedure to collect a sample:

1. If necessary, penetrate the soil to the appropriate sampling depth.
2. Using a clean tool, remove and discard a thin layer of soil from the area. Record the characteristics of the soils, including grain size, content, staining, and color.
3. To collect a discrete soil sample for VOC analysis, a 5-gram EnCore® sampler will be used. After pressing the sampler into the soil at the sampling location, cap the coring body while it is still in the EnCore® sampler T-handle. To collect a discrete soil sample for other parameters, use a stainless steel laboratory spoon or equivalent. Homogenize the non-VOC samples as necessary.
4. Place the homogenized sample into appropriate sample containers. In addition to analytical samples, a reference sample considered representative of the soil may also be collected in a wide mouth jar and stored for possible future physical analyses such as grain size analysis.
5. Check that the cap of each sample container has a Teflon® liner, if required for the analytical method. Secure the cap tightly.
6. Label the sample container with the appropriate sample tag. The tags could be permanent labels or clean tape. Label the tag carefully and clearly using indelible ink. Complete appropriate sampling forms and record in the field notebook. Pre-labeled containers are handy, particularly if you are wearing gloves or if the weather is inclement.
7. Initiate the chain-of-custody form.
8. Place the capped EnCore® sampler core bodies and other sample containers on ice in a cooler to maintain the samples at approximately 4°C. Ship the cooler to the laboratory for analysis within 48 hours of sample collection.
9. Decontaminate equipment between sample locations and after use as described below.

Subsurface Soil Sample Collection

The sampling procedure will be as follows.

1. Borings will be advanced via direct push technology (Geoprobe®). The Geoprobe® will hydraulically drive a stainless steel, acetate-lined MacroCore® sampler (2-inch diameter by 4-foot length) to the desired subsurface sample depth. Following sample collection, the sampler will be retrieved to the surface and the soil sample removed from the disposable acetate liner within the sampler.
2. One subsurface soil sample will be collected from 0.5 to 6 feet within each boring. The soil from 0.5 to 6 feet will be screened, in the field, for evidence of impact with visual and olfactory observation and a photoionization detector (PID). The soil interval exhibiting the greatest impact will be submitted to the laboratory for analysis.
3. A 5-gram EnCore® sampler will be used to collect VOC samples from the subsurface soil. Use the EnCore® sampler to collect a VOC sample from the top portion of sample in the MacroCore® sampler.
4. Of the four subsurface soil samples collected within the site, visual and olfactory observation and PID readings will also be used to identify the most impacted sample. This sample will be used for dioxin analysis.
5. Descriptive logs of each boring will be prepared as described in Appendix D.
6. Follow chain-of-custody procedures.
7. All borings will be grouted to the surface, following retrieval of both the waste and soil samples.

Boring equipment will be decontaminated and investigation-derived waste will be disposed of as described below.

APPENDIX D

Test Boring Logs

URS

LOG OF BORING _____

PROJECT NAME/NUMBER **Sauget Area 2 Site/23-20010024.02** LOCATION **Sauget Illinois**		DATE STARTED	DATE COMPLETED
DRILLING CONTRACTOR	FOREMAN	GROUND ELEVATION (FT. MSL)	WATER DEPTH (FT BGS):
DRILLING EQUIPMENT		COMPLETION DEPTH (FT BGS)	ROCK DEPTH (FT BGS)
GEOLOGIST/ENGINEER		BORING LOCATION	

DESCRIPTION	Sample Run	Depth (FT BGS)	Water Table	SAMPLES Recov. (in)	SAMPLES Penetra. Tons/ft^2	USC	PID Readings Head Space (ppm)	REMARKS

APPENDIX E

Guidance for Soil Sample Logs

APPENDIX E

Guidance for Soil Sample Logs

At the outset of sample logging, the on-site geologist will record field notes with waterproof ink in a bound field notebook. At a minimum, the daily field notes will include:

- Project name and number
- Date and time
- Weather conditions
- Sampler's name
- Project objective(s).

Throughout the sampling round, the following items will be recorded as appropriate:

- Sample location(s)
- Sample identifications
- Limiting field conditions
- Problems encountered.

A copy of the boring log to be used is included as Appendix D.

Unconsolidated soil samples will be described as follows:

- Descriptive information:
  - Color name (Munsell Color Chart) of the logged interval or sample
  - Color notation including chroma, hue, value, and qualifiers

1. Mottling with abbreviations, descriptors, and criteria for descriptions of mottles as identified below

Descriptors for Mottling

Abundance	Size	Contract
f: few (<2%)	fine (<5 mm)	faint
c: common (2%-20%)	medium (5-15 mm)	distinct
m: many (>20%)	coarse (>15 mm)	prominent

2. Degree of saturation (dry, damp, moist, wet, saturated, or combinations); note depth to groundwater table, if observed

3. Degree of density. Count the blows of each 12-inch increment of the sampler (ASTM-1586-84). Use the values and the density table presented below to determine the degree of density.

Degree of Density

Cohesive Clays		Non-cohesive Granular Soils	
0-2	very soft	0-3	very loose
2-4	soft	4-9	loose
5-7	firm	10-29	medium dense
8-15	stiff	30-49	dense
16-29	hard	50-80	very dense
30-49	very hard	80+	extremely dense
50-80	extremely hard		

4. Soil description according to ASTM's Unified Soil Classification System (USC) and by soil structure:

- ASTM Unified Soil Classification: The Grade Limits and Grade Standards table presented below provides the grade limits and grade names used by engineers according to ASTM standards D422-63 and D643-78.

Grade Limits and Grade Standards

Grade Limits		Grade Names	
mm	inch	US standard sieve series	
			boulders
305	12.0		
			cobbles
76.2	3.0	3.0 inch	
			gravel
4.75	0.19	No. 4	
2.00	0.08	No. 10	
			medium sand
0.425		No. 40	
0.074		No. 200	
			silt
0.005			
			clay size

Source: AGI data sheet 29.2

- Course-grained soils include clean gravels and sands and silty or clayey gravels and sands with more than 50% retained on the No. 200 sieve. A table of USC symbols and names for coarse-grained soils is presented below.

APPENDIX E

Guidance for Soil Sample Logs

USCS Symbols and Names for Coarse-grained Soils

USCS Symbol	Typical Names
GW	Well graded gravels, gravel-sand mixtures, little or no fines
GP	Poorly graded gravels, gravel-sand mixtures, little or no fines
GM	Silty gravels, gravel-sand-silt mixtures
GC	Clayey gravels, gravel-sand-clay mixtures
SW	Well graded sands, gravelly sands, little or no fines
SP	Poorly graded sands, gravelly sands, little or no fines
SM	Silty sand, sand-silt mixtures
SC	Clayey sands, sand-clay mixtures

- Fine-grained soils include inorganic and organic silts and clays; gravelly, sandy, or silty clays; and clayey silts with more than 50% passing the No. 200 sieve. A table of USC symbols and names for fine-grained soils is presented here.

USCS Symbols and Names for Fine-grained Soils

USCS Symbol	Typical Names
ML	Inorganic silts and very fine sands, rock flour, silty, or clayey fine sands, or clayey silts with slight plasticity
CL	Inorganic clays of low to medium plasticity, gravelly clays, sandy clays, silty clays, lean clays
OL	Organic silts and organic silty clays of low plasticity
MH	Inorganic silts, micaceous or diatomaceous fine sandy or silty soils, elastic silts
CH	Inorganic clays or high plasticity (residual clays), fat clays
OH	Organic clays of medium to high plasticity, organic silts
Pt	Peat and other highly organic soils

A table of soil descriptors is presented below. (this goes with #4, needs hyphened bullet)

Soil Descriptors

Calcareous:	containing appreciable quantities of calcium carbonate
Fissured:	containing shrinkage cracks, often filled with fine sand or silt, usually more less vertical
Interbedded:	containing alternating layers of different soil types

Soil Descriptors

Intermixed:	containing appreciable, random, and disoriented quantities of varying color, texture, or constituency
Laminated:	containing thin layers of varying color, texture, or constituency
Layer:	thickness greater than 3 inches
Mottled:	containing appreciable random speckles or pockets of varying color, texture, or constituency
Parting:	paper thin
Poorly graded (well sorted):	primarily one grain size, or having a range of sizes with some intermediate size missing
Slickensided:	having inclined planes of weakness that are slick and glossy in appearance and often result in lower unconfined compression cohesion
Split graded:	containing two predominant grain sizes with intermediate sizes missing
Varved:	sanded or layered with silt or very fine sand (cyclic sedimentary couplet)
Well graded (poorly sorted):	containing wide range of grain sizes and substantial amounts of all intermediate particle sizes
Modifiers:	Predominant type - 50% to 100% Modifying type - 12% to 50% With - 5% to 12% Trace - 1% to 5%

5. Degree of plasticity. The following table presents the terms used to denote the various degrees of plasticity of soil that passes the No. 200 sieve.

Degrees of Plasticity

Descriptive Term	Degree of Plasticity	Plasticity Index Range
SILT	none	non-plastic
Clayey SILT	slight	1-5
SILT & CLAY	low	5-10
CLAY & SILT	medium	10-20
Silty CLAY	high	20-40
CLAY	very high	over 40

6. Drilling information:

   - Drill rig manufacturer, model, and driller (if applicable)
   - Geologist or geotechnical engineer
   - Project name, sample point identification, and location

- Date samples obtained (and times if required)
- Type of sampler (e.g., split spoon, Shelby, California), measurements or method of advancing boring or equipment, method of driving sampler, and weight of hammer
- Drill fluids (if applicable)
- Ground surface or grade elevation (if known)
- Depth penetrated and blow counts/6-inch interval of penetration for ASTM 1586-84 and sample number (if applicable)
- Closed hole intervals and advancement (if applicable)
- Recovery
- Strata changes and changes within samples
- Sampling tool behavior
- Drill string behavior
- Use(s) of borehole
- Disposition(s) of residual soil or cuttings
- Signature or sampling of log (as required)

APPENDIX F

Sample Chain-of-Custody

CHAIN OF CUSTODY RECORD

Page ___ of ___

Project Name	Project No.
Project Location	Project Manager
Sampler(s)	

Sample		Type		Sample Identification	Matrix	Containers		Analytical Parameters										Remarks
Date	Time	Comp.	Grab			No.	Type											

Signatures	Date	Time	Shipping Details	Special Instructions
Relinquished by:			Method of Shipment	
Received by:			Airbill No.	
Relinquished by:			Lab Address	
Received for Laboratory by:				

Custody.frm/jdg 3-09-92

White copy - Laboratory Yellow copy - Laboratory Pink copy - WCC

APPENDIX G Typical Well Construction Diagrams and Well Installation SOP

APPENDIX G Typical Well Construction Diagrams and Well Installation SOP

Well Construction SOP

- Well materials will be inspected for proper specifications and integrity.
- The well screen, bottom cap, plug, and riser will be certified clean from the manufacturer. If they are not, they will be cleaned with a high-pressure steam cleaner.
- The total depth of the borehole will be measured, referenced to existing grade, and recorded. The quantities and lengths of all materials placed in the borehole will be measured and recorded. These materials include, but are not limited to: screen interval, blank casing or riser length, filter pack, bentonite seal, grout, and protective casing.
- The well must be straight and vertical. Centralizers will be used as necessary to keep the monitoring well centered in the borehole.
- The filter pack will consist of an appropriately graded, washed silica sand. The volume of filter pack necessary to fill the annular space will be computed and used to monitor the progress of installing the filter pack. The filter pack will be emplaced in increments to prevent bridging. If bridging occurs, the bridge will be broken before proceeding. The depth of the filter pack will be continuously checked with a weighted tape. The filter pack will extend a minimum of 2 feet above the top of the well screen.
- The augers or temporary casing will be withdrawn in no more than 5-foot increments to limit borehole collapse during emplacement of the filter pack. The lowest point of the casing or auger will not be more than 2 feet higher than the top of the filter material.
- A bentonite slurry seal will be tremied in place above the filter pack. The bentonite slurry seal will extend a minimum of 2 feet and not more than 3 feet above the top of the filter pack.
- A cement and bentonite grout mixture will be tremied in place above the top of the bentonite slurry seal to 3 feet below existing grade. The grout mixture will be installed from the top of the bentonite seal upward to reduce the opportunity for the development of void spaces in the emplaced grout. The grout mixture must be pH neutral so as not to modify the pH of the groundwater.
- A protective casing will be installed which extends from below the frost line to slightly above the top of the well casing. A weep hole will be drilled into the protective casing so accumulated water can drain.

- The concrete to be used to complete surface installation will be a commercially available, premixed cement, sand, and gravel mixture (e.g., Quickrete).

MONITORING WELL CONSTRUCTION DIAGRAM

GROUND SURFACE ELEVATION _____

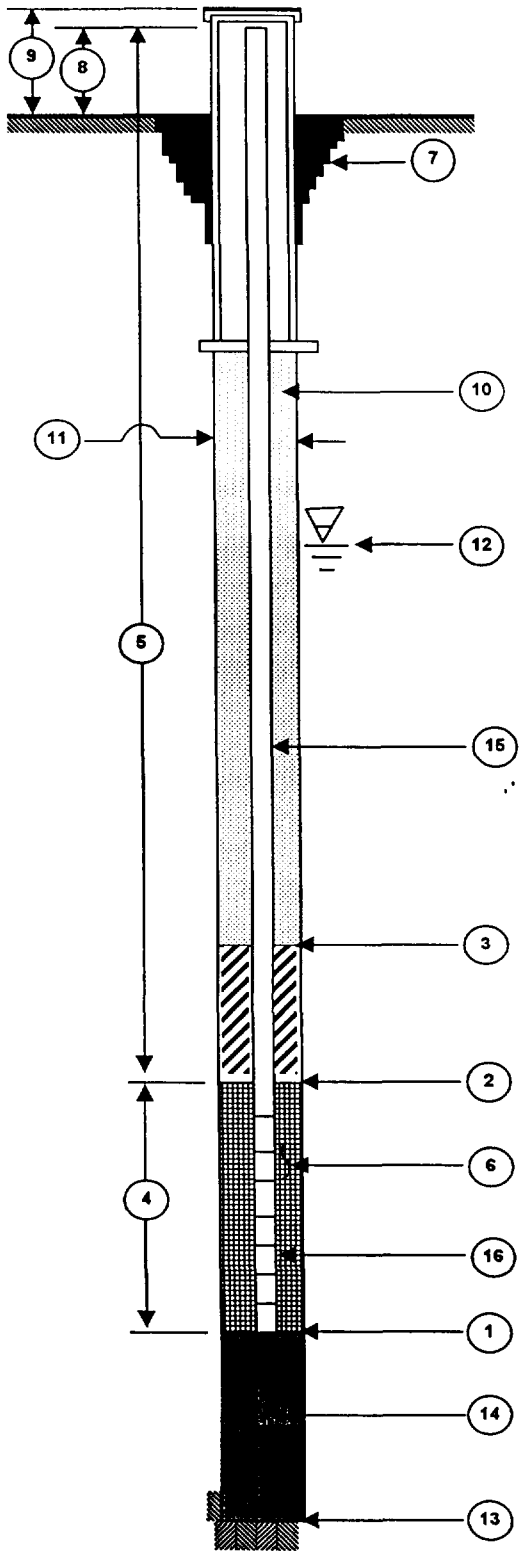
TOP OF INNER WELL CASING ELEVATION _____

JOB NUMBER _____

BORING NUMBER _____

INSTALLATION DATE _____

LOCATION _____



1. DEPTH TO BOTTOM OF WELL POINT OR SLOTTED PIPE _____ FEET.*
2. DEPTH TO BOTTOM OF SEAL (IF INSTALLED) _____ FEET.*
3. DEPTH TO TOP OF SEAL (IF INSTALLED) _____ FEET.*
4. LENGTH OF WELL SCREEN _____ FEET.
   SLOT SIZE _____ INCHES.
5. TOTAL LENGTH OF RISER PIPE _____ FEET AT _____ INCH DIAMETER.
6. TYPE OF PACK AROUND WELL POINT OR SLOTTED PIPE _____.
7. CONCRETE CAP? YES NO (CIRCLE ONE)
8. HEIGHT OF WELL CASING ABOVE GROUND _____ FEET.
9. PROTECTIVE CASIING YES NO (CIRCLE ONE)
   HEIGHT ABOVE GROUND _____ FEET.
   LOCKING CAP? YES NO (CIRCLE ONE)
10. TYPE OF UPPER BACKFILL _____.
11. BOREHOLE DIAMETER _____ FEET BELOW TOP.
12. DEPTH TO GROUND WATER _____ FEET.
13. TOTAL DEPTH OF BOREHOLE _____ FEET.*
14. TYPE OF LOWER BACKFILL _____.
15. PIPE MATERIAL _____.
16. SCREEN MATERIAL _____.

* (DEPTH FROM GROUND SURFACE)

URS Corporation

MONITORING WELL CONSTRUCTION DIAGRAM

GROUND SURFACE ELEVATION _____

TOP OF INNER WELL CASING ELEVATION _____

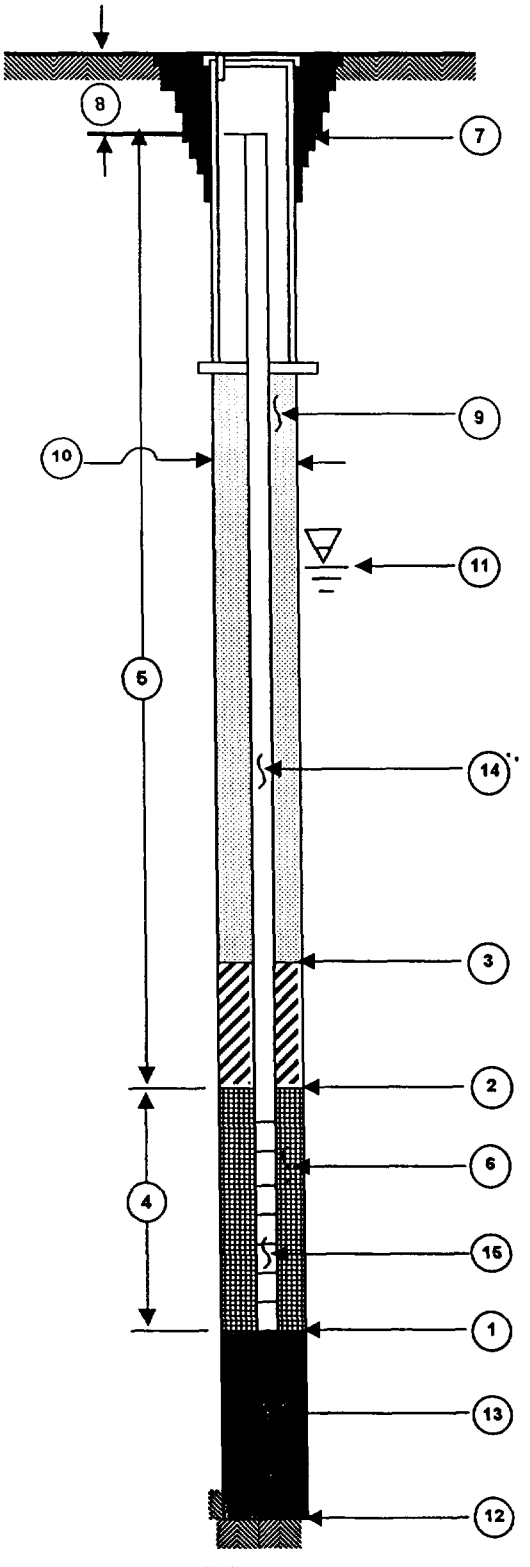
DATUM _____

JOB NUMBER _____

BORING NUMBER _____

INSTALLATION DATE _____

LOCATION _____



(1) DEPTH TO BOTTOM OF WELL POINT OR SLOTTED PIPE _____ FEET.*

(2) DEPTH TO BOTTOM OF SEAL (IF INSTALLED) _____ FEET.*

(3) DEPTH TO TOP OF SEAL (IF INSTALLED) _____ FEET.*

(4) LENGTH OF WELL SCREEN _____ FEET. SLOT SIZE _____.

(5) TOTAL LENGTH OF RISER PIPE _____ FEET AT _____ INCH DIAMETER.

(6) TYPE OF PACK AROUND WELL POINT OR SLOTTED PIPE _____.

(7) CONCRETE CAP? YES NO (CIRCLE ONE)

(8) DEPTH TO TOP OF INNER CASING BELOW GROUND SURFACE _____ FEET.

(9) TYPE OF UPPER BACKFILL _____.

(10) BOREHOLD DIAMETER _____ INCHES.

(11) DEPTH TO GROUNDWATER _____ FEET BELOW TOP OF INNER CASING _____ HOURS AFTER WELL DEVELOPMENT.

(12) TOTAL DEPTH OF BOREHOLE _____ FEET.*

(13) TYPE OF LOWER BACKFILL _____.

(14) PIPE MATERIAL _____.

(15) SCREEN MATERIAL _____.

* (DEPTH FROM GROUND SURFACE)

MONITOR WELL INSTALLATION DETAILS

URS Corporation

P:/BOILER/EXCEL/MONITORWELLFLUSH

APPENDIX H Well Development and Well Purging SOPs

APPENDIX H Well Development and Well Purging SOPs

Well Development

The objective of groundwater monitoring well development is to clear the well of accumulated sediments, when 10% or more of the well screen has been occluded by sediment, so that representative groundwater samples may be collected. The accumulated sediments need to be re-suspended in the water column in order to be removed. A variety of techniques can be used to re-suspend the sediments. Some of the common methods that can be used to re-suspend sediments include using a surge block, injection of air into the water column of the well, or using a bailer. Once the sediment is re-suspended, the water and sediment can then be removed from the well using a submersible pump, an air bladder pump, or a bailer. Development will be considered to be complete when the fine-grained materials have been removed.

The preferred method for development will be surging and removing water with dedicated, disposable, polyethylene bailers or a submersible pump. The following procedures will be used when developing an existing well.

1. Place a clean, plastic drop cloth on the ground around the well to be developed.
2. Unlock the protective well cover and remove the well cap.
3. Check the well for NAPL using an interface probe, as outlined in the water level measurement section below.
4. Measure the depth to groundwater and/or NAPL to the nearest hundredth of a foot.
5. Measure the total depth of the well to the nearest hundredth of a foot. Note whether the bottom of the well feels hard or soft.
6. Attach the decontaminated surge block to the appropriate lengths of pole section and push the surge block to the bottom of the well, or send a bailer to the bottom of the well.
7. Pull and push the surge block/bailer up and down to agitate the water and suspend the sediments in the well.
8. Once sufficient re-suspension has occurred, pull the surge block/bailer out of the well.
9. Attach an appropriate length of polyethylene tubing to a submersible pump, and lower the pump to near the bottom of the well, out of sediment that may be remaining in the bottom of the well.

10. Place the discharge end of the tubing such that purged water will be collected in a 55-gallon drum.
11. Turn on the pump and adjust the flow rate to pump at a sufficiently high rate to allow the sediments to be removed without causing the pump to clog.
12. Continue pumping until relatively sediment-free water is obtained.
13. Remove the pump and allow the well to recover for half an hour. Re-measure the total well depth. If the measured depth indicates 10% or more occlusion, repeat steps 8 through 14. If the measured depth indicates less than 10% well screen occlusion, disconnect the tubing from the pump and place into the appropriate waste container. Dismantle the surge block and pole connectors for decontamination. Pick up and appropriately dispose of plastic sheeting and other disposables into the appropriate waste container. Close and properly label the 55-gallon drum(s).
14. Decontaminate the pump, wiring, and any other equipment, using the steam cleaner.

Note in the field log book the approximate number of gallons of water removed during development of each well.

Well Purging

Prior to initiating the well purging process, the following information will be recorded in a field notebook and on the groundwater sampling logs (Appendix N).

- Well number
- Day, date, and time
- Weather conditions
- Condition of the well and surrounding area
- Sampling team members
- Instrument calibration information
- Water level prior to purging
- Depth to the bottom of the well
- Volume of water to be purged

- Physical properties of evacuated water: color, odor, turbidity, presence of non-aqueous phase liquids
- Deviations from planned sampling methodology
- Ambient air monitoring readings

Low-flow purging techniques will be used to purge the well in accordance with RCRA Groundwater Monitoring TEGD guidelines. These guidelines state that purging will be conducted by removing a minimum of three well volumes of fluid. A well volume of water is calculated using the following formula: $V = \pi r^2 h(7.48)$ where

V = Standing water volume in gallons to be purged

r^2 = Inside radius of well in feet, squared

h = Linear feet of standing water in the casing

One well volume will be calculated so field personnel know when to perform field measurements. Such measurements are performed after the removal of each well volume.

In groundwater systems, naturally occurring metals tend to adsorb to the surfaces of solids. The level of adsorbance depends on the pH of the soil and water. The concentration of metals in dissolved form, therefore, is limited by this adsorption and by the metals' low solubilities. Sediment in water is likely to have metal ions adsorbed to its particles, which analytical methods may not be able to differentiate from metal ions dissolved in the water. Groundwater samples that contain sediment, therefore, may yield analytical results that do not represent the concentration of metals in the groundwater itself.

Moreover, the transport of sediment is generally not due to the natural flow of groundwater, but is induced by the sampling. Samples that are collected for metals analysis should exhibit low turbidity, and they are generally filtered to remove sediment. When possible, low turbidity samples should be obtained without filtering. A turbidity meter will be used to monitor turbidity during sampling. Following the extraction of each well volume, turbidity will be monitored in the field. Additionally, pH, conductivity, and temperature will be measured and recorded after each well volume removed. Purging is deemed complete when these parameters have stabilized within 10% over a minimum of two successive well volumes. Samples will be collected when turbidity levels are below 5 nephelometric turbidity units (NTU). Should a turbidity level of 5

NTU be unachievable after 2 hours of purging, the samples will be collected and the turbidity recorded.

The procedures for well purging are described as follows:

- The low-flow pump will be lowered into the well, and the pump intake will be located at the approximate midpoint of the screened interval. Once the pump is in place, the controller will be set for the desired flow rate. The optimum flow rate is dependent on the site-specific hydrogeology and will be determined in the field, however, the flow rate will not exceed 1 L/min.
- Pump the groundwater into a graduated pail. Continue pumping until the turbidity reading is at or below 5 NTU unless that is unattainable then the turbidity reading is within 10% for two consecutive well volumes, the well is pumped dry.
- If the well is purged dry, allow sufficient time for the well to recover before proceeding. Record this information on the groundwater sampling log.
- In addition to the turbidity readings, in wells which exhibit sufficient recharge, also collect pH, conductivity, and temperature measurements. A minimum of two consecutive measurements should be within the following criteria:
  - ±0.25 units for pH
  - ± 10% for specific conductivity
  - ± 1 C^{o} for temperature

  Record this information on the groundwater sampling log.

Discharge the water removed during purging or possible decontamination procedures into 55-gallon drums for disposal.

APPENDIX I Well Gauging and Groundwater Sampling SOPs

APPENDIX I Well Gauging and Groundwater Sampling SOPs

Water Level Measurements (Well Gauging)

Groundwater level measurements will be collected as follows:

- A pre-cleaned, electric water level or NAPL interface probe will be used to measure the depth to water from the top-of-casing reference point and/or check for NAPLs in the water column, where applicable. Record the depth of water and/or NAPLs, as applicable. This procedure will also be used to measure the depth of the well. Measurements will be made to the nearest 0.01 feet.
- After obtaining the water level, the volume of water within the well will be calculated.

Decontaminate the water level and NAPL interface probe used in the well by thoroughly scrubbing with Alconox® and a potable water wash. Rinse with potable water, and then rinse twice with distilled water.

Pre-sampling Procedures

As part of a sampling event, the following steps will initially be taken by personnel responsible for sampling:

- Obtain appropriate containers for sample collection. Containers will be provided by the laboratory performing the analyses.
- Examine sampler, containers, and preservatives; contact laboratory immediately if problems are found.
- Confirm sample delivery time and method of sample shipment with the laboratory.
- Assemble and inspect field equipment to be used for sample collection; verify that equipment is clean and in proper working order.
- Calibrate field instruments and/or meters to manufacturers' specifications. Conductivity, pH, and turbidity meters will be calibrated to known calibration standard solutions. Re-check calibration prior to the start of each day and after four hours of use. Calibration activities will be recorded on the groundwater sampling log (Appendix N) and in the field notebook.
- Perform NAPL interface probe function test in accordance with QAPP guidelines.

- Establish well location and well identification.
- Obtain necessary keys for wells or gates.
- As feasible, begin sampling procedures at monitoring wells that are least impacted and proceed to those that historically have been impacted. A review of previous analytical data will be required prior to sampling.
- Examine each well for damage, tampering, erosion around the well casing, etc., and note on respective field log sheet.
- Place clean plastic sheeting around well to provide a barrier between the surrounding ground surface and sampling equipment used
- Put on a new pair of disposable gloves.
- Open well cap and make a visual check down the casing and note the condition of the well casing and whether a permanent groundwater level reference point has been established on the casing. Note on respective field log sheet.
- Perform ambient air monitoring for hazardous conditions on a continuous basis following opening of the well using a PID and CGM. Record readings in the field notebook.

Groundwater Well Sampling Procedures

The following method will be used to collect leachate samples:

1. Remove appropriate sample containers from the transport container, and prepare the sample containers for receiving samples.
2. Fill out a self-adhesive label with the appropriate information and affix it to the appropriate sample container. Place clear polyethylene tape over the completed label to protect it from dirt and water. Sample labels can be prepared prior to sample collection except for time and date. Labels can be filled in on the date of sample collection and just prior to collecting the sample. Sample containers will be kept cool with their caps on until they are ready to receive samples.
3. Place clean plastic sheeting around the well to provide a barrier between the surrounding ground surface and sampling equipment.

4. Groundwater samples will be collected in accordance with RCRA Groundwater Monitoring TEGD guidelines. Using a low-flow sampling system such as the MicroPurge Basic System.
5. Put on a clean pair of disposable gloves.
6. The low-flow pump will be lowered into the well, and the pump intake will be located at the approximate midpoint of the screened interval. Once the pump is in place, the controller will be set for the desired flow rate. The optimum flow rate is dependent on the site-specific hydrogeology and will be determined in the field, however, the flow rate will not exceed 1 L/min.
7. Samples will be transferred from the bailer to appropriate sample containers. Agitation and aeration will be minimal.
8. Fill sample containers for VOC samples prior to filling other sample containers.
9. Fill remaining sample containers.
10. If the sample containers cannot be filled quickly, keep sample containers cool with the cap on until finished. Sample containers will be preserved as described in the QAPP.
11. Return each sample container to its proper transport container. Preserve samples by reducing the temperature within the containers to approximately 4° Celsius, using ice. Samples must not be allowed to freeze.
12. Begin chain-of-custody procedures. A sample chain-of-custody form is included in Appendix F.
13. Record the physical appearance of the groundwater observed during sampling on the groundwater sampling log or in the field notebook.
14. Replace the well cap and lock the well protection assembly before leaving the well location.
15. The pump and all downhole equipment will be decontaminated prior to each use.

Groundwater Borehole Sample Collection

The following method will be used to collect groundwater samples:

1. Remove appropriate sample containers from the transport container, and prepare the sample containers for receiving samples.
2. Fill out a self-adhesive label with the appropriate information and affix it to the appropriate sample container. Place clear polyethylene tape over the completed label to protect it from dirt and water. Sample labels can be prepared prior to sample collection except for time and date. Labels can be filled in on the date of sample collection and just prior to collecting the sample. Sample containers will be kept cool with their caps on until they are ready to receive samples.
3. The Geoprobe® will hydraulically push the screened sampler to the desired sample depth (e.g., the first sample will be collected at 20 feet below ground surface). The sampler will fill with groundwater.
4. Send a bailer or ball and check valve down to the screened section of the sampler to collect the groundwater sample. Pull the bailer or ball and check valve to the surface.
5. Unfiltered samples will be collected at each sample location and depth.
6. Fill sample containers for VOC samples prior to filling other sample containers.
7. Fill remaining sample containers.
8. If the sample containers cannot be filled quickly, keep sample containers cool with the cap on until filled. Sample containers will be preserved as described in the QAPP.
9. Return each sample container to its proper transport container. Preserve samples by reducing the temperature within the containers to approximately 4° Celsius using ice. Samples must not be allowed to freeze.
10. The Geoprobe® will then push the screened sampler to the next desired depth (e.g., 60 feet). As before, send either a bailer or ball and check valve down into the sampler to collect the groundwater. Bring the sample to the surface and fill the appropriate sample containers. Continue to repeat this process until all samples have been collected.
11. Begin chain-of-custody procedures. A sample chain-of-custody form is included in Appendix F.
12. Record the physical appearance of the groundwater observed during sampling on the groundwater sampling log or in the field notebook.

APPENDIX J Rock Lithology, Log Order of Presentation and Selection

APPENDIX J Rock Lithology Log Order of Presentation and Selection

1. COLOR

Color (from Munsell Color Chart) of logged interval or mass (sample)

2. ROCK QUALITY

The rock quality designation (%RQD) is computed in the following way:

%RQD = 100 x [length of core in pieces $\geq$ 4] / [hole length drilled or attempted (cored)]

Guidelines:

- Measure from the center of natural breaks
- Exclude joints that dip within 5 degrees of core axis
- Exclude drill breaks (See criteria for identification of drill breaks)
- Do not calculate RQD for soft semi-indurate rock or severely weathered rock ("Weathering" is addressed below)

Scale:

90 – 100	Excellent	Massive
75 – 90	Good	Lightly fractured
50 – 75	Fair	Moderately fractured
25 – 50	Poor	Highly fractured
0 – 25	Very poor	Sheared

It is important to think of RQD in conditions of equal effect; that is, group the RQD ranges as equivalent to rock type, structural domain, shear zones, and so forth.

Criteria for identifying drilling breaks:

- A rough, brittle surface with fresh cleavage planes in individual rock minerals indicates an artificial fracture
- A generally smooth or somewhat weathered surface with soft coating or infilling materials such as talc, gypsum, chlorite, mica, or calcite obviously indicates a natural discontinuity

APPENDIX J Rock Lithology Log Order of Presentation and Selection

- In rocks showing foliation, cleavage, or bedding, it may be difficult to distinguish between natural discontinuities and artificial fractures when these are parallel with the incipient planes of weakness. If drilling has been carried out carefully, then the questionable breaks should be counted as natural features, to make the conservative assumption.
- Depending on the drilling equipment, part of the length of core being drilled may occasionally rotate with the inner barrels in such a way that grinding of the surfaces of discontinuities and fractures occurs. In weak rock types, it may be difficult to decide if the resulting rounded surfaces are present natural or artificial features. When in doubt, the conservative assumption should be made; that is, assume that they are natural.
- It is appropriate to keep a separate record of the frequency of artificial fractures for assessing the possible influence of blasting on the weaker sedimentary and foliated or schistose metamorphic rocks.

The occurrence of impurities is qualified with the following terms:

consolidated, unconsolidated, semi-consolidated round, sub-round, sub-angular, angular, ellipsoidal, spherical

masses	brecciated	trace remnants
pockets	chaotically intermixed	disseminated throughout matrix
nodules	fine wispy layers	scattered
blebs	stringers	streaks or specks
lenses	subtle network	narrow zones
oolites	chicken wire pattern	
zones	dendritic	
transitions		

3. POROSITY

Use the following descriptions:

none

medium

moderate

very

pinhole porosity

visual porosity

4. BEDS

Bedding, horizontal or inclined:

planar

mylonitic

folded

contorted

wavy banding

Bedding, beds, cleavage, and foliation:

Very thin	1-3 cm (0.4-1")
Thin	3-10 cm (1-4")
Medium	10-30 cm (4"-1')
Thick	30-100 cm (1-3')
very thick	>100 cm (>3')

Lamina:

laminated: 0.3-1 cm (0.4-1")

thinly laminated: <0.3 cm (<0.4")

5. THICKNESS, LAMINATIONS, LAMELLA, SEAMS

smooth

broken

irregular

convuluted

up/down criteria

6. **CONTACT**

distinct

vague

gradational

7. **FOLIATION**

fissile (planar splitting)

non-fissile

8. **JOINTS**

planar	irregular break	infilled with
parting planes	scalloped	healed fracture
	conchoidal	mylonitic

Spacing

Very thin	1-3 cm (0.4-1")
thin	3-10 cm (1-4")
medium	10-30 cm (4"-1')
thick	30-100 cm (1-3')
Very thick	>100 cm (>3')

9. WEATHERING

Fresh	Rock fresh; crystals or grains bright; a few joints may show slight staining; crystalline rocks ring if struck with a hammer
Slight	Rock generally fresh; joints stained and may show clay filling if open; staining may extend into rock fabric adjacent to weathered planes; if present, feldspars may be dull and discolored; crystalline rocks ring if struck with hammer
Moderate	Except for quartz, most of the rock mass shows discoloration and weathering; most feldspar is dull and discolored and kaolinitization (alteration to clay minerals) is common; rock gives a dull sound if struck with hammer; rock shows overall loss of strength; potions may be removed with a geologist's pick
Severe	All minerals except quartz discolored or stained; rock fabric still discernible; intergranular or intercrystalline disassociation virtually complete; internal structure essentially that of soil; fragments of strong rock may remain; may be called saprolite
Complete	Rock is decomposed to a soil; fabric not discernible or only barely discernible; quartz may remain as dikes or stringers

10. SURFACE

Solid	Contains no voids
Pitted	Small voids generally restricted to joint surfaces, bedding planes, or other surfaces which provide access for attacking fluids
Vuggy	Use restricted to solution voids in carbonate rocks and hydrothermally altered rocks; voids may be found throughout the rock face; voids up to 9 inch diameter
Vesicular	Use restricted to voids in igneous (occasionally metamorphic) rocks, void origin usually due to gas bubbles; voids up to 3-inch average diameter
Cavernous	Applicable in any rock; voids and channels greater than 9-inch average diameter; voids large enough to cause serious leakage or structural problems

11. HARDNESS

The following scale (not to be confused with Moh's scale for hardness of minerals) is used for a rock:

Very hard	Cannot be scratched with knife or sharp pick; breaking of hand specimens require several hard blows of geologist's pick
Hard	Can be scratched with knife or pick, only with difficulty; hard blow of hammer required to detach hand specimen
Moderately	Can be scratched with knife or pick; gouges or grooves to 1/8-inch deep can be excavated by hard blow of point of geologist's pick; hand specimen can be detached by moderate blow
Medium	Can be grooved or gouged 1/16-inch deep by firm pressure on knife or pick point; can be excavated in small chips to pieces about 1-inch maximum size by hard blows of the point of a geologist's pick
Soft	Can be gouged or grooved readily with knife or pick point; can be excavated in chips to pieces several inches in size by moderate blows of a pick point; small thin pieces can be broken by finger pressure
Very soft	Can be carved with knife; can be excavated readily with point of pick; pieces 1-inch or more in thickness can be broken by finger pressure; can be scratched readily by fingernail

12. TEXTURE

American Geological Institute data sheets

Fine	<1 mm
Medium	1.5 mm
coarse	>5 mm

13. GRAIN SHAPE

very angular

angular

sub-angular

sub-rounded

rounded

well rounded

14. SORTING (for sedimentary rocks)

very well sorted

well sorted (poorly graded)

moderately sorted

poorly sorted (well graded)

very poorly sorted

15. MINERAL COMPONENTS

16. ROCK CLASSIFICATION

American Geological Institute data sheets

Abbreviations of rock descriptions will conform to the standard abbreviation list. This list is presented below. A word that is not on this list will be spelled out. An initial capital letter will be used for each rock type. Capital letters will be for formation names and rock types.

Punctuation will also be standardized. The following convention will be used for punctuation:

- Comma after each item of description
- Semi-colon between each rock-type description
- No full stops (periods).

In addition, remarks such as *A/A* ("as above"), *same as above*, *see above*, or *same* are undesirable.

APPENDIX J Rock Lithology Log Order of Presentation and Selection

Accepted abbreviations:

A	
about	ABT
above	ABV
abundant	ABDT
accumulation	ACCUM
acicular	ACIC
aggregate	AGG
agglomerate	AGLM
algae	ALG
altered	ALT
amorphous	AMOR
amount	AMT
angular	ANG
anhedral	ANHED
anhydrite	ANHY
anhydritic	ANHYDRIC
apparent	APR
appears	APRS
approximate	APPROX
aragonite	ARAG
arenaceous	AREN
argillaceous	ARG
arkose	ARK
asphalt	ASPH
at	@
average	AV

bed	BED
bedded	BEDD
bedding	BEDG
bentonite	BENT
biotite	BIOT
bitumen	BIT
black	BLK
bleeding	BLDG
blocky	BLKY
botryoida	BTRI
bottom	BTM
boulder	BLDR
brachiopod	BRAC
breccia	BREC
brittle	BRIT
bright	BRI
broken	BRKN
brown	BRN
bryozoa	BRY

C	
calcite	CA
calcareous	CALC
carbonaceous	CARB
cavernous	CAV
caving	CVG
cement	CMT

APPENDIX J Rock Lithology Log Order of Presentation and Selection

B	
band	BND
banded	BNDD
barite	BAR
basalt	BAS
chitin	CHIT
chlorite	CHL
chloritic	CHLTC
clastic	CLAS
clay	CLY
claystone	CLYST
clean	CLN
clear	CLR
cleavage	CLV
cluster	CLS
coal	COAL
coarse	C
cobble	CBL
color	COL
common	COM
compact	COMP
conchoidal	CONCH
concentric	CNCN
conodont	CONO
conglomerate	CGL
contact	CONT
contorted	CONTRT
coquina	COQ
covered	COV
center	CNTR
cephalopod	CEPH
chalcedony	CHAL
chalk	CHK
chert	CHT
determine	DTRM
detrital	DTRL
diameter	DIAM
diatoms	DIAT
difference	DIF
disseminated	DISM
dolocast	DOLC
dolomite	DOL
dolomitic	DOLIC
dolomoid	DOLM
drusey	DRSY
E	
earthy	ETHY
echinoid	ECH
eliptical	ELIP
elongate	ELNG
embedded	EMBEDD
enlarged	ENL
epidote	EP
equivalent	EQUIV
euhedral	EUHED
evaporitic	EVAP
expose	EXP

APPENDIX J Rock Lithology Log Order of Presentation and Selection

cream	CRM	extrusive	EXTRU
crenelated	CREN		
crevice	CREV	**F**	
crinkled	CRNK	faceted	FAC
crinoid	CRIN	faint	FNT
crossbedded	XBEDD	fair	R
crosslaminated	XLAM	fault	FLT
cross-stratified	XSTRAT	fauna	RAU
cryptocrystalline	CRPXLN	feldspar	FELS
cryptograined	CRPGR	ferruginous	FE
crystal	XL	fibrous	FIB
crystalline	XLN	figured	FIG
cuttings	CTGS	fine,-ly	F
		fissile	FISS
D		flaggy	FLGY
dark	DK	flake,-y	FLK,-Y
dead	DD	flinty	FLTY
debris	DEB	floating	FLTG
degree	DEGR	fluorescence	FLUOR
dendritic	DEND	foliated,-ion	FOL
dense	DNS	foraminifera	FORAM
formation	FMTN	**I**	
fossil	FOSS	igneous	IG
fossiliferous	FOSSIF	imbedded	IMBEDD
fracture,-ed	FRAC	impregnated	IMPRG
fragment	FRAG	impressions	IMP
fresh	FRSH	included	INCL
friable	FRI	inclusion	INCLSN
frosted	FROS	increase	INCR

APPENDIX J Rock Lithology Log Order of Presentation and Selection

fusilinid	FUS
G	
gabro	GAB
gastropod	GAST
glassy	GL
glauconite	GLAUC
globular	GLOB
gloss	GLOS
gneiss	GN
good	G
grade	GRD
grading	GRDG
grain	GRN
granite	GRNT
granular	GRAN
granule	GRNL
graptolite	GRAP
gravel	GVL
gray	GRY
graywacke	GYWKE
greasy	GRSY
green	GREEN
gritty	GRTY
gypsum	GYP
gypsiferous	GYPS
H	
hard	HD

indistinct	IND
interbedded	INTBEDD
intercrystalline	INTXLN
intergranular	INTGRAN
intergrown	INTGWN
interlaminated	INTLAM
interstitial	INTSTL
interval	INTVL
intraformational	INTRM
intrusion	INTR
invertebrate	INVRTB
iron	FE
iron oxides	FE-OX
ironstone	FE-ST
irregular	IREG
iridescent	IRID
J	
jasper	JASP
jointed	JTD
jointing	JTG
joints	JTS
K	
kaolin,-ite	KAOL
L	
laminated	LAM
large	LRG

APPENDIX J Rock Lithology Log Order of Presentation and Selection

heavy	HVY
hematite	HEM
high	HI
horizontal	HOR
hornblende	HBD
hydrocarbon	HYDC
limonite	LMNT
limy	LMY
lithic	LITH
lithographic	LITHG
little	LTL
long	LONG
loose	LSE
lower	LOW
lumpy	LMPY
luster	LSTR
M	
macro-fossil	MACFOS
magnetic	MAGN
magnetite	MAG
marl	ML
marlstone	MRLST
maroon	MAR
massive	MASS
material	MAT
matrix	MTX

lavender	LAV
layer	LYR
leached	LCHD
ledge	LDG
lenticular	LENT
light	LT
lignite	LIG
limestone	LS
numerous	NUM
O	
object	OBJ
occasional	OCC
ocher	OCH
odor	ODOR
oil	OIL
olive	OLV
oolitic	OOL
opaque	OPG
opposite	OPP
orange	ORNG
organic	ORG
orthoclase	ORTH
ostracod	OST
oxidized	OX
P	
patchy	PCHY
part	PT

APPENDIX J Rock Lithology Log Order of Presentation and Selection

maximum	MAX
medium	M
member	MBR
metamorphic	METAM
mica	MIC
micaceous	MICAC
microcrystalline	MICXLN
microfossil	MICFOS
micrograined	MICGR
micromicaceous	MMIC
middle	MID
mineral	MNRL
minimum	MIN
minor	MNR
minute	MNUT
moderate	MOD
mollusca	MOL
mottled	MOT
mudstone	MDST
muscovite	MUSC
N	
nacreous	NAC
nodule	NOD
preserved	PRES
primary	PRIM
prismatic	PRIS
probably	PROB
prominent	PROM

parting	PTG
pearl	PRL
pebble	PBL
pegmatite	PEG
pelecypod	PLCY
pellet	PEL
permeability	PERM
petroleum	PET
phosphate	PHOS
pink	PNK
pinpoint porosity	PPP
pisolite	PISO
pitted	PIT
plagioclase	PLAG
plant fossils	PL FOS
plastic	PLAS
platy	PLTY
polish	POL
poor	PR
porcelaneous	PORC
porosity	POR
porphyry	PORPH
possible	POS
predominant	PRED
scattered	SCAT
schist	SCH
scolecondonts	SCOL
secondary	SEC
sediment	SED

APPENDIX J Rock Lithology Log Order of Presentation and Selection

pseudo	PSDO	selenite	SEL
purple	PURP	sericite	SER
pyrite	PYR	severe	SEV
pyrobitumen	PYRBIT	shale,-ly	SH,SHY
pyroclastic	PYRCLAS	siderite	SID
		silica	SIL
Q		sillceous	SILIC
quartz	QTZ	silky	SLKY
quartzite	QTZT	silt	SLT
quartizitic	QTZTC	siltstone	SLTST
quartzose	QTZS	size	SZ
		slickensided	SLKS
R		slight	SL
radiate	RAD	small	S
range	RNG	smooth	SMTH
random	RAND	soft	SFT
rare	RR	soluble	SOLB
red	R	solution	SOL
regular	REG	sort	SRT
remains	RMN	speck	SPCK
replaced	RPL	sphalerite	SPHAL
residue	RESD	spherules	SPH
resinous	RSNS	spicule	SPIC
rhombohedral	RHMB-L	splintery	SPL
rock	RK	sponge	SPG
round	RND	spore	SPR
rounded	RNDD	spot	SP
rubbly	RBLY	stain	STN
rusty	RST	stained	STND

APPENDIX J Rock Lithology Log Order of Presentation and Selection

S	
salt	SALT
saccharoidal	SACC
sample	SMPL
sand	SD
sandstone	SS
sandy	SDY
saturated	SAT
scales	SC
scarce	SCS
sucrose	SUC
sulphur	SULF
surface	SURF
T	
tabular	TAB
texture	TEX
thick	THK
thin	THN
through	THRU
tight	TT
tourmaline	TOUR
trace	TR
transparent	TRNSP
trilobite	TRILO
tripolitic	TRIP
tubular	TUB
tuff	TUFF
staining	STNG
stippled	STIP
strata	STRAT
streak	STR
striated	STRI
stringer	STRG
stromatoparoids	STROM
structure	STRUC
styolite	STYL
subangular	SUBANG
subhedral	SUBHED
W	
water	WTR
wavy	WVY
waxy	WXY
weather	WTHR
weathered	WTHRD
white	WH
with	W/
Y	
yellow	YEL
Z	
zone	ZN

APPENDIX J Rock Lithology Log Order of Presentation and Selection

U	
unconformity	UNCONF
unconsolidated	UNCONS
upper	UP
V	
variable	VAR
varicolored	VCOL
variegated	VGTD
varved	VRVD
vein	VN
vertebrate	VRTB
very	V
vesicular	VES
vitreous	VIT
volcanics	VOLC
vug,-gy,-ular	VUG

APPENDIX K

Slug Test Field Log

APPENDIX K — Slug Test Field Log

Standard Operating Procedure (SOP) for *In Situ* Hydraulic Conductivity Tests (Slug Tests)

Equipment Requirements

- A pressure transducer connected to a data logger system
- An inert solid slug of sufficient diameter and length to artificially raise or lower the water level 1 foot or more in the well (commonly either a PVC or Teflon® slug)
- A timing device

Test Design

1. Identify the test objectives and document them.
2. Identify potential limitations of test and interpretation methods as they relate to the project and site.
3. Identify the available database for correlation purposes (other hydraulic conductivity test data, maps, or logs of subsurface soils).
4. Evaluate access to wells and obstructions or siltation in wells.
5. Review boring and well completion logs for wells to be tested for lithology, natural discontinuities, possible well yield, screen length, location of groundwater table with respect to the screen interval, and type of sand/gravel pack.
6. Identify the type of in situ hydraulic conductivity test to be used.
   - Only use a rising head test if the screened interval of the well straddles the water table. The introduction of water into the unsaturated portion of the formation during a falling head test will result in an inaccurate estimation of hydraulic conductivity.
   - If the screened interval of the well is fully submerged below the water, use both the rising and falling head test and average the results.
7. Evaluate the amount of head change to be induced in the well.
8. Evaluate the water level measurement frequency needed.
   - During the early portions of the test, measure water levels as closely spaced intervals. The frequency of measurements will be governed by the rate of recovery of the water level in the well. The faster the recovery, the more frequently the measurements need to

be taken. Measurement frequency can decline logarithmically during the test (the length of time between measurements increasing during the test). Water levels should be recorded until the water level has recovered to 95% of static pre-test conditions.

9. Identify the type of slug and water level recording device to be used.
   - Choose the manual or electronic method based upon previously calculated hydraulic conductivity (K) values or expected K based upon grain size encountered within the well:
   - If $K > 10^{-3}$ cm/sec, use pressure transducer
   - If $K < 10^{-3}$ cm/sec, use pressure transducer or manual method

Field Protocols

1. Record the following information in the project notebook and the slug test field log at the end of this appendix:
   - Name
   - Date
   - Project name and description
   - Project number
   - Well number and well location in sufficient detail to relocate
2. Measure and document static head. If a pressure transducer is to be used, lower transducer into well, and secure the pressure transducer cable to the well to prevent movement. Connect the pressure transducer to the electronic data logger. Measure the static head with both the transducer and manually, then start the automatic recording by the data logger.
3. Insert the slug into or withdraw the slug from the groundwater in the well.
   - Given the variability of test conditions, there is no absolute requirement for the magnitude of the change in water level. It is suggested that a minimum of 1-foot instantaneous hydraulic head change be created to allow for effective measurement of aquifer response. About 75% of the estimated displacement by the slug should be documented in the water level recordings.
4. Measure the recovery of the water level in the well until 95% recovery to static conditions has been achieved.

- For manual measurements, record the time (real or elapse time) and the depth to groundwater in the well in the project field book. All measurements should be from the same point on the well casing using the same well probe.
- For the pressure transducer, the time and water level will be automatically recorded.

5. Data Review

   a. Make sure the necessary information is documented for each test within the field notebook and on a slug test field log.

   b. Make a preliminary analysis of data before leaving the field to evaluate if test was successful:

- Did the slug create an instantaneous head change in the well of sufficient magnitude to observe a meaningful water level response?
- Did you collect a sufficient number of data points to define the water level recovery for the test?
- Is the test data generally consistent with your pre-test expectations?
- If the test was not successful, re-evaluate the test design and complete a new test.

   c. For electronic tests, copy the data file onto a disk and label the disk with the project number, date, test well, and file name.

Sauget Area 2 Site
Slug Testing Form
URS Job No. 23-20010024.02

Monitoring Well - _____ Date: _____
Diameter - two inches
Total Depth - _____ feet below top of casing
Screened Interval - _____ feet to _____ feet below top of casing
Length of Water Column - _____ feet
Circle one: Slug In / Slug Out

Time (min:secs)	Depth to Water (feet)		Time (min:secs)	Depth to Water (feet)		Time (min:secs)	Depth to Water (feet)
0:02			1:20			8:30	
0:04			1:30			9:00	
0:06			1:40			9:30	
0:08			1:50			10:00	
0:10			2:00			11:00	
0:12			2:15			12:00	
0:14			2:30			13:00	
0:16			2:45			14:00	
0:18			3:00			15:00	
0:20			3:30				
0:25			4:00				
0:30			4:30				
0:35			5:00				
0:40			5:30				
0:45			6:00				
0:50			6:30				
0:55			7:00				
1:00			7:30				
1:10			8:00				

APPENDIX L

Air Sampling Methods

APPENDIX L Air Sampling Methods

Standard Operating Procedures will be developed and provided for the air sampling and analysis program upon selection of the laboratories who will perform these services.

URS

October 30, 2001

Mr. Mike Ribordy
U.S. EPA – Region 5
77 West Jackson Boulevard (SR-6J)
Chicago, IL 60604-3590

RE: Sauget Area 2 Sites **Deliver by Overnight Mail**

Dear Mike:

This letter is intended to resolve and clarify several issues that have been raised by Mr. Richard Byvik in his review of the Sauget Area 2 Quality Assurance Project Plan (Volume 2B). Specifically, this letter addresses Item Number 4 in Mr. Byvik's most recent comments, which relates to Appendix L, Air Sampling Methods. Based upon a review of the most current information, the following methods will be utilized for the sampling and analysis of air samples for the specified parameters:

VOCs - TO15

This is a modification from the original plan, which had specified Method TO1. A copy of Severn Trent Laboratories (STL) standard operating procedure (SOP) for TO15 (SOP No. LM-AT-TO15) including target compounds and associated reporting limits, was previously supplied to USEPA on September 7, 2001.

SVOCs - TO13

This is consistent with the original plan, and a copy of STL's SOP for TO13 (SOP No. AR:01:21:98:1) was previously supplied to USEPA on September 7, 2001. This SOP is applicable for Methods TO4, TO10, and TO13. Please note that Method TO13 is applicable only for PAH compounds. A table listing the target analytes and their associated reporting limits for this method is enclosed.

Pesticides - TO4

This is a modification from the original plan, which had specified Method TO13. A copy of STL's SOP for TO4 (SOP No. AR:01:21:98:1) was previously supplied to USEPA on September 7, 2001. This SOP is applicable for Methods TO4, TO10, and TO13. A table listing the target analytes and their associated reporting limits for this method is enclosed.

URS Corporation
2318 Millpark Drive
Maryland Heights, MO 63043
Tel: 314.429.0100
Fax: 314.429.0462

Herbicides – NA

Upon review of the commercially available, approved sampling and analysis methods for air samples, we do not believe that there is currently a method available which is suitable for the analysis of herbicides. Therefore, this group of compounds will be deleted from the air-sampling program.

PCBs – TO4

This is a modification from the original plan, which had specified Method TO13. A copy of STL's SOP for TO4 (SOP No. AR:01:21:98:1) was previously supplied to USEPA on September 7, 2001. This SOP is applicable for Methods TO4, TO10, and TO13. A table listing the target analytes and their associated reporting limits for this method is enclosed.

Dioxin – TO9

This is consistent with the original plan. A copy of STL's SOP for Method 8290 (SOP SAC-ID-0005) was previously supplied to USEPA on October 15, 2001. This SOP is also used for ambient air samples (TO-9). The following sections pertain specifically to ambient air analyses: 2.3, 3.6, 7.8, 7.10, 8.3, 9.7, 11.4.16 and 17.1.9.

Metals – PM2.5/IO3.1

This is consistent with the original plan. A copy of URS' SOP for Method PM2.5 is enclosed, as are STL SOPs ME54:10:29:01:1 (Digestion and Preparation Procedures for Metals in Air) and ME70:03:07:01:7 (Elements by ICP – 200.7 and 6010B). A table listing the target analytes and their associated reporting limits for this method is enclosed.

I trust that this information resolves any outstanding issues as they pertain to approval of the QAPP for this program. Please do not hesitate to call Steve Smith if you have any questions on this information.

Sincerely,

Robert B. Veenstra
Principal

cc: Steve Smith, SA2SG Project Manager

MODIFIED: TO-15
STANDARD OPERATING PROCEDURES FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR BY GAS CHROMATOGRAPHY/MASS SPECTROSCOPY

Applicable matrix or matrices: ambient air
Standard Compound List and Reporting Limits: see Table 1

Approvals and Signatures

Laboratory Director:	Christopher A. Ouellette	Date:	5/24/01
QA Manager:	Kim B. Watson	Date:	6/1/01
Organics Lab Manager:	Bryce E. Stearns	Date:	5/24/01

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1.0 SCOPE AND APPLICATION

1.1 This document describes a procedure for analysis of 60 polar and non-polar volatile organic compounds (VOCs) in ambient air. The VOCs are separated by gas chromatography and measured by a mass spectrometer. This method presents procedures for sampling into canisters to final pressures both above and below atmospheric pressure (respectively referred to as pressurized and subatmospheric pressure sampling).

MODIFIED: TO-15
STANDARD OPERATING PROCEDURES FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR BY GAS CHROMATOGRAPHY/MASS SPECTROSCOPY

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Standard Compound List and Reporting Limits: see Table 1

Approvals and Signatures

Laboratory Director:	Christopher A. Ouellette	Date:
QA Manager:	Kim B. Watson	Date:
Organics Lab Manager:	Bryce E. Stearns	Date:

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1.0 SCOPE AND APPLICATION

1.1 This document describes a procedure for analysis of 60 polar and non-polar volatile organic compounds (VOCs) in ambient air. The VOCs are separated by gas chromatography and measured by a mass spectrometer. This method presents procedures for sampling into canisters to final pressures both above and below atmospheric pressure (respectively referred to as pressurized and subatmospheric pressure sampling).

1.2 This method is applicable to specific VOCs that have been tested and determined to be stable when stored in pressurized and sub-atmospheric pressure canisters. Numerous compounds, many of which are chlorinated VOCs, have been successfully tested for storage stability in pressurized canisters. However, minimal documentation is currently available demonstrating stability of VOCs in subatmospheric pressure canisters.

1.3 The target list is shown in Table 1. These compounds can be recovered from canisters near their original concentrations after storage times of up to thirty days (18.2).

Table 1. Analytes, Chemical Abstract Services Numbers and Reporting Limits (RL)

Analyte	CAS No.	RL (ppbv)	Quant Mass Signal	Qualifier Mass
Dichlorodifluoromethane	75-71-8	0.5	85	87
Chloromethane	74-87-3	0.5	50	52
Dichlorotetrafluoroethane	76-14-2	0.5	85	135
Vinyl Chloride	75-01-4	0.5	62	64
1,3-Butadiene	106-99-0	0.5	39	54
Bromomethane	74-83-9	0.5	94	96
Chloroethane	75-00-3	0.5	64	66
Bromoethene	593-60-2	0.5	106	108
Acetone	67-64-1	0.5	43	58
Trichlorofluoromethane	75-69-4	0.5	101	103
Isopropyl Alcohol (2-Propanol)	67-63-0	0.5	45	43
1,1-Dichloroethene	75-35-4	0.5	96	61
Methylene Chloride	75-09-2	0.5	49	84
3-Chloropropene (Allyl Chloride)	107-05-1	0.5	41	46
Carbon Disulfide	75-15-0	0.5	76	
Trichlorotrifluoroethane	76-13-1	0.5	101	151

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Analyte	CAS No.	RL (ppbv)	Quant Mass Signal	Qualifier Mass
trans-1,2-Dichloroethene	156-60-5	0.5	61	96
1,1-Dichloroethane	75-34-3	0.5	63	65
Methyl tertiary-butyl ether	1634-04-4	0.5	73	43
Methyl Ethyl Ketone (2-Butanone)	78-93-3	0.5	43	72
cis-1,2-Dichloroethene	156-59-2	0.5	61	96
Hexane	110-54-3	0.5	57	86
Chloroform	67-66-3	0.5	83	85
Tetrahydrofuran	109-99-9	0.5	42	72
1,2-Dichloroethane	107-06-2	0.5	62	98
1,1,1-Trichloroethane	71-55-6	0.5	97	99
Benzene	71-43-2	0.5	78	77
Carbon Tetrachloride	56-23-5	0.5	117	119
Cyclohexane	110-82-7	0.5	56	84
1,2-Dichloropropane	78-87-5	0.5	63	41
Bromodichloromethane	75-27-4	0.5	83	85
Trichloroethene	79-01-6	0.5	95	130
1,4-Dioxane	123-91-1	0.5	88	58
2,2,4-Trimethylpentane (Isooctane)	540-84-1	0.5	57	41
n-Heptane	142-82-5	0.5	43	71
cis-1,3-Dichloropropene	10061-01-5	0.5	75	110
trans-1,3-Dichloropropene	10061-02-6	0.5	75	110
Methyl Isobutyl Ketone (4-Methyl-2-Pentanone)	108-10-1	0.5	43	58
1,1,2-Trichloroethane	79-00-5	0.5	83	97
Toluene	108-88-3	0.5	92	91
Methyl Butyl Ketone (2-Hexanone)	591-78-6	0.5	43	58

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Analyte	CAS No.	RL (ppbv)	Quant Mass Signal	Qualifier Mass
Dibromochloromethane	124-48-1	0.5	129	127
1,2-Dibromoethane	106-93-4	0.5	107	109
Tetrachloroethene	127-18-4	0.5	166	168
Chlorobenzene	108-90-7	0.5	112	77
Ethylbenzene	100-41-4	0.5	91	106
m,p-Xylene	108-38-3	0.5	106	91
Bromoform	75-25-2	0.5	173	175
Styrene	100-42-5	0.5	104	78
1,1,2,2-Tetrachloroethane	79-34-5	0.5	83	131
o-Xylene	95-47-6	0.5	106	91
2-Chlorotoluene	95-49-8	0.5	91	63
4-Ethyltoluene	622-96-8	0.5	105	120
1,3,5-Trimethylbenzene	108-67-8	0.5	105	120
1,2,4-Trimethylbenzene	95-63-6	0.5	105	120
1,3-Dichlorobenzene	541-73-1	0.5	146	111
1,4-Dichlorobenzene	106-46-7	0.5	146	111
1,2-Dichlorobenzene	95-50-1	0.5	146	111
1,2,4-Trichlorobenzene	120-82-1	0.5	180	182
Hexachlorobutadiene	87-68-3	0.5	225	223

2.0 SUMMARY OF METHOD

2.1 Both subatmospheric pressure and pressurized sampling modes typically use an initially evacuated canister and pump-ventilated sample line during sample collection. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of ambient air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into a pre-evacuated specially prepared passivated canister.

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2.2 After the air sample is collected, the canister valve is closed, an identification tag annotated and attached to the canister, a chain-of-custody (COC) form completed, and the canister is transported to the laboratory for analysis.

2.3 Upon receipt at the laboratory, the canister pressure and tag data is recorded on the analysis sheet, the COC completed, and the canister is attached to the analytical system. During analysis, VOCs are concentrated by collection in a cryogenically cooled trap. The cryogen is then removed and the temperature of the trap is raised. The VOCs originally collected in the trap are revolatilized, separated on a GC column, then detected by one or more detectors for identification and quantitation.

2.4 General Method - The mass spectrometer is calibrated to recognize m/z values in the range of 35-260 amu. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples. The performance of the mass spectrometer is verified by the injection of 4-Bromofluorobenzene (BFB). Next, the instrument must demonstrate acceptable chemical calibration and linearity by the analysis of five concentrations of a standard mix containing the analytes of interest, as well as the internal standards. Before any samples are analyzed, a method blank must be analyzed to demonstrate that the instrument is free from contamination. All analyses must occur within 24 hours of the injection of the passing BFB. Another analytical sequence may be started by the analysis of a passing BFB MS tune followed by a continuing calibration standard, a laboratory control sample, and a method blank.

3.0 DEFINITIONS

Absolute Pressure-pressure measured with reference to absolute zero pressure (as opposed to atmospheric pressure), usually expressed as kPa, mm Hg, or psi.

Cryogen-a refrigerant used to obtain very low temperatures in the cryogenic trap of the analytical system. A typical cryogen is liquid nitrogen (bp –195.8°C) or liquid argon (bp –185.7°C).

Dynamic Calibration-calibration of an analytical system using calibration gas standard concentrations in a form identical or very similar to the samples to be analyzed and by introducing such standards into the inlet of the sampling or analytical system in a manner very similar to the normal sampling or analytical process.

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Gauge Pressure-pressure measured above ambient atmospheric pressure (as opposed to absolute pressure). Zero gauge pressure is equal to ambient atmospheric (barometric) pressure.

MS/SCAN-the GC is coupled to a MS programmed in the SCAN mode to scan all ions repeatedly during the GC run.

MS/SIM-the GC is coupled to a MS programmed to acquire data for only specified ions and to disregard all others. This is performed using SIM coupled to retention time discriminators. The GC/SIM analysis provides quantitative results for selected constituents of the sample gas as programmed by the user.

Pressurized Sampling-collection of an air sample in a canister with a (final) canister pressure above atmospheric pressure, using a sample pump.

Qualitative Accuracy-the ability of an analytical system to correctly identify compounds.

Quantitative Accuracy-the ability of an analytical system to correctly measure the concentration of an identified compound.

Static Calibration-calibration of an analytical system using standards in a form different from the samples to be analyzed. An example of a static calibration would be injecting a small volume of a high concentration standard directly onto a GC column, bypassing the sample extraction and preconcentration portion of the analytical system.

Sub-atmospheric Sampling-collection of an air sample in an evacuated canister at a (final) canister pressure below atmospheric pressure, without the assistance of a sampling pump. The canister is filled as the internal canister pressure increases to ambient or near ambient pressure. An auxiliary vacuum pump may be used as part of the sampling system to flush the inlet tubing prior to or during sample collection context, this procedure serves as a qualitative identification and characterization of the sample.

Internal Standards (IS)-Non-target analyte compounds that are similar to the target analytes but are not expected to be found in environmental media (generally, isotopically labeled target analytes are used for this purpose) and are added to every standard, quality control sample, and field sample at a known concentration prior to analysis. IS responses are used as the basis for quantitation of target analytes.

Stock solutions-A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

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Primary Dilution Standard Solution-A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

Calibration Standard (CAL)-A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

Continuing Calibration Verification (CCV)-An analytical standard solution containing all target analytes and internal standard compounds that is used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

Method Blank (ABLK, similarly known as the LABORATORY REAGENT BLANK)-A canister of ambient air or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The ABLK is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

Trip Blank-A canister of ambient air or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the trip blank is to determine if method analytes or other interferences are present in the field environment (originating from the proximity of sample containers to one another during shipment and storage).

Laboratory Control Sample (LCS)-The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. Its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. When the results of the matrix spike analysis indicates a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

Initial Calibration Verification (ICV)-An analytical standard solution containing all target analytes and internal standard compounds that are prepared from a source external to the laboratory and independent from the source of the initial calibration standards. The purpose of the ICV is to verify that the initial calibration is in control.

4.0 Interferences

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4.1 Contamination may occur in the sampling system if canisters are not properly cleaned before use. Additionally, all other sampling equipment (e.g., pump and flow controllers) should be thoroughly cleaned to ensure that the filling apparatus would not contaminate samples.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

5.2 STL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in these methods. Material Safety Data Sheets (MSDS) are made available to all personnel involved in the chemical analysis. STL also has a written environmental health and safety plan.

5.3 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichlorethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood.

6.0 EQUIPMENT AND SUPPLIES

6.1 Sample Containers

- SUMMA® passivated stainless steel canisters are available from a number of commercial suppliers. STL's major suppliers are Restek and Scientific Instrumentation Specialists.
- Tedlar bags

6.2 Instrumentation:

- VOC Autosampler: Nutech model 3600 automated sytem. This system is capable of introducing samples from up to sixteen canisters in an automated sequence.

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- Cryogenic Concentrator: Nutech model 3550A cryogenic concentrator. The concentrator incorporatesTO-15 cryotrapping techniques.

- CDT Multibed Cryotrap: Effectively removes water and CO_2 while trapping polar and non-polar compounds.

- Electronic Mass Flow Controllers: The Nutech cryogenic concentrator is equipped with an electronic mass flow controller to maintain a constant flow for carrier gas and sample over a range of 0-200 cc/min.

- Cryofocussing Accessory: The Nutech 354A Cryofocussing accessory cryogenically refocuses the sample onto the column head.

- Gas Chromatograph: Hewlett-Packard 5890 Series II

- Mass Spectrometer: Hewlett-Packard 5971 MSD

- Primary Column: Fused silica capillary column, J&W DB-1 60m x 0.35 mm x 1.0 µm or equivalent

- Vacuum Pumps: General purpose vacuum pumps of the type specified in EPA Method TO-15.

6.3 Syringes-1.0mL - 1.0-L gas tight syringes with Luer-Lok tip

6.4 Data System: DOS based PC software for Nutech instrumentation. Hewlett-Packard ChemStation software is used for data acquisition and Hewlett-Packard ChemServer, Target 3.5 software is used for data processing.

6.5 Canister Cleaning System: Entech auto-canister cleaning system (Model 3000)

- Vacuum Pump: Capable of evacuating sample canisters to an absolute pressure of -29.9" Hg.

- Manifold: Equipped with stainless steel and Teflon transfer lines and connections for cleaning up to eight canisters simultaneously.

- Vacuum Gauge: Capable of measuring vacuum in the manifold to an absolute pressure of 0.05-mm Hg or less.

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- Heating Manifolds: Individually thermal-stated heating manifolds used to heat canisters during the cleaning cycle.

7.0 Reagents and Standards

7.1 Gas cylinders of ultrahigh purity helium and zero air.

7.2 Low pressure liquid nitrogen for the cryogenic concentrator and cryofocuser.

7.3 4-Bromofluorobenzene (BFB) for monitoring mass spectral tuning.

7.4 Calibration Standards: The primary standard is purchased through Spectra Gases. The 1 ppmv standard has 60 TO-15 target compounds and is traceable to a NIST standard. The calibration standards are prepared by adding a known amount of the primary standard into a humidified SUMMA canister and pressurizing with zero air to achieve the concentration wanted. The calibration levels (0.5, 5, 10, 20, 40 ppbv) are then achieved by injecting different volumes or further diluting.

7.5 Internal standards (Bromochloromethane, 1,4-Difluorobenzene, and Chlorobenzene-d5) are purchased through Spectra Gases at the 1 ppmv level. They are introduced automatically through the concentrator to achieve a final concentration of 10 ppbv.

7.6 Laboratory Control Samples: The 62 component standard is purchased through Spectra Gases at the 1 ppmv level. The concentration of the LCS is achieved by adding a known amount of the 1 ppmv standard to a humidified canister and then pressurized to achieve the target concentration, which is the midpoint of the calibration curve.

8.0 SAMPLE COLLECTION AND STORAGE

8.1 All canisters must be clean and free of any contaminants before sample collection.

8.2 All canisters are leak tested by evacuating them to approximately –29.5"Hg. The initial vacuum is measured, the canister valve is closed, and the final vacuum is

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checked after at least 8 hours. If acceptable, the vacuum should not vary more than 2"Hg over the time period.

8.3 The canister(s) are connected to the manifold. The vent shut-off valve and the canister valve(s) are opened to release any remaining pressure in the canister(s). The heating band(s) are then attached to the canister(s) and turned on allowing them to heat to 100°C. The number of cycles (≥3) are chosen on the Entech 3000 cleaning system and the "Auto" button is depressed. The canister(s) are first evacuated for 5 minutes by an oiless pump and then they are pressurized with humid zero air to ~10 psig.

8.4 At the end of the evacuation/pressurization cycles, the canister is pressurized to 10 psig with humid zero air. The canister is then analyzed by a GC/MS analytical system. Any canister that has not tested clean (compared to direct analysis of humidified zero air of less than 0.5 ppbv of targeted VOCs) should not be used. 100% of the canisters will be analyzed by GC/MS until they are proven to be clean. From this point on, the canister with the highest TIC in the batch of 8 canisters being cleaned at one time will be analyzed. If this canister is proven to be clean, then the rest of the batch will be certified clean as well.

8.5 The canister is reattached to the cleaning manifold and is then reevacuated to <-29.5" Hg. The canister valve is closed. The canister is removed from the cleaning system and the canister connection is capped with a stainless steel fitting. The canister is now ready for collection of an air sample. An identification tag is initialed, dated, and attached to the inlet of each canister for field notes and chain-of-custody purposes.

8.6 The analytical system is comprised of a GC equipped with a mass-selective detector set in the SCAN mode. All ions are scanned by the MS repeatedly during the GC run over a mass range of 35-265 amu. The system includes a computer and appropriate software for data acquisition, data reduction, and data reporting. A 200-mL air sample is collected from the canister into the analytical system. The sample air is first passed through a mass flow controller, then routed into a cryogenic trap.

8.6.1 The trap temperature is ramped from –40°C to 0°C within 2 minutes and then is dry purged to remove water and CO_2. The trap is then ramped to 150°C and the sample is transferred and trapped again onto the cryofocus assembly. The sample is then injected onto the DB-1 capillary column (0.32-mm x 60-m). *Note: Rapid heating of the trap provides efficient transfer of the sample components onto the gas chromatographic column.]*

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8.6.2 Upon sample injection unto the column, the MS computer is signaled by the GC computer to begin detection of compounds, which elute from the column. The gas stream from the GC is scanned within a preselected range of atomic mass units (amu). For detection of compounds in Table 1, the range should be 35 to 265 amu.

8.7 Sample collection is described in method TO-15.

8.8 Samples collected in SUMMA® canisters are analyzed within twenty days of collection. Other holding times may be selected by the client to conform with local regulatory requirements. Samples collected in Tedlar bags are analyzed within three days of collection.

8.9 The overall condition of each sample container is observed upon receipt and any signs of damage is reported immediately to the client. The pressure of each sample canister is checked by attaching a pressure gauge to the canister inlet and briefly opening the canister valve to obtain the pressure reading. The measurement is recorded on the laboratory analysis sheet. Samples received at a vacuum less than -4.0" Hg must be pressurized to ensure that there is enough sample for analysis. The canisters are pressurized with zero grade air and the dilution factor is calculated and applied to the final results of analysis.

8.10 Samples received in Tedlar bags are inspected for condensation. If it is present, the bag is gently warmed by holding it between your hands in hope that the sample will return to its gaseous state. However, resampling may be necessary if this procedure does not work.

9.0 QUALITY CONTROL

9.1 4-Bromofluorbenzene - Prior to the acquisition of a calibration curve or the analysis of samples, an aliquot of BFB (1 ppmv) is automatically introduced into the GC by way of the Nutech automated sytem. If the spectrum does not meet all criteria in Table 2, another BFB tune is injected into the instrument. If the second BFB tune fails the criteria in Table 2, the MS should be retuned and adjusted to meet all criteria before proceeding with the calibration or the analysis.

9.2 Method Detection Limits - Method detection limits (MDLs) are determined annually in accordance with the method described in 40 CFR, Part 136, Appendix B. The results of these studies are kept on file by the QA Manager.

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9.3 Initial Calibration Verification - An ICV must be run following the acquisition of the five-point initial calibration. The ICV is prepared from a source external to the laboratory and independent from the source of the initial calibration standards. The compounds should be at a concentration of 10 ppbv. The ICV recovery limits are shown in Table 3.

9.4 Internal Standards - The internal response shall be +/- 40% of the mean internal standard response recorded during the analysis of the continuing calibration standard. The retention time shift should not be more than +/-20 seconds from the latest daily calibration check.

9.5 Laboratory Control Sample - A laboratory control sample should be included with each analytical batch. The compounds should be at a concentration of 10 ppbv. The LCS recovery limits are shown in Table 3.

9.6 Method Blank - One blank must be run with every batch of samples after the LCS. A 200-mL sample of laboratory zero air must be analyzed prior to any samples. An acceptable blank must not contain any volatile target analytes at concentrations greater than their reporting limits with the exception of acetone and methylene chloride which must be less than or equal to five times (5X) its reporting limit. If the method blank exceeds these criteria, the analytical system may be out of control. The source of the contamination must be investigated and appropriate corrective measures must be taken and documented before further sample analysis proceeds.

10.0 CALIBRATION AND STANDARDIZATION

10.1 BFB - The ion abundances shown in Table 2 must be met before analysis of calibration standards may proceed.

10.2 Initial Calibration (IC) - The five concentrations for the initial calibration are 0.5, 5, 10, 20, and 40 ppbv. A response factor (RF) is calculated for each analyte and/or isomer pair for each calibration solution using the appropriate internal standard. The calculation is performed as follows:

$$RF = \frac{(A_x)(Q_{is})}{(A_{is})(Q_x)}$$

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where:

A_x = area of the quantitation ion of the analyte
A_{is} = area of the quantitation ion of the internal standard
Q_x = quantity of analyte purged in nanograms or concentration units
Q_{is} = quantity of internal standard purged in ng or concentration units

10.2.1 For each analyte calculate the mean response factor from analyses of the calibration solutions. Calculate the standard deviation (SD) and relative standard deviation (RSD) from each mean (M).

$$RSD = 100\frac{SD}{M}$$

10.2.2 The %RSD average of all analytes must be ≤ 30% (2 compounds are allowed to be ≤40%). The RRT for each target compound at each calibration level must be within 0.06 RRT units of the mean RRT for the compound. The retention time shift for each of the internal standards at each calibration level must be within 20 s of the mean retention time over the initial calibration range for each internal standard.

10.3 Independent Calibration Verification (ICV)- An ICV must be run following the initial calibration. The ICV is purchased from an independent source and is run at a concentration of 10 ppbv. The percent recovery for each compound should be 70-130% for 90% of the compounds. In addition, the internal standard retention time should not change by more than 20 s. from the mid-point standard level of the most recent curve sequence. The integrated areas of the internal standards in the calibration verification standard should not change by more +/-40% from that in the mid-point standard level of the most recent calibration.

10.4 Continuing Calibration Verification (CCV) - Verify the BFB MS tune and perform a continuing calibration verification at the beginning of each 24-hr work shift. The concentration of the CCV is 10 ppbv. The RF is calculated for each analyte compound from the data measured in the continuing calibration check. The percent difference is calculated using the following equation:

$$\%Difference = \frac{RF - RF_v}{RF}(100)$$

RF = mean Response Factor from the initial calibration
RF_v = Response Factor from the analyses of the verification standard

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The percent difference for each CCV should be ≤ 30% for 90% of the compounds. In addition, the internal standard retention time should not change by more than 20 s. from the mid-point standard level of the most recent initial curve sequence. The integrated areas of the internal standards in the calibration verification standard should not change by more than +/-40% from that in the mid-point standard level of the most recent calibration sequence. If the above criterion is not met maintenance is performed on the instrument and/or a new calibration curve is acquired. Alternatively, in keeping with the approach described for the IC, if the average of the responses for all analytes is within 30% for 90% of the compounds, then the calibration has been verified. If the calibration still does not meet the 30% for 90% of the compounds limit, check the instrument operating conditions, and if necessary inject another aliquot of the calibration verification standard. If the response for the analyte is still not within +/-30% for 90% of the compounds, then a new IC must be prepared.

10.5 Laboratory Control Sample (LCS) - One LCS must be run in each 24-hour window following the CCV. The LCS is run at the concentration of 10 ppbv. The percent recovery for each compound should be 70-130% for 90% of the compounds. In addition, the internal standard retention time should not change by more than 20 s. from the mid-point standard level of the most recent curve sequence. The integrated areas of the internal standards in the calibration verification standard should not change by more +/-40% from that in the mid-point standard level of the most recent calibration.

10.6 Method Blank - A method blank is run following the passing of the BFB tune, CCV, and LCS. A 200-mL aliquot of zero grade air is run to verify that the analytical system is clean. An acceptable method blank verifies that there are no volatile organic compounds present above their reporting limits. In addition, the internal standard retention time should not change by more than 20 s. from the mid-point standard level of the most recent calibration. The integrated areas of the internal standards in the method blank should not change by more +/-40% from that in the mid-point standard level of the most recent calibration sequence.

11.0 PROCEDURE

11.1 The analytical system is comprised of a GC equipped with a mass-selective detector set in the SCAN mode. All ions are scanned by the MS repeatedly during the GC run. The system includes a computer and appropriate software for data

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acquisition, data reduction, and data reporting. A 200-mL air sample is collected from the canister or Tedlar bag into the analytical system. The sample air is first passed through the mass flow controller then routed onto a cryogenic trap. The internal standards are then loaded onto the trap. The trap is heated, dry purged, then desorbed onto the cryofocus. The sample is next injected onto the DB-1 capillary column (0.32-mm x 60-m).

[Note: Rapid heating of the trap provides efficient transfer of the sample components onto the gas chromatographic column.]

Upon sample injection unto the column, the MS computer is signaled by the GC computer to begin detection of compounds, which elute from the column. The gas stream from the GC is scanned within a preselected range of atomic mass units (amu). Data is acquired and stored over the nominal mass range 35-260 with a total cycle time (including scan overhead time) of two seconds or less. The cycle time is adjusted to measure five or more spectra during the elution of each GC peak. A multi-stage temperature ramp is used to separate the components of interest for this analysis. A typical GC temperature program is described below.

- Initial temperature: 30° C, initial time 4 min.
- Ramp1: 9° C/min. to 175° C.
- Ramp2: 40° C/min. to 260° C, hold for 1.60 min.

11.2 Identification of Analytes - A sample is identified by comparison of its mass spectrum (after background subtraction) to a reference spectrum in the user-created database. The GC retention time for each analyte should be within +/- 0.5 minutes of the midpoint standard's retention time in the initial calibration curve.

11.2.1 In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component and should agree within absolute 20%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 10-50%. Some ions, particularly the molecular ion, are of special importance, and should be evaluated even if they are below 10% relative abundance.

11.2.2 Identification requires expert judgment when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously represent more than one sample component (i.e., broadened peak with

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shoulder(s) or valley between two or more maxima), appropriate analyte spectra and background spectra can be selected by examining plots of characteristic ions for tentatively idehtified components. When analytes coelute (i.e., only one GC peak is apparent), the identification criteria can be met but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

11.2.3 Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC retention times. Acceptable resolution is achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks. Otherwise, structural isomers are identified as isomeric pairs. Two of the three isomeric xylenes are examples of structural isomers that are not resolved on the capillary column. These groups of isomers will be reported as isomeric pairs.

12.0 CALCULATIONS

12.1 Dilution factor:

$$DF = \frac{P_1}{P_2}$$

P_1 = Canister pressure before dilution (psig)
P_2 = Canister pressure after dilution (psig)

12.2 Concentrations of Calibrated Compounds:

$$C_x = \frac{(A_x)(C_{IS})}{(A_{IS})(\overline{RRF})}(DF)$$

$\overline{RRF}$ = Average Relative Response Factor from five-point initial calibration.
C_x = Concentration of compound (ppbv)
C_{IS} = Concentration of associated internal standard (ppbv).
DF = Dilution Factor.
A_{IS} = Area of quantitation ion for associated internal standard.
A_x = Area of quantitation ion for compound.

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12.3 Calculation of Recovery - Calculate the recovery of each spiked analyte in the LCS and ICV by the following equation:

$$\text{Recovery} = \%R = \frac{C_s - C_u}{C_n}(100)$$

C_s = Measured concentration of the spiked sample aliquot
C_u = Measured concentration of the unspiked sample aliquot (use 0 for LCS and ICV)
C_n = Nominal (theoretical) concentration increase that results from spiking the sample, or the nominal concentration of the spike aliquot (for LCS and ICV)

12.4 Calculation of Precision - Precision is estimated from the relative percent difference (RPD) of the concentrations (not the recoveries) measured for matrix spike/ matrix spike duplicate pairs, or for duplicate analyses of unspiked samples. The RPD is calculated according to the following equation below.

$$RPD = \frac{(C_1 - C_2)}{\left(\frac{C_1 + C_2}{2}\right)}(100)$$

C_1 = Measured concentration of the first sample aliquot
C_2 = Measured concentration of the second sample aliquot

12.5 Data Reporting - Based on the mass spectra, it is appropriate to report values between the MDL and the RL. In this region, an analyte can be qualitatively detected, but not accurately quantified. Any data point reported in this region is flagged with a "J". STL reports sample specific RL's. Sample specific RL's are derived by taking into account various sample specific data, which can include the amount of the sample subject to testing, % moisture, dilution factor, interferences and the base RL's for the analysis.

12.5.1 Reporting Qualifiers

B = Analyte is found in the associated method blank as well as the sample
D = Compound is identified in an analysis at a secondary dilution factor

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E = Compound quantitation is above the instrument's calibration range for this analysis
J = Indicates an estimated quantitation value
U = Compound was analyzed for but not detected
X = The reported compound is a suspected laboratory contaminant
Y = An additional qualifier which will be defined at the time of use by the data reviewer
Z = The reported result is based on the combined responses from coeluting compounds

12.5.2 Data Package Definitions - Three levels of reporting are available. The difference between these levels has nothing to do with the quality of the work being performed, only how it is presented.

Level 2: A level 2 data package consists of sample results only, and may be available as either an Analytical Report or in a format similar to the OLM Form 1A's.
Level 3: A level 3 data package consists of sample, CLP-like forms with Quality Control results.
Level 4: A level 4 data package consists of a full set of RAS forms, and all supporting documentation.

Electronic-Diskettes are available upon request

13.0 METHOD PERFORMANCE

Method detection limits are calculated using the formula:

$$MDL = S\ t_{(n-1,\ 1\text{-alpha} = 0.99)}$$

Where:
$t_{(n-1,\ 1\text{-alpha} = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom
n = number of replicates
S = the standard deviation of the replicate analyses

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities

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for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

14.2 The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N.W. Washington D.C. 20036, (202) 872-4477.

15.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA AND CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

15.1 Data assessment, acceptance criteria and corrective action for out of control data is summarized in Table 4.

15.2 Corrective actions for out of control data is summarized in Table 4.

16.0 CONTINGENCIES FOR HANDELING OUT OF CONTROL OR UNACCEPTABLE DATA

Summarized in Table 4.

17.0 WASTE MANAGEMENT

The samples that are not utilized in the analysis are vented in the Volatiles Prep Lab hood and further disposed of during the canister cleaning process. The U.S. Environmental Protection Agency requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. Excess reagents, samples, and method process wastes should be characterized and disposed of in a an acceptable manner. The Agency urges laboratories to protect the air, water and land by minimizing and controlling

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all release from hoods, and bench operations, complying with the letter and spirit of any waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the "Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 14.3.

18.0 REFERENCES

18.1 Compendium Method TO-15, "Determination of Volatile Organic Compounds in Ambient Air using Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry", US EPA, January, 1997.

18.2 Kelly T. J. and Holdren, M.W., "Applicability of Canisters for Sample Storage in the Determination of Hazardous Air Pollutants," *Atmos. Environ.*, Vol. 29, 2595-2608, May 1994.

19.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

Table 2. BFB Criteria

BFB Key Ions and Ion Abundance Criteria	
Mass	Ion Abundance Criteria
50	8.0-40.0 percent of mass 95
75	30.0-66.0 percent of mass 95
95	base peak, 100 percent relative abundance
96	5.0-9.0 percent of mass 95

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173	less than 2.0 percent of mass 174
174	50.0-120.0 percent of mass 95
175	4.0-9.0 percent of mass 174
176	93.0-101.0 percent of mass 174
177	5.0-9.0 percent of mass 176

Table 3. Internal Standards

Internal Standard	CAS No.	Quant Mass	Qualifier
Bromochloromethane	74-97-5	128	49
1,4-Difluorobenzene	540-36-3	114	
Chlorobenzene-d5	3114-55-4	117	

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Table 4. TO-15 Quality Control Criteria

Quality Control Criteria	Frequency	Acceptance	Corrective Action
BFB	24 hours	Per Method	Reshoot, Retune
ICAL: 0.5, 5, 10, 20, 40 ppbv	As Required	Average %RSD must be ≤ 30% (2 compounds allowed to ≤40%)	System check, Mix new standards, Recalibrate, Reanalyze
ICV (10 ppbv)	Following Initial Calibration Curve	Average %RSD must be ≤ 30% for 90% of the compounds	System check, Mix new standards, Recalibrate, Reanalyze
CCV (10 ppbv)	Beginning of each 24 hour window	%Difference each CCC ≤30% for 90% of the compounds	System Check, Recalibrate
LCS (10 ppbv)	Following the CCV	%Difference each CCC ≤30% for 90% of the compounds	System Check, Recalibrate
Method Blank	Following each LCS/ICV	Targets < Reporting Limits (Methylene Chloride 5xs RL)	Check for contamination, Reanalyze, correct as required
Internal Standards	In every sample, blank, and QC samples	+/-40%RF from last acceptable calibration; +/-.33 min	System Check, Recalibrate
Samples	Per Request	ISTD must meet their criteria and the concentration must fall within the calibrated range	A dilution is applied to the sample when needed; the target concentration will be the midpoint of the high end of the calibration curve. If the ISTD criterion is failing, the sample is ran again. If the ISTD fail again, the sample is reported out as is.

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SEMIVOLATILE ORGANIC COMPOUNDS IN AMBIENT AIRBNA AND PESTICIDES COLLECTED ON PUF AND PUF/RESIN CARTRIDGES (TO4/TO10/TO13)

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1.0 SCOPE AND APPLICATION

1.1 This method describes sampling media cleaning and certification procedures, the extraction procedures, and references the analytical methods for the determination of semivolatile organic compounds (SVOC) in ambient air.

1.2 The reporting limit, the method detection limit, and the accuracy and precision limits are listed in Section 5 of the STL Corporate Quality Assurance Plan. Note that the target compounds for the BNA parameters do not correspond exactly to the routine TCL list reported by STL. Several of the target compounds cannot be quantitatively extracted from the media.

2.0 SUMMARY OF METHOD

2.1 Air samples may be collected using a high volume sampler (>1000 L/min) or using a low volume sampler (1-5 L/min.). The types of media used are described in Section 6. A sampling cartridge containing only polyurethane foam may be used to collect samples for pesticides and high molecular weight compounds. If low molecular weight compounds are to be determined, a dual media cartridge containing PUF and XAD-2 resin should be used.

2.2 After sampling, the sampling media cartridges are returned to the laboratory. The glass fiber filter and the XAD-2 resin/PUF are extracted for 16 h in a Soxhlet apparatus. The extract is filtered, concentrated, and analyzed. The extract may be split and/or exchanged to another solvent depending on the analysis required.

2.3 This SOP based on the guidance given in EPA Method TO-4, TO-10, and TO13.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 The analyst should wear protection for the eyes (lab glasses or face shield), the hands (latex gloves), and the clothes (lab coat or apron).

3.3 The analyst should be familiar with the Material Safety Data Sheets (MSDS) for the standards and reagents used in this procedure.

4.0 INTERFERENCES

4.1 Inadequately cleaned and monitored sampling media can contribute contamination that makes identification and quantitation of the target compounds difficult.

4.2 High levels of non-target compounds can cause problems with the chromatography and can affect the sensitivity and specificity of the detector.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Air samples for SVOC should be wrapped securely and iced after collection. The sample media should be stored at 4C (0-6C) in the lab. The media should be extracted within 7 days of collection and the extract analyzed within 40 days of extraction.

6.0 APPARATUS AND MATERIALS

6.1 Media for High Volume Sampler

If the client supplies a cartridge compatible with the General Metal Works PS-1 High Volume Sampler, the following media are required:

XAD-2 resin - Supelco 1-0357 (500 g) 20-60 mesh

Polyurethane foam (PUF) plugs: 1" General Metals Works (GPSI-18)

Polyurethane foam (PUF) plugs: 3" General Metals Works (GPSI-18)

Glass fiber filters: 4" Circle General Metal Works GQMA4

One compatible cartridge is: General Metal Works GPSI-4

The high volume cartridges can also be obtained from SKC as a pre-cleaned unit:

SKC Cat #	Application	Description	Sorbent/ Amount
226-129	Fits GMW PS1 TO13	Glass, open 65mmOD x 125mm L	PUF/XAD-2/PUF 50mm/10g/50mm
226-131	Fits GMW PS1 TO4	Glass, open 65mmOD x 125mm L	PUF 75mm

6.2 Low Volume Sampler

The low volume media are purchased as pre-cleaned cartridges from SKC:

SKC Cat #	Application	Description	Sorbent/ Amount
226-143	TO10, TO13	Glass, open 22mm x 100mm L	PUF/XAD-2/PUF 30mm/1.5g/30mm
226-126	TO10	Glass, open 22mm x 100mm L	Glass fiber filter/ PUF 75mm

6.3 Glass pipettes

6.4 Aluminum foil

6.5 Cotton gloves

6.6 Glass or metal rod

6.7 Volumetric glassware

6.8 Microsyringes

6.9 Soxhlet extraction apparatus (glassware and heaters)

6.10 Glass wool

7.0 REAGENTS

7.1 Methylene chloride, pesticide residue grade

7.2 Hexane, pesticide residue grade

7.3 Diethyl ether

7.4 Five- percent diethyl ether in hexane: Add 50mL of diethyl ether to a 1-L volumetric flask and dilute to volume with hexane

7.5 Acetone-pesticide residue grade or equivalent

8.0 STANDARDS

The spiking solutions are given in SOP EX70: *Preparation of Semivolatile Surrogate and Matrix Spiking Solutions*

Compounds	Method	Surrogate Spiking Solution	Matrix Spiking Solution
BNA	8270	1mL BNA surrogate	1mL 8270 or 1mL 625
Pesticides/PCBs	8080	1mL PEST	1mL 608
PAH	8310	1mL 8310-PAH	1mL 8310-MS

9.0 SAMPLE PREPARATION

The General Method Works dual sampling module consists of a filter holder and glass cartridge. Each component of the sampling module must be cleaned and checked prior to the sampling.

9.1 Media

The media may be purchased pre-cleaned or cleaned in the lab. If purchased pre-cleaned, a certificate must be received with the media. If the media is cleaned in the lab, one set of media from each batch of prepared media is extracted and analyzed as a sample to demonstrate that the media has been properly cleaned.

9.1.1 Polyurethane Foam (PUF) Plugs

The PUF plugs are cleaned by extracting in a Soxhlet extraction apparatus for 12 or more hours with hexane.

9.1.1.1 Place up to five PUF plugs in the Soxhlet body. The PUFs should fit snugly but should not be
"crammed " into the Soxhlet extractor. The cleaning solvent must be allowed to penetrate each PUF.

9.1.1.2 Charge the receiving flask with 300-400 mL of methylene chloride.

9.1.1.3 Set up the Soxhlet apparatus and set the heater to cycle every 15-min for 12 hours.

9.1.1.4 After 12 hours, turn off the heater and allow the apparatus to cool.

9.1.1.5 Remove the PUF plugs using stainless steel tweezers and place the PUFs on a sheet of aluminum foil.

9.1.1.6 Allow the PUFs to completely dry at ambient temperature under a fume hood.

9.1.1.7 Store the PUF plugs in a glass jar in the dark.

9.1.2 XAD-2 Resin

9.1.2.1 Place a small wad of glass wool in the bottom of the Soxhlet body.

9.1.2.2 Using a spatula or spoon, transfer the resin to the Soxhlet body. Approximately 100 g of resin can be
cleaned in each Soxhlet body.

9.1.2.3 Place a wad of glass wool on top of the resin to keep it in place during the extraction.

9.1.2.4 Charge the receiving flask with 300-400 mL of methylene chloride.

9.1.2.5 Set up the apparatus and set the heater to cycle every 15-min for 12 hours.

9.1.2.6 Turn off the heater and allow the apparatus to cool.

9.1.2.7 Tilt the apparatus to cause the solvent to drain from the Soxhlet body into the receiving flask.

9.1.2.8 Carefully remove the resin using a metal spatula and place it on aluminum foil under a fume hood.
Allow the resin to completely dry and store in sealed glass jars.

9.1.3 Glass Fiber Filters

The glass fiber filters may be cleaned by Soxhlet extraction with methylene chloride (recommended) or by placing the filters in the muffle furnace at 600°C. The filters should be cooled and stored in glass jars or between sheets of aluminum foil until ready for sampling.

9.2 Assembly of the Glass Cartridge

The glass cartridge contains two one-inch PUF plugs sandwiching ~ 25 g of XAD-2 resin or one three-inch PUF (if no resin is required).

9.2.1 Wear cotton gloves while assembling the glass cartridge component of the sampling media. The gloves used when cleaning the HP mass spectrometers are acceptable.

9.2.2 Rinse the <u>inside</u> of the glass cartridge with acetone and hexane in succession to remove any organic contaminants that may adhere to the surface of the glass.

9.2.3 Using stainless steel tweezers or tongs, place a clean 1-inch PUF plug in the glass cartridge. A glass rod may be used to help position the plug securely against the retaining screen. Make sure that there are no gaps or channels present along the interface of the

PUF and the glass wall.

NOTE: If a PUF-only cartridge is to be used, place a single 3-inch PUF securely into the sampling cartridge.

9.2.4 Using a metal spatula, carefully transfer the XAD-2 resin to the glass cartridge. The resin should be
added to form a 1.5 - 2.0" layer. The layer should be uniform with no gaps or channels. Gently tap the side of the glass cartridge to settle the resin.

9.2.5 Place the second 1 inch PUF plug in the glass cartridge to form a PUF/resin/PUF "sandwich." The second (top) plug should rest securely on the resin bed to keep the resin in place during the sampling event.

9.2.6 Wrap the glass cartridge in aluminum foil and store it in a glass jar. The glass jar should have a label that identifies the cartridge, the preparation batch, date of preparation, and the initials of the analyst.

9.3 Extraction

Prior to extracting, the target analytes and analytical procedures must be selected. The ambient air sample can be used to determine the following:

Compounds	Method	Extraction Solvent	Final Volume	Final Solvent
BNA	8270	MeCl2	1.0 mL	$MeCl_2$
Pesticides/PCBs	8080	5% ether in hexane	10 mL	Hexane
PAH	8310	MeCl2 or 5% ether in hexane	1.0 mL	Acetonitrile

The method blank and lab control spike are prepared using the same type of cartridge that was utilized for sampling. The spiking solution is added to the PUF or PUF/resin after it has been placed in the Soxhlet extractor.

9.3.1 Carefully inspect the glass cartridge and glass fiber filter for cracks or holes. Notify the project manager if there are problems with the sampling media.

9.3.2 Wearing cotton gloves, fold the filter twice. The exposed sides should be pointed towards each other.

9.3.3 Place a small plug of glass wool in the bottom of the Soxhlet body.

9.3.4 Using stainless steel tweezers, carefully remove the top foam plug from the glass cartridge and place it into the Soxhlet body.

9.3.5 Using a stainless steel spatula, carefully transfer the XAD-2 resin to the Soxhlet body.

9.3.6 Place the folded filter on top of the resin and carefully remove the second PUF plug. Place it in the
Soxhlet body. This second PUF plug should fit snugly enough to keep the filter and resin from floating on top of the solvent during the extraction. If the low volume sampler is

extracted, place a second plug of glass wool over the media to keep the resin in place.

NOTE: In some cases, the second PUF may be used to check for breakthrough and is extracted separately from the filter and front PUF.

9.3.7 Add the surrogate solution to the media in the Soxhlet body.

9.3.8 Rinse the **inside** of the glass cartridge with several milliliters of extraction solvent and allow the rinsings to flow into the Soxhlet body.

9.3.9 Charge the receiving flask with 300-400 mL of the extraction solvent and extract at approximately 4 cycles per hour for 16 hours.

9.3.10 Allow the unit to cool. Tilt the Soxhlet unit to drain any solvent left in the body into the receiving flask. Dispose of the extracted media in accordance with SOP CA70:*Waste Management*.

9.3.11 Concentrate the extract to the appropriate final volume.

9.3.12 Analyze the sample extract by the appropriate analytical method.

10.0 ANALYTICAL PROCEDURE

Compounds	Method	SOP
BNA	8270	SM05
Pesticides/PCBs	8080	SG45
PAH	8310	LC50

11.0 CALCULATIONS

11.1 Air samples for SVOC are routinely reported as mg/m3 (milligrams of target compound per cubic meter of air sampled). This unit is equivalent to ug/L (micrograms of target compounds per liter of air sampled).

$$\frac{mg}{m3} = \frac{ug}{L} = \frac{C \otimes FV \otimes DF}{V}$$

where

C = concentration of the target compound in the extract(ug/mL)
FV = final volume of the extract in milliliters(mL)
DF = dilution factor
V = volume of air sampled

NOTE: If the volume of sample is not supplied by the sampler, the results are reported as "micrograms per sample", assuming V=1 in the equation.

11.2 The percent recovery of the surrogates or matrix spiking compounds is determined by dividing the micrograms of compound detected by the micrograms of compound spiked:

$$\%REC = \frac{C \otimes FV \otimes DF}{Cs \otimes Vs} \otimes 100$$

where

C = concentration of the target compound in the extract(ug/mL)
FV = final volume of the extract in milliliters(mL)
DF = dilution factor
Cs = concentration of the surrogate or matrix spiking solution (ug/mL)
Vs = volume of surrogate or matrix spiking solution added to the sample(mL)

11.3 Precision is expressed as the relative percent difference between two duplicate samples or two spiked samples:

$$\%RPD = \left| \frac{C1 - C2}{\frac{C1 + C2}{2}} \right| \otimes 100$$

where

C1 = concentration of sample
C2 = concentration of sample duplicate

$$\%RPD = \left| \frac{\%REC1 - \%REC2}{\frac{\%REC1 + \%REC2}{2}} \right| \otimes 100$$

where

%REC1 = percent recovery of the LCS or MS
%REC2 = percent recovery of the LCSD or MSD

12.0 QUALITY CONTROL/QUALITY ASSURANCE

12.1 For every batch of twenty or fewer samples, a method blank/reagent blank, a laboratory control standard (LCS), and laboratory control standard duplicate(LCSD) will be extracted and analyzed. If duplicate samples are supplied, only an LCS will be extracted and analyzed.

12.2 The QC items will be evaluated against the control limits in Section 5 of the Corporate Quality Assurance Plan.

12.3 The method detection limit will be determined in accordance with SOP CA95:*Procedure for the Determination Of Method Detection Limit(MDL)* by spiking cleaned cartridges with the target compounds and analyzing the spiked cartridges in accordance with this SOP.

13.0 PREVENTIVE MAINTENANCE

No items in this revision.

14.0 TROUBLE-SHOOTING

No items in this revision.

15.0 REFERENCES

15.1. STL *Corporate Quality Assurance Plan*, current revision

15.2. TO-4, *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* (Rev 6/88).

15.3. TO-10, *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* (Rev 6/88).

15.4. TO-13, *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* (Rev 6/88).

SEVERN TRENT SERVICES

STL Savannah

Air Parameters

PARAMETER	RL(ug)
Metals by IO-3(6010B)	
Aluminum	4
Antimony	1.2
Arsenic	0.2
Barium	4
Beryllium	0.1
Cadmium	0.1
Calcium	100
Chromium	0.2
Cobalt	1
Copper	0.5
Iron	2
Lead	0.06
Magnesium	100
Manganese	0.3
Nickel	0.8
Potassium	100
Selenium	0.1
Silver	0.2
Sodium	100
Thallium	0.2
Vanadium	1
Zinc	0.4
PAH by TO13(8270C)	
Acenaphthene	10
Acenaphthylene	10
Anthracene	10
Benzo(a)anthracene	10
Benzo(b)fluoranthene	10
Benzo(k)fluoranthene	10
Benzo(g,h,i)perylene	10
Benzo(a)pyrene	10
Chrysene	10
Dibenz(a,h)anthracene	10
Fluoranthene	10
Fluorene	10
Indeno(1,2,3-cd)pyrene	10
Naphthalene	10
Phenanthrene	10
Pyrene	10

PARAMETER	RL(ug)
Pesticides by TO4(8081A)	
Aldrin	0.050
alpha BHC	0.050
beta BHC	0.050
delta BHC	0.050
gamma BHC (Lindane)	0.050
alpha Chlordane	0.050
gamma Chlordane	0.050
4,4'-DDD	0.10
4,4'-DDE	0.10
4,4'-DDT	0.10
Dieldrin	0.10
Endosulfan I	0.050
Endosulfan II	0.10
Endosulfan sulfate	0.10
Endrin	0.10
Endrin aldehyde	0.10
Endrin ketone	0.10
Heptachlor	0.050
Heptachlor epoxide	0.050
Methoxychlor	0.50
Toxaphene	5.0
PCBS by TO4(EPA 680)	
Monochlorobiphenyls	0.10
Dichlorobiphenyls	0.10
Trichlorobiphenyls	0.10
Tetrachlorobiphenyls	0.20
Pentachlorobiphenyls	0.20
Hexachlorobiphenyls	0.20
Heptachlorobiphenyls	0.30
Octachlorobiphenyls	0.30
Nonachlorobiphenyls	0.50
Decachlorobiphenyl	0.50
RL = reporting limit	

1.0 PRINCIPLE AND APPLICABILITY

1.1 An air sampler, properly located at the measurement site, draws a measured quantity of ambient air into a covered housing and through a filter during a 24-hr (nominal) sampling period. The sampler flow rate and the geometry of the shelter favor the collection of particles up to 25-50 µm (aerodynamic diameter), depending on wind speed and direction. The filters used are specified to have a minimum collection efficiency of 99 percent for 0.3 µm (DOP) particles.

1.2 The filter is weighed (after moisture equilibration) before and after use to determine the net weight (mass) gain. The total volume of air sampled, corrected to EPA standard conditions (25° C, 760 mm Hg [101 kPa]), is determined from the measured flow rate and the sampling time. The concentration of total suspended particulate matter in the ambient air is computed as the mass of collected particles divided by the volume of air sampled, corrected to standard conditions, and is expressed in micrograms per standard cubic meter (µg/std m3). For samples collected at temperatures and pressures significantly different than standard conditions, these corrected concentrations may differ substantially from actual concentrations (micrograms per actual cubic meter), particularly at high elevations. The actual particulate matter concentration can be calculated from the corrected concentration using the actual temperature and pressure during the sampling period.

2.0 INHERENT SOURCES OF ERROR

2.1 Airflow variation. The weight of material collected on the filter represents the (integrated) sum of the product of the instantaneous flow rate times the instantaneous particle concentration. Therefore, dividing this weight by the average flow rate over the sampling period yields the true particulate matter concentration only when the flow rate is constant over the period. The error resulting from a non-constant flow rate depends on the magnitude of the instantaneous changes in the flow rate and in the particulate matter concentration. Normally, such errors are not large, but they can be greatly reduced by equipping the sampler with an automatic flow controlling mechanism that maintains constant flow during the sampling period. Use of a constant flow controller is recommended.

2.2 Air volume measurement. If the flow rate changes substantially or non-uniformly during the sampling period, appreciable error in the estimated air volume may result from using the average of the pre-sampling and post-sampling flow rates. Greater air volume measurement accuracy may be achieved by (1) equipping the sampler with a flow controlling mechanism that maintains constant air flow during the sampling period, (2) using a calibrated, continuous flow rate recording device to record the actual flow rate during the

sampling period and integrating the flow rate over the period, or (3) any other means that will accurately measure the total air volume sampled during the sampling period. Use of a continuous flow recorder is recommended, particularly if the sampler is not equipped with a constant flow controller.

2.3 Loss of volatiles. Volatile particles collected on the filter may be lost during subsequent sampling or during shipment and/or storage of the filter prior to the post-sampling weighing. Although such losses are largely unavoidable, the filter should be reweighed as soon after sampling as practical.

2.4 Artifact particulate matter. Artifact particulate matter can be formed on the surface of alkaline glass fiber filters by oxidation of acid gases in the sample air, resulting in a higher than true TSP determination. This effect usually occurs early in the sample period and is a function of the filter pH and the presence of acid gases. It is generally believed to account for only a small percentage of the filter weight gain, but the effect may become more significant where relatively small particulate weights are collected.

2.5 Humidity. Glass fiber filters are comparatively insensitive to changes in relative humidity, but collected particulate matter can be hygroscopic. The moisture conditioning procedure minimizes but may not completely eliminate error due to moisture.

2.6 Filter handling. Careful handling of the filter between the pre-sampling and post-sampling weightings is necessary to avoid errors due to loss of fibers or particles from the filter. A filter paper cartridge or cassette used to protect the filter can minimize handling errors

2.7 Non-sampled particulate matter. Particulate matter may be deposited on the filter by wind during periods when the sampler is inoperative. It is recommended that errors from this source be minimized by an automatic mechanical device that keeps the filter covered during non-sampling periods, or by timely installation and retrieval of filters to minimize the non-sampling periods prior to and following operation.

2.8 Timing errors. Samplers are normally controlled by clock timers set to start and stop the sampler at midnight. Errors in the nominal 1,440-min sampling period may result from a power interruption during the sampling period or from a discrepancy between the start or stop time recorded on the filter information record and the actual start or stop time of the sampler. Such discrepancies may be caused by (1) poor resolution of the timer set-points, (2) timer error due to power interruption, (3) missetting of the timer, or (4) timer malfunction. In general, digital electronic timers have much better set-point resolution than mechanical timers, but require a battery backup system to maintain continuity of

operation after a power interruption. A continuous flow recorder or elapsed time meter provides an indication of the sampler run-time, as well as indication of any power interruption during the sampling period and is therefore recommended.

2.9 Recirculation of sampler exhaust. Under stagnant wind conditions, sampler exhaust air can be re-sampled. This effect does not appear to affect the TSP measurement substantially, but may result in increased carbon and copper in the collected sample. This problem can be reduced by ducting the exhaust air well away, preferably downwind, from the sampler.

3.0 PRECISION AND BIAS

3.1 The high-volume sampling procedure used to collect ambient air particulate matter has a between-laboratory relative standard deviation of 3.7 percent over the range 80 to 125 µg/m3. The combined extraction-analysis procedure has an average within-laboratory relative standard deviation of 5 to 6 percent over the range 1.5 to 15 µg metals/ml, and an average between laboratory relative standard deviation of 7 to 9 percent over the same range. These values include use of either extraction procedure.

4.0 APPARATUS

4.1 Filter.

4.1.1 Size: 20.3±0.2xK25.4±0.2 cm (nominal 8xK10 in).

4.1.2 Nominal exposed area: 406.5 cm2 (63 in\2\).

4.1.3 Material: Glass fiber or other relatively inert, non-hygroscopic material.

4.1.4 Collection efficiency: 99 percent minimum as measured by the DOP test (ASTM-2986) for particles of 0.3µm diameter.

4.1.5 Recommended pressure drop range: 42-54 mm Hg (5.6-7.2 kPa) at a flow rate of 1.5 std m3/min through the nominal exposed area.

4.1.6 pH: 6 to 10.

4.1.7 Integrity: 2.4 mg maximum weight loss.

4.1.8 Pinholes: None.

4.1.9 Tear strength: 500 g minimum for 20 mm wide strip cut from filter in weakest dimension. (See ASTM Test D828-60).

4.1.10 Brittleness: No cracks or material separations after single lengthwise crease.

4.2 Sampler. The air sampler shall provide means for drawing the air sample, via reduced pressure, through the filter at a uniform face velocity.

4.2.1 The sampler shall have suitable means to:

a. Hold and seal the filter to the sampler housing.

b. Allow the filter to be changed conveniently.

c. Preclude leaks that would cause error in the measurement of the air volume passing through the filter.

d. Manually adjust the flow rate to accommodate variations in filter pressure drop and site line voltage and altitude. The adjustment may be accomplished by an automatic flow controller or by a manual flow adjustment device. Any manual adjustment device must be designed with positive detents or other means to avoid unintentional changes in the setting.

4.2.2 Minimum sample flow rate, heavily loaded filter: 1.1 m3/min (39 ft3/min).

4.2.3 Maximum sample flow rate, clean filter: 1.7 m3/min (60 ft3/min).K

4.2.4 Blower Motor: The motor must be capable of continuous operation for 24-hr periods.

4.3 Sampler shelter.

4.3.1 The sampler shelter shall:

a. Maintain the filter in a horizontal position at least 1 m above the sampler supporting surface so that sample air is drawn downward through the filter.

b. Be rectangular in shape with a gabled roof.

c. Cover and protect the filter and sampler from precipitation and other weather.

d. Discharge exhaust air at least 40 cm from the sample air inlet.

e. Be designed to minimize the collection of dust from the supporting surface by incorporating a baffle between the exhaust outlet and the supporting surface.

4.3.2 The sampler cover or roof shall overhang the sampler housing somewhat and shall be mounted so as to form an air inlet gap between the cover and the sampler housing walls. This sample air inlet should be approximately uniform on all sides of the sampler. The area of the sample air inlet must be sized to provide an effective particle capture air velocity of between 20 and 35 cm/sec at the recommended operational flow rate. The capture velocity is the sample air flow rate divided by the inlet area measured in a horizontal plane at the lower edge of the cover. Ideally, the inlet area and operational flow rate should be selected to obtain a capture air velocity of 25 ±2 cm/sec.

4.4 Flow rate measurement devices.

4.4.1 The sampler shall incorporate a flow rate measurement device capable of indicating the total sampler flow rate. Two common types of flow indicators covered in the calibration procedure are (1) an electronic mass flow meter and (2) an orifice or orifices located in the sample air stream together with a suitable pressure indicator such as a manometer, or aneroid pressure gauge. A pressure recorder may be used with an orifice to provide a continuous record of the flow. Other types of flow indicators (including rotameters) having comparable precision and accuracy are also acceptable.

4.4.2 The flow rate measurement device must be capable of being calibrated and read in units corresponding to a flow rate which is readable to the nearest 0.02 std m3/min over the range 1.0 to 1.8 std m3/min.

4.5 Thermometer, to indicate the approximate air temperature at the flow rate measurement orifice, when temperature corrections are used.

4.5.1 Range: -40° to +50° C (223-323 K).

4.5.2 Resolution: 2° C (2 K).

4.6 Barometer, to indicate barometric pressure at the flow rate measurement orifice, when pressure corrections are used.

4.6.1 Range: 500 to 800 mm Hg (66-106 kPa).

4.6.2 Resolution: #5 mm Hg (0.67 kPa).

4.7 Timing/control device.

4.7.1 The timing device must be capable of starting and stopping the sampler to obtain an elapsed run-time of 24 hr ±1 hr (1,440 ±60 min).

4.7.2 Accuracy of time setting: #30 min, or better

4.8 Flow rate transfer standard, traceable to a primary standard

4.8.1 Approximate range: 1.0 to 1.8 m3/min.

4.8.2 Resolution: 0.02 m3/min.

4.8.3 Reproducibility: #2 percent (2 times coefficient of variation) over normal ranges of ambient temperature and pressure for the stated flow rate range.

4.8.4 Maximum pressure drop at 1.7 std m3/min; 50 cm H2O (5 kPa).

4.8.5 The flow rate transfer standard must connect without leaks to the inlet of the sampler and measure the flow rate of the total air sample.

4.8.6 The flow rate transfer standard must include a means to vary the sampler flow rate over the range of 1.0 to 1.8 m3/min (35-64 ft3/min) by introducing various levels of flow resistance between the sampler and the transfer standard inlet.

4.8.7 The conventional type of flow transfer standard consists of: An orifice unit with adapter that connects to the inlet of the sampler, a manometer or other device to measure orifice pressure drop, a means to vary the flow through the sampler unit, a thermometer to measure the ambient temperature, and a barometer to measure ambient pressure. A preferable design has a variable flow restriction that can be adjusted externally without disassembly of the unit. Use of a conventional, orifice-type transfer standard is assumed in the calibration procedure.

4.9 Filter conditioning environment

4.9.1 Controlled temperature: between 15° and 30° C with less than ±3° C variation during equilibration period.

4.9.2 Controlled humidity: Less than 50 percent relative humidity, constant within ±5 percent.

4.10 Analytical balance.

4.10.1 Sensitivity: 0.1 mg.

4.10.2 Weighing chamber designed to accept an unfolded 20.3 x 25.4 cm (8 x 10 in) filter.

4.11 Area light source, similar to X-ray film viewer, to backlight filters for visual inspection.

4.12 Numbering device, capable of printing identification numbers on the filters before they are placed in the filter-conditioning environment, if not numbered by the supplier.

5.0 REAGENTS

5.1 Glass fiber filters. The specifications given below are intended to aid the user in obtaining high quality filters with reproducible properties.

5.1.1 Metals content. The absolute metals content of filters is not critical, but low values are, of course, desirable. EPA typically obtains filters with a metals content of 75 µg/filter.

It is important that the variation in lead content from filter to filter, within a given batch, be small.

5.1.2 Testing.

5.1.2.1 For large batches of filters (500 filters) select at random 20 to 30 filters from a given batch. For small batches (500 filters) a lesser number of filters may be taken. Cut one 3/4''x8'' strip from each filter anywhere in the filter. Analyze all strips, separately, according to the directions in sections 7 and 8.

5.1.2.2 Calculate the total metal in each filter as

Fb = ug Metals/ml x 100ml/strip x 12 strips/filter

where:

Fb = Amount of lead per 72 square inches of filter, µg.

5.1.2.3 Calculate the mean, Fb, of the values and the relative standard deviation (standard deviation/mean x 100). If the relative standard deviation is high enough so that, in the analyst's opinion, subtraction of Fb, may result in a significant error in the µg Pb/m3, the batch should be rejected.

5.1.2.4 For acceptable batches, use the value of Fb to correct all lead analyses of particulate matter collected using that batch of filters. If the analyses are below the LDL no correction is necessary.

6.0 Calculation.

6.1 Determine the average sampler flow rate during the sampling period according to either 6.1.1 or 6.1.2 below.

6.1.1 Determine Qstd for the initial flow rate from the sampler calibration curve, either graphically or from the transposed regression equation:

Qstd = 1/m([Appropriate expression from table 2]-b)

Similarly, determine Qstd from the final flow reading, and calculate the average flow Qstd as one-half the sum of the initial and final flow rates.

6.1.2 For a sampler with a continuous flow recorder, determine the average flow rate device reading, I, for the period. Determine Qstd from the sampler calibration curve, either graphically or from the transposed regression equation:

Qstd = 1/m([Appropriate expression from table 2]-b)

If the trace shows substantial flow change during the sampling period, greater accuracy may be achieved by dividing the sampling period into intervals and calculating an average reading before determining Qstd.

6.2 Calculate the total air volume sampled as:

V-Qstd(t)

Where V = total air volume sampled, in standard volume units (std m3);
Qstd = average standard flow rate, std m3/min.; and
T = sampling time, min.

6.3 Calculate and report the particulate matter concentration as:

$$TSP = \frac{(Wf - Wi)10^6}{v}$$

where:

TSP = mass concentration of total suspended particulate matter, µg/std m3;
Wi = initial weight of clean filter, g;
Wf = final weight of exposed filter, g;
V = air volume sampled, converted to standard conditions, std m3,
10^6 = conversion of g to µg.

6.4 If desired, the actual particulate matter concentration can be calculated as follows:

4.10.2 Weighing chamber designed to accept an unfolded 20.3 x 25.4 cm (8 x 10 in) filter.

4.11 Area light source, similar to X-ray film viewer, to backlight filters for visual inspection.

4.12 Numbering device, capable of printing identification numbers on the filters before they are placed in the filter-conditioning environment, if not numbered by the supplier.

5.0 REAGENTS

5.1 Glass fiber filters. The specifications given below are intended to aid the user in obtaining high quality filters with reproducible properties.

5.1.1 Metals content. The absolute metals content of filters is not critical, but low values are, of course, desirable. EPA typically obtains filters with a metals content of 75 µg/filter.

It is important that the variation in lead content from filter to filter, within a given batch, be small.

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5.1.2.1 For large batches of filters (500 filters) select at random 20 to 30 filters from a given batch. For small batches (500 filters) a lesser number of filters may be taken. Cut one 3/4''x8'' strip from each filter anywhere in the filter. Analyze all strips, separately, according to the directions in sections 7 and 8.

5.1.2.2 Calculate the total metal in each filter as

Fb = ug Metals/ml x 100ml/strip x 12 strips/filter

where:

Fb = Amount of lead per 72 square inches of filter, µg.

5.1.2.3 Calculate the mean, Fb, of the values and the relative standard deviation (standard deviation/mean x 100). If the relative standard deviation is high enough so that, in the analyst's opinion, subtraction of Fb, may result in a significant error in the µg Pb/m3, the batch should be rejected.

5.1.2.4 For acceptable batches, use the value of Fb to correct all lead analyses of particulate matter collected using that batch of filters. If the analyses are below the LDL no correction is necessary.

6.0 Calculation.

6.1 Determine the average sampler flow rate during the sampling period according to either 6.1.1 or 6.1.2 below.

6.1.1 Determine Qstd for the initial flow rate from the sampler calibration curve, either graphically or from the transposed regression equation:

Qstd = 1/m([Appropriate expression from table 2]-b)

Similarly, determine Qstd from the final flow reading, and calculate the average flow Qstd as one-half the sum of the initial and final flow rates.

6.1.2 For a sampler with a continuous flow recorder, determine the average flow rate device reading, I, for the period. Determine Qstd from the sampler calibration curve, either graphically or from the transposed regression equation:

Qstd = 1/m([Appropriate expression from table 2]-b)

If the trace shows substantial flow change during the sampling period, greater accuracy may be achieved by dividing the sampling period into intervals and calculating an average reading before determining Qstd.

6.2 Calculate the total air volume sampled as:

V-Qstd(t)

Where V = total air volume sampled, in standard volume units (std m3);
Qstd = average standard flow rate, std m3/min.; and
T = sampling time, min.

6.3 Calculate and report the particulate matter concentration as:

$$TSP = \frac{(Wf - Wi)10^6}{v}$$

where:

TSP = mass concentration of total suspended particulate matter, µg/std m3;
Wi = initial weight of clean filter, g;
Wf = final weight of exposed filter, g;
V = air volume sampled, converted to standard conditions, std m3,
10^6 = conversion of g to µg.

6.4 If desired, the actual particulate matter concentration can be calculated as follows:

$$(TSPa = TSP(P3 / Pstd)(298 / T3)$$

where:

(TSP)a = actual concentration at field conditions, µg/m3;
TSP = concentration at standard conditions, µg/std m3;
P3 = average barometric pressure during sampling period, mm Hg;
Pstd = 760 mn Hg (or 101 kPa);
T3K = average ambient temperature during sampling period, K.

7.0 Quality Control

¾ inch x 8 inch glass fiber filter strips containing 80 to 2000 µg metals/strip (as metals salts) and blank strips with zero metal content should be used to determine if the method-as being used-has any bias. Quality control charts should be established to monitor differences between measured and true values. The frequency of such checks will depend on the local quality control program.

8.0 Procedure

8.1 Number each filter, if not already numbered, near its edge with a unique identification number.

8.2 Backlight each filter and inspect for pinholes, particles, and other imperfections; filters with visible imperfections must not be used.

8.3 Equilibrate each filter in the conditioning environment for at least 24-hr.

8.4 Following equilibration, weigh each filter to the nearest milligram and record this tare weight (Wi) with the filter identification number.

8.5 Do not bend or fold the filter before collection of the sample.

8.6 Open the shelter and install a numbered, pre-weighed filter in the sampler, following the sampler manufacturer's instructions. During inclement weather, precautions must be taken while changing filters to prevent damage to the clean filter and loss of sample from or damage to the exposed filter. Filter cassettes that can be loaded and unloaded in the laboratory may be used to minimize this problem.

8.7 Close the shelter and run the sampler for at least 5 min to establish run-temperature conditions.

8.8 Record the flow indicator reading and, if needed, the barometric pressure (P3) and the ambient temperature (T3) see NOTE following step 8.12). Stop the

sampler. Determine the sampler flow rate; if it is outside the acceptable range (1.1 to 1.7 m3/min [39-60 ft3/min]), use a different filter, or adjust the sampler flow rate. Warning: Substantial flow adjustments may affect the calibration of the orifice-type flow indicators and may necessitate recalibration.

8.9 Record the sampler identification information (filter number, site location or identification number, sample date, and starting time).

8.10 Set the timer to start and stop the sampler such that the sampler runs 24-hrs, from midnight to midnight (local time).

8.11 As soon as practical following the sampling period, run the sampler for at least 5 min to again establish run-temperature conditions.

8.12 Record the flow indicator reading and, if needed, the barometric pressure (P3) and the ambient temperature (T3).

Note: No onsite pressure or temperature measurements are necessary if the sampler flow indicator does not require pressure or temperature corrections (e.g., a mass flow meter) or if average barometric pressure and seasonal average temperature for the site are incorporated into the sampler calibration. For individual pressure and temperature corrections, the ambient pressure and temperature can be obtained by onsite measurements or from a nearby weather station. Barometric pressure readings obtained from airports must be station pressure, not corrected to sea level, and may need to be corrected for differences in elevation between the sampler site and the airport. For samplers having flow recorders but not constant flow controllers, the average temperature and pressure at the site during the sampling period should be estimated from weather bureau or other available data.

8.13 Stop the sampler and carefully remove the filter, following the sampler manufacturer's instructions. Touch only the outer edges of the filter. See the precautions in step 8.6.

8.14 Fold the filter in half lengthwise so that only surfaces with collected particulate matter are in contact and place it in the filter holder (glassine envelope or manila folder).

8.15 Record the ending time or elapsed time on the filter information record, either from the stop set-point time, from an elapsed time indicator, or from a continuous flow record. The sample period must be 1,440 ± 60 min. for a valid sample.

8.16 Record on the filter information record any other factors, such as meteorological conditions, construction activity, fires or dust storms, etc., that might be

pertinent to the measurement. If the sample is known to be defective, void it at this time.

8.17 Equilibrate the exposed filter in the conditioning environment for at least 24-hrs.

8.18 Immediately after equilibration, reweigh the filter to the nearest milligram and record the gross weight with the filter identification number.

9.0 Calibration.

9.1 Calibration of the high volume sampler's flow indicating or control device is necessary to establish traceability of the field measurement to a primary standard via a flow rate transfer standard.

Note: The following calibration procedure applies to a conventional orifice-type flow transfer standard and an orifice-type flow indicator in the sampler (the most common types). For samplers using a pressure recorder having a square-root scale, other acceptable calibration procedures may apply. Other types of transfer standards may be used if the manufacturer or user provides an appropriately modified calibration procedure.

9.2 Certification of the flow rate transfer standard.

9.2.1 Equipment required: Positive displacement standard volume meter traceable to the National Bureau of Standards (such as a Roots meter or equivalent), stop-watch, manometer, thermometer, and barometer.

9.2.2 Connect the flow rate transfer standard to the inlet of the standard volume meter. Connect the manometer to measure the pressure at the inlet of the standard volume meter. Connect the orifice manometer to the pressure tap on the transfer standard. Connect a high-volume air pump (such as a high-volume sampler blower) to the outlet side of the standard volume meter.

9.2.3 Check for leaks by temporarily clamping both manometer lines (to avoid fluid loss) and blocking the orifice with a large-diameter rubber stopper, wide cellophane tape, or other suitable means. Start the high-volume air pump and note any change in the standard volume meter reading. The reading should remain constant. If the reading changes, locate any leaks by listening for a whistling sound and/or retightening all connections, making sure that all gaskets are properly installed.

9.2.4 After satisfactorily completing the leak check as described above, unclamp both manometer lines and zero both manometers.

9.2.5 Achieve the appropriate flow rate through the system, either by means of the variable flow resistance in the transfer standard or by varying the voltage to the air pump. At least five different but constant flow rates, evenly distributed, with at least three in the specified flow rate interval (1.1 to 1.7 m3/min [39-60 ft\3Vmin]), are required.

9.2.6 Measure and record the certification data on a standard form according to the following steps.

9.2.7 Observe the barometric pressure and record as P1.

9.2.8 Read the ambient temperature in the vicinity of the standard volume meter and record it as T1.

9.2.9 Start the blower motor, adjust the flow, and allow the system to run for at least 1 min for a constant motor speed to be attained.

9.2.10 Observe the standard volume meter reading and simultaneously start a stopwatch. Record the initial meter reading (Vi).

9.2.11 Maintain this constant flow rate until at least 3 m3 of air have passed through the standard volume meter. Record the standard volume meter inlet pressure manometer reading as ^P, and the orifice manometer reading as ^H. Be sure to indicate the correct units of measurement.

9.2.12 After at least 3 m3 of air have passed through the system, observe the standard volume meter reading while simultaneously stopping the stopwatch. Record the final meter reading (Vf) and the elapsed time (t).

9.2.13 Calculate the volume measured by the standard volume meter at meter conditions of temperature and pressures as Vm=Vf-Vi.

9.2.14 Correct this volume to standard volume (std m3) as follows:

$$Vstd = Vm \frac{P1 - dP}{Pstd} \frac{Tstd}{T1}$$

where:

Vstd = standard volume, std m3;
Vm = actual volume measured by the standard volume meter;
P1 = barometric pressure during calibration, mm Hg or kPa;
DP = differential pressure at inlet to volume meter, mm Hg or kPa;
Pstd = 760 mm Hg or 101 kPa;
Tstd = 298 K;
T1 = ambient temperature during calibration, K.

Calculate the standard flow rate (std m3/min) as follows:

$$Qst = \frac{Vstd}{t}$$

where:

Qstd = standard volumetric flow rate, std m3/min
t = elapsed time, minutes.

Record Qstd to the nearest 0.01 std m3/min.

9.2.15 Repeat steps 9.2.9 through 9.2.14 for at least four additional constant flow rates, evenly spaced over the approximate range of 1.0 to 1.8 std m3/min (35-64 ft\3V/min).

9.2.16 For each flow, compute

¤(5)•H (P1/Pstd)(298/T1)

and plot these value against Qstd. Be sure to use consistent units (mm Hg or kPa) for barometric pressure. Draw the orifice transfer standard certification curve or calculate the linear least squares slope (m) and intercept (b) of the certification curve:

¤(6)•H (P1/Pstd)(298/T1)=mQstd+b.

A certification graph should be readable to 0.02 std m3/min.

9.2.17 Recalibrate the transfer standard annually or as required by applicable quality control procedures.

9.3 Calibration of sampler flow indicator.

Note: For samplers equipped with a flow controlling device, the flow controller must be disabled to allow flow changes during calibration of the sampler's flow indicator, or the alternate calibration of the flow controller given in 9.4 may be used. For samplers using an orifice-type flow indicator downstream of the motor, do not vary the flow rate by adjusting the voltage or power supplied to the sampler.

9.3.1 A standard form should be used to record the calibration data.

9.3.2 Connect the transfer standard to the inlet of the sampler. Connect the orifice manometer to the orifice pressure tap. Make sure there are no leaks between the orifice unit and the sampler.

9.3.3 Operate the sampler for at least 5 minutes to establish thermal equilibrium prior to the calibration.

9.3.4 Measure and record the ambient temperature, T2, and the barometric pressure, P2, during calibration.

9.3.5 Adjust the variable resistance or, if applicable, insert the appropriate resistance plate (or no plate) to achieve the desired flow rate.

9.3.6 Let the sampler run for at least 2 min to re-establish the run-temperature conditions. Read and record the pressure drop across the orifice (•H) and the sampler flow rate indication (I).

9.3.7 Calculate ¤(7)H(P2/Pstd)(298/T2) and determine the flow rate at standard conditions (Qstd) either graphically from the certification curve or by calculating Qstd from the least square slope and intercept of the transfer standard's transposed certification curve: Qstd=1/m ¤(8)H(P2/Pstd)(298/T2)-b. Record the value of Qstd.

9.3.8 Repeat steps 9.3.5, 9.3.6, and 9.3.7 for several additional flow rates distributed over a range that includes 1.1 to 1.7 std m3/min.

9.3.9 Determine the calibration curve by plotting values of I against Qstd. The choice of expression from depends on the flow rate measurement device used and also on whether the calibration curve is to incorporate geographic average barometric pressure (Pa) and seasonal average temperature (Ta) for the site to approximate actual pressure and temperature. Where Pa and Ta can be determined for a site for a seasonal period such that the actual barometric pressure and temperature at the site do not vary by more than ±60 mm Hg (8 kPa) from Pa or ±15° C from Ta, respectively, then using Pa and Ta avoids the need for subsequent pressure and temperature calculation when the sampler is used. The geographic average barometric pressure (Pa) may be estimated from an altitude-pressure table or by making an (approximate) elevation correction of -26 mm Hg (-3.46 kPa) for each 305 m (1,000 ft) above sea level (760 mm Hg or 101 kPa). The seasonal average temperature (Ta) may be estimated from weather station or other records. Be sure to use consistent units (mm Hg or kPa) for barometric pressure.

9.3.10 Draw the sampler calibration curve or calculate the linear least squares slope (m), intercept (b), and correlation coefficient of the calibration curve. Calibration curves should be readable to 0.02 std m3/min.

9.3.11 For a sampler equipped with a flow controller, the flow controlling mechanism should be re-enabled and set to a flow near the lower flow limit to allow maximum control range. The sample flow rate should be verified at this time with a clean filter installed. Then add two or more filters to the sampler to see if the flow controller maintains a constant flow; this is particularly important at high altitudes where the range of the flow controller may be reduced.

9.4 Alternate calibration of flow-controlled samplers. A flow-controlled sampler may be calibrated solely at its controlled flow rate, provided that previous operating history of the sampler demonstrates that the flow rate is stable and reliable. In this case, the flow indicator may remain un-calibrated but should be used to indicate any relative change between initial and final flows, and the sampler should be recalibrated more often to minimize potential loss of samples because of controller malfunction.

9.4.1 Set the flow controller for a flow near the lower limit of the flow range to allow maximum control range.

9.4.2 Install a clean filter in the sampler and carry out steps 9.3.2, 9.3.3, 9.3.4, 9.3.6, and 9.3.7.

9.4.3 Following calibration, add one or two additional clean filters to the sampler, reconnect the transfer standard, and operate the sampler to verify that the controller maintains the same calibrated flow rate; this is particularly important at high altitudes where the flow control range may be reduced.

10.0 References.

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TABLE 1. EXPRESSIONS FOR PLOTTING SAMPLER CALIBRATION CURVES

Type of sampler flow rate measuring device	Expression: For actual pressure and temperature corrections	Expression: For incorporation of geographic average pressure and seasonal average temperature
Mass flowmeter	I	I
Orifice and pressure indicator	$\sqrt{I\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	$\sqrt{I\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$
Rotameter, or orifice and pressure recorder having square root scale*	$I\sqrt{\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	$I\sqrt{\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$

*This scale is recognizable by its nonuniform divisions and is the most commonly available for high-volume samplers.

TABLE 2. EXPRESSIONS FOR DETERMINING FLOW RATE DURING SAMPLER OPERATION

Type of sampler flow rate measuring device	Expression: For actual pressure and temperature corrections	Expression: For use when geographic average pressure and seasonal average temperature have been incorporated into the sampler calibration
Mass flowmeter	I	I
Orifice and pressure indicator	$\sqrt{I\left(\frac{P_3}{P_{std}}\right)\left(\frac{298}{T_3}\right)}$	$\sqrt{I}$
Rotameter, or orifice and pressure recorder having square root scale*	$I\sqrt{\left(\frac{P_3}{P_{std}}\right)\left(\frac{298}{T_3}\right)}$	I

*This scale is recognizable by its nonuniform divisions and is the most commonly available for high-volume samplers.

DIGESTION AND PREPARATION PROCEDURES FOR METALS IN AIR

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1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe the procedures used to prepare and digest air samples collected on filter paper prior to the analysis by ICP (SOP ME70). This preparation may be performed on samples tested for Suspended Particle Matter (SPM). However, the gravimetric determination of SPM is beyond the scope of this procedure.

2.0 SUMMARY OF METHOD AND DEFINTIONS

2.1 An ambient air sample is routinely collected on 8" x 10" quartz/glass fiber filter paper. A 1" x 8"strip of the filter is removed and placed in a digestion vessel. A nitric acid/hydrochloric acid extraction solution is added and the sample is digested for 20 minutes. After cooling, 10mL of deionzed water is added and the sample is allowed to stand for 30 minutes. The digest is filtered, adjusted to a final volume of 20mL, and analyzed by ICP (Method 6010B, SOP ME70). The results are reported as micrograms of metal on the filter paper.
Definitions

Digestate - the digested sample
ICP - inductively coupled (argon) plasma
HCl –hydrochloric acid
HNO3 – nitric acid

2.3 The SOP is based on the guidance in Compendium Method IO-3.1 and SW-846 Method 6010B.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 The samples are digested in strong acid solutions and contain acid concentrations of 10-20% by volume. The analyst must wear protective clothing such as a lab coat or apron. The acids used in this procedure will destroy unprotected clothing. The analyst must wear proper eye protection such as lab glasses or face shield. Acid can be splashed into the eyes from many sources. Gloves must be worn to protect hands from acid burns.

3.3 The acid digestion procedures must be performed under a properly functioning fume hood. The acid fumes from the digestion can cause mild to severe respiratory problems if breathed.

3.4 Each digestion lab must have acid spill kits. These kits must be located in a highly accessible area of the lab. Each digestion lab must be equipped with a properly working shower.

3.5 The standards and reagents used to prepare the standards in this method should be treated as potential hazards. Lab coats, gloves, and other protective equipment should be used when preparing and using the standards and reagents.

3.6 The Material Safety Data Sheets (MSDS) for each reagent and standard are located in each laboratory. These sheets denote the type of hazard that each reagent poses and the safe handling instructions for these compounds.

3.7 Care must be taken when handling the digestion beakers. Before handling a vessel that has been in use, check the temperature to make sure that it is not hot. Make sure that the digestion vessels are placed on a stable platform during and after the digestion. Vibrations from the hood or an unstable platform can cause the beakers to move and possibly to fall and splatter an analyst with a hot acid solution. Hot acids can cause severe skin burns and destroy unprotected clothing.

4.0 INTERFERENCES

Contamination of the sample can occur when the preparation glassware and/or reagents contain the target elements. Reagent blanks (method blanks) must be analyzed as a check on contamination due to the sample digestion.

5.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Ambient quartz filters should be received folded in half lengthwise with the particulate material inward and enclosed in protective envelopes. Some filters may be provided in a shipping envelope with an unused filter covering the exposed surface. At least one blank filter must also be received for use as the blank and the lab control sample. If one or more blank filters are not received, notify the project manager immediately.

Inspect the filters upon receipt into the preparation lab for tears or holes in the filters. Note if any of the particulate material has fallen off of the filter. Capture any "loose particulate material in a tared plastic container. Notify the project manger via an Anomaly Report.

Check the identification of the filter. If. any discrepancy is noted or if the filter cannot be unambiguously identified, notify the project manger via an Anomaly Report.

The samples are stored at ambient (room) temperature and must be prepared and analyzed within 180 days of collection.

6.0 APPARATUS AND MATERIALS

6.1 Hot plate or digestion block-capable of maintaining a sample temperature of 95C+/-5C. The temperature of the hot plate or digestion block must be monitored and recorded each day samples are digested. The temperature is measured in a beaker or digestion vessel containing reagent water.

6.2 Digestion vessels, appropriate volume for use with digestion block

6.3 Teflon or Pyrex beakers, appropriate volumes, Recommend 150mL or 250mL beakers for use with hot plates

6.4 Watch glasses, for use with beakers (block digestion vessels do not require watch glasses)

6.5 Teflon vials-25mL

6.5 Volumetric flasks- appropriate volumes

6.6 Graduated cylinder-appropriate volume

6.7 Pipettes

6.8 Analytical balance

6.9 Top-loading balance

7.0 REAGENTS

Reagents must be tracked in accordance with SOP AN44: *Reagent Traceability*.

7.1 Reagent water-lab generated deionized water. ASTM Type I or Type II. The conductivity must be checked daily in accordance with SOP AN35: *Conductivity Checks for Laboratory Deionized Water*.

7.2 Nitric acid (HNO_3)-reagent grade. The assay sheet of each lot of acid received into the lab must be reviewed to make sure that the quality of the acid is sufficient for trace analysis of metals. Each lot of acid must be assayed in the laboratory to ensure that each particular lot can be used for trace analysis.

7.3 Hydrochloric acid (HCl)-reagent grade. The assay sheet of each lot of acid received into the lab must be reviewed to make sure that the quality of the acid is sufficient for trace analysis of metals. Each lot of acid must be assayed in the laboratory to ensure that each particular lot can be used for trace analysis.

7.4 Extraction solution_ Add ~500mL of reagent water, 55.5mL of concentrated HNO_3, and 167.5mL of concentrated HCl to a 1.0-L volumetric flask. Dilute to volume with reagent water.

8.0 STANDARDS

The preparation of the spiking solutions must be tracked in accordance with SOP AN41: *Standard Material Traceability*. General guidance on the preparation of standards is given in SOP AN43: *Standard Preparation*.

The lab should purchase certified solutions from STL-approved vendors, if available. The lab should prepare standards from neat materials only if a certified solution is not available. See SOP AN43 for guidance for standard preparation.

8.1 ICP Matrix Spiking Solution 1 is a solution purchased from SPEX. The catalogue number is SPIKE-1. Store this solution at room temperature. Prepare this solution every six months or sooner if needed or required.

8.2 Preparation of the ICP Matrix Spiking Solution 2

Add 20-mL to 30-mL of reagent water to a clean100-mL volumetric flask. Add 1-mL of concentrated nitric acid (HNO_3) and 5-mL of hydrochloric acid (HCl) to the volumetric flask. The standard will have an acid concentration of 1% HNO_3 and 5% HCl when diluted to volume.

Add the volumes of the stock standards given in the following table to the volumetric flask:

Element	Conc. of Stock (mg/L)	mL of Stock	Final Volume (mL)	Conc. of std. (mg/L)
Boron (B)	1000	10	100	100
Calcium (Ca)	10000	5.0		500
Magnesium (Mg)	10000	5.0		500
Molybdenum (Mo)	1000	5.0		50
Potassium (K)	10000	5.0		500
Sodium (Na)	10000	5.0		500
Strontium (Sr)	1000	5.0		50
Tin (Sn)	1000	10		100
Titanium (Ti)	1000	10		100

Dilute to a final volume of 100-mL with reagent water. Store the standard at room temperature. Prepare this solution every six months or sooner if needed or required.

9.0 SAMPLE PREPARATION

This digestion procedure is used for the preparation of filter material for the determination of total metals by ICP. This digestion procedure is not suitable for some analytes that will be analyzed by graphite furnace atomic absorption (GFAA) because HCl can cause interferences during furnace atomization.

Wear gloves during this entire procedure. Do not touch the exposed area of the filter.

9.1 Place the sample filter paper on a plastic or inert surface with the exposed side up (the side with the particulate material-this will usually be the side with the sample identification number). A sheet of plastic wrap (e.g., Saran Wrap) may be used to cover the surface.

9.2 Place two wooded rulers on each lengthwise side of the filter paper, parallel to each other. The rulers must not touch the particulate material but should be positioned so that they contact the filter paper about ½ inch from the side.

9.3 Place a straight edge on the two rulers-the straight edge will be above but must not touch the particulate material. Place the straight edge in the middle of the filter paper, perpendicular tot he rulers. Using a stainless steel razor, cut the filter paper. Move the straight edge one inch and make a second cut. This will result in a 1" x 8" strip.

Cut a 1" x 8" strip for the blank and for the LCS. The same filter may be used and two 1" x 8" strips taken from the same 8" x 10" filter.

9.4 Carefully transfer the strips to labeled digestion vessels.

9.5 Add 1.0-mL of the appropriate spiking solution to the designated laboratory control spike.

9.6 Record the following information on the digestion log:

- date
- analyst's initials
- beaker ID#
- sample identification
- the weight of sample digested
- batch identification
- fume hood #
- temperature of the hot plate or digestion block (daily)
- the lot number of the acids used for the digestion
- the lot number of the ICP spiking solutions
- the time that the digestion was started
- the SOP/method number

9.7 Add 10mL of extraction solution (7.4) to each digestion vessel. The acid solution must cover the strip completely. If the acid does not cover the strip, add reagent water so that the strip is immersed in liquid. Mix gently and cover the beaker with a watchglass.

9.8 Carefully heat the beaker until a gentle reflux is achieved-the sample is not heated to boiling; that is, bubbles are not formed in the liquid in the bottom of the beaker. The sample/acid solution is refluxing when the liquid evaporates and drops of liquid condense on the watch glass and the sides of the beaker and fall back into the beaker. Do not allow the samples to boil. Reflux for 30 minutes.

9.9 Remove the beakers from the hot plate or digestion block and allow the beakers to cool to room temperature. Add 10mL of reagent water and allow the sample to stand for 30 minutes.

9.10 Wash down the inside of the beaker and the watchglass with reagent water. Filter and dilute the sample digestate to a final volume of 20mL with reagent water.

9.11 Record the analyst's initials, the final volume of the sample digestate, and the date that the digestion was completed in the digestion logbook. The sample is now ready for analysis.

10.0 PROCEDURES

The digestion procedure is described in Section 9.0. The analytical procedure is given in SOP ME 70: *Elements by ICP*.

11.0 CALCULATIONS

Calculations for the determination of metals by ICP in the sample digest are given in SOP ME70: *Elements by ICP*. The calculation of metals on the filter follows:

$$Mass(ug) = Cdigest \otimes F \otimes DF \otimes 9$$

Mass(ug) = mass of metal in micrograms
Cdigest = concentration of the metal in the digest (ug/L)
F = final volume of the digest in liters(L)
DF = dilution factor
9 = multiplier for strip of filter-a 1" x 8" strip is one ninth of the exposed area of the filter paper

The sample is then corrected for the blank. If the metal is not detected in the blank, then Mb = 0.

$$Mass(corr) = Ms - Mb$$

where
M(corr) = mass of metal in sample corrected for blank (ug)
Ms = mass of metal in sample uncorrected for bank(ug)
Mb = mass of metal in blank (ug)

12.0 QUALITY CONTROL/QUALITY ASSURANCE

The analytical batch consists of up to twenty (20) client samples and the associated quality control items. The quality control items consist of a method (reagent) blank and a lab control standard (LCS).

SOP AN02: *Analytical Batching* contains guidance for evaluating the QC in an analytical batch. The accuracy and precision limits are published in the current LQM.

13.0 PREVENTIVE MAINTENANCE AND TROUBLESHOOTING

The temperature of the hot plate or digestion block must be monitored daily. If the temperature required for sample preparation cannot be maintained the heating device must be removed from service and repaired or replaced.

14.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

Excess samples, reagents, and digestates must be disposed in accordance with SOP CA70: *Waste Management*.

15.0 REFERENCES

Compendium Method IO-3.0: Selection, Preparation, and Extraction of Filter Material. Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air, June 1999, published by the Center for Environmental Research Information, Office of Research and Development, USEPA< Cincinnati, OH..

ELEMENTS BY ICP (200.7 and 6010)

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Date
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STL X Savannah __ Tallahassee __ Mobile __ Tampa West

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the procedures to determine the concentration of various elements by inductively coupled plasma (ICP) atomic emission spectroscopy. This method contains the analytical procedures for the determination of metals in surface and ground water, wastewater, soil, sediment, leachate (EP or TCLP), and waste samples after digestion.

1.2 Table 1 lists the elements that may be determined by ICP and the characteristic wavelength used for each element. The reporting limit (RL) for each element, the method detection limit (MDL) for each element, and the accuracy and precision criteria for each element are in the Laboratory Quality Manual (LQM) prepared by and for STL Savannah, STL Tallahassee, STL Mobile, and STL Tampa West.

2.0 SUMMARY OF METHOD AND DEFINITIONS

2.1 Prior to analysis by ICP, the sample must be solubilized or digested using the sample preparation method appropriate to the matrix. Sample digestates are aspirated and nebulized into a spray chamber. A stream of argon gas carries the sample aerosol through the innermost of three concentric tubes and injects it into the middle of the donut-shaped plasma. The sample elements are dissociated, atomized, and exited to a higher energy level. As the elements fall to a lower energy level, radiation characteristic of the elements present in the plasma is emitted. The light is directed through an entrance slit, dispersed by the diffraction grating, and projected on to the photomultiplier tube (PMT). The PMTs, located behind the exit slits, convert the light energy to an electrical current. This signal is then digitized and processed by the data system. Background correction is required for trace element determination.

2.2 Definitions

ICP -inductively coupled (argon) plasma; sometimes referred to a "ICAP"
TCLP-toxicity compound leaching procedure
EP (tox)-extraction procedure (toxicity)
Analytical Spike or Post-Digestion Spike - addition of a known concentration of analyte to an aliquot of sample after the preparation steps have been performed
RL - reporting limit, the lowest calibration standard or the sample equivalent of the lowest calibration standard; published in LQM or project-specific quality assurance plan (QAPP); sometimes referred to as the "practical quantitation limit(PQL).
MDL - method detection limit, the concentration that can be reported with 99% confidence that the result is greater than zero; published in LQM

2.3 This method is based on EPA Method 200.7 and SW-846 Method 6010B. Note that EPA has promulgated two versions of method 200.7-one for NPDES samples and one for drinking water. The calibration sequence for drinking water by 200.7 requires a multi-point curve with a minimum of three standards and a calibration blank.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 Each digestion lab must have acid spill kits. These kits must be located in a highly accessible area of the lab. Each digestion lab must be equipped with a properly working shower.

3.3 The standards and reagents used to prepare the standards in this method should be treated as potential hazards. Lab coats, gloves, and other protective equipment should be used when preparing and using the standards and reagents.

3.4 The Material Safety Data Sheets (MSDS) for each reagent and standard are located in each laboratory. These sheets denote the type of hazard that each reagent poses, the safe handling instructions for these compounds, and first aid instructions.

4.0 INTERFERENCES

4.1 Spectral interferences are caused by (1) the overlap of a spectral line from another element, (2) unresolved overlap of molecular band spectra, (3) background contribution from continuous phenomena, and (4) stray light from the line emissions of highly concentrated elements.

4.1.1 Spectral overlap may be compensated for by the use of inter-element correction factors.

4.1.2 Background contribution and stray light can be compensated for by a background correction adjacent to the analyte line.

4.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity can cause significant inaccuracies, especially in samples containing high concentrations of dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample digestate, by using a peristaltic pump, or by using the method of standards additions(MSA), or use of an internal standard

4.3 Contamination of the sample can occur when the preparation glassware and/or reagents contain the target elements. Reagent blanks (method blanks) must be analyzed as a check on contamination due to the sample digestion.

5.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

5.1 Aqueous Samples

5.1.1 Liquid samples are routinely collected in 250-mL or 500-mL plastic containers. The sample is preserved with HNO_3 to a pH <2. The sample must be digested and analyzed within 6 months of collection. Samples may be stored at room temperature.

5.1.2 Samples for dissolved metals should be filtered in the field before acid is added to the sample. If the sample is to be filtered in the lab, no preservative is added to the sample until the sample is filtered.

5.2 Soil/Sediment Samples
Soil and sediment samples are routinely collected in 500-mL plastic containers. The sample is iced at the time of collection and is stored in the lab at 4C (less than 6C but not frozen) until time of digestion and analysis. The sample must be digested and analyzed within 6 months of collection.

5.3 TCLP or EP Toxicity Leachate Samples
The leachate is transferred to a plastic container after the extraction procedure. The sample is preserved with HNO_3 to a pH <2. The leachate sample must be digested and analyzed within 6 months of completion of the leaching procedure.

5.4 Waste Samples
Waste samples are routinely collected in 500-mL plastic containers. The sample must be digested and analyzed within 6 months of collection.

6.0 APPARATUS AND MATERIALS

6.1 Thermo Jarrell Ash TJA ICAP61E-trace, or other suitable inductively coupled plasma emission spectrometer with data system

6.2 Argon gas supply and appropriate fittings

6.3 Cooling water supply

6.4 Peristaltic pump

6.5 Volumetric flasks

6.6 Pipettes

7.0 REAGENTS
Reagents are tracked in accordance with STL SOP AN44:*Reagent Traceability.*

7.1 Reagent water-lab generated deionized water, ASTM Type I or Type II. The conductivity is monitored in accordance with STL SOP AN35.

7.2 Nitric acid (HNO_3)-reagent grade. The assay sheet of each lot of acid received into the lab must be reviewed to make sure that the quality of the acid is sufficient for trace analysis of metals.

7.4 Hydrochloric acid (HCl)-reagent grade. The assay sheet of each lot of acid received into the lab must be reviewed to make sure that the quality of the acid is sufficient for trace analysis of metals.

8.0 STANDARDS
Calibration and spike solutions are prepared from either certified stock solutions or from stock solutions purchased from vendors. Certificates of analysis or purity must be received with all neat compounds or stock solutions. All preparation steps must be in accordance with STL SOP AN41: *Standard Materials Traceability.* SOP AN43 contains guidance for the preparation of standards.

8.1 Recommended concentrations for the calibration standards are given in Table 1. Appendix A contains examples for the preparation of the initial calibration and calibration verification standards for both 6010 and 200.7. if the laboratory uses "recipes' other than those listed in Appendix A, the recipe must be documented in the standard material traceability logbook or as controlled posting. All standards must have be prepared in 5% hydrochloric acid and 1% nitric acid by volume.

NOTE: Standards must be prepared every six months "or sooner if needed or required." "If needed" means the standard has been exhausted; "if required" means that the standard does not meet the QC criteria.

8.2 Preparation of the Linearity Check Solutions

The linearity check solutions are prepared individually according to the following equation:

$$Vs = \frac{Vlc \otimes Clc}{Cs}$$

where
Vs = volume of stock standard (mL)
Cs = concentration of stock standard (mg/L)
Vlc = volume of linearity check standard to prepare (mL)
Clc = concentration of linearity check standard to prepare (mg/L)

The linearity check solutions are prepared at the concentrations specified in Table 1. Prepare sufficient volume to perform the linearity check, maintaining the hydrochloric acid concentration at 5% by volume and the nitric acid concentration at 1% by volume.

9.0 SAMPLE PREPARATION

The sample preparation and digestion procedures are listed in the following SOPs:

MATRIX	SOP
Aqueous and leachate samples	ME50
Soils and Sediments	ME51
Wastes and oils	ME51

10.0 ANALYSIS PROCEDURE

The analytical sequence, including standardization and calibration verification, is included in the SOP Summary in Appendix A. The SOP Summary also included the acceptance criteria for QC, including recommended corrective actions.

10.1 Initial Calibration/Standardization

10.1.1 Turn the ICP on and allow it to become thermally stable before beginning to analyze the calibration standards. It will take about an hour for the instrument to warm up. If optics were turned off, allow 2 hours warm up time.

10.1.2 Run the "Automatic Profile" program. The "automatic profile" of the instrument should be checked twice a day to compensate for changes in air pressure, humidity, and temperature. If the environment of the instrument is such that daily changes in the instrument profile are extreme, the instrument should be "profiled" every few hours.

10.1.3 Analyze the calibration standards and calibrate the ICP. ***If using a multi-point calibration, use the Calibration/Analysis and Curvefit programs to calibrate the instrument.***

10.1.4 The highest concentration calibration standard is reanalyzed after the instrument is standardized as an "unknown". The results for the re-analysis of the highest concentration calibration standard must be within +/- 5% of the true value for each target analyte. If the result for any target analyte is outside of this range, the ICP may need to be "profiled" and the standardization/calibration repeated.

10.1.5 The QC Check standards (ICV) and the Calibration Blank (ICB) are analyzed as a check on the instrument calibration.

10.1.5.1 (EPA Method 6010) The results for the target compounds in the initial calibration verification (ICV) must be within the +/- 10 % of the true value.

10.1.5.2 (EPA Method 200.7) The results for the target compounds in the initial calibration verification (ICV) must be within the +/-5.0 % of the true value. **When performing 200.7 work, note that this solution should be prepared fresh weekly.**

10.1.5.3 (EPA 6010/200.7) The results for the target compounds in the initial calibration blank (ICB) must be less than the RL.

10.1.6 The RL/PQL Check Solution is analyzed to demonstrate that the ICP is capable of detecting the target compounds at or near the reporting limit (RL). The determined concentration must within +/- 50% of the true concentration.

10.1.7 The ICP Interference Check Sample is analyzed. The concentrations of the target analytes must be within 20% of the true concentrations. Pay particular attention to false positives and false negatives for elements not present in the interference check solutions.

10.2 Continuing Calibration Verification (CCV)

10.2.1 The calibration of the ICP must be verified every 10 samples by the analysis of the analysis of the QC Check Solutions (CCV) and the Calibration Blank (CCB).

10.2.1.2 (EPA Method 6010/200.7-DW) The results for the target compounds in the continuing calibration verification (CCV) must be within the +/- 10 % of the true value.

10.2.1.2 (EPA Method 200.7-NPDES) The results for the target compounds in the continuing calibration verification (CCV) must be within the +/-5.0 % of the true value.

10.2.1.3 (EPA 6010/200.7) The results for the target compounds in the continuing calibration blank (CCB) must be less than the Reporting Limit (RL).

10.2.2 ICP Interference Check Solution and the RL check solution are analyzed at the beginning and end of each analytical sequence.

10.3 Sample Analysis

10.3.1 The samples are analyzed only after the ICB/CCB and ICV/CCV criteria are met.

10.3.2 The samples are analyzed in a sequence as follows:

INSTRUMENT WARM-UP
PROFILE
INITIAL CALIBRATION (STANDARDIZATION/CALIBRATION OF THE ICP)
REANALYSIS OF HIGH CONCENTRATION CALIBRATION STANDARD AS A SAMPLE
INITIAL CALIBRATION VERIFICATION (ICV)
INITIAL CALIBRATION BLANK (ICB)
DETECTION LIMIT CHECK SOLUTION
ICP INTERFERENCE CHECK SOLUTION A (ICSA)
ICP INTERFERENCE CHECK SOLUTION AB (ICSAB)
CONTINUING CALIBRATION VERIFICATION (CCV)
CONTINUING CALIBRATION BLANK (CCB)
10 SAMPLES
CONTINUING CALIBRATION VERIFICATION (CCV)
CONTINUING CALIBRATION BLANK (CCB)
10 SAMPLES
CCV
CCB
10 SAMPLES
CCV
CCB
10 SAMPLES
CCV
CCB

The analytical sequence must end with the analysis of the detection limit check standard, ICSA, ICSAB, CCV and CCB. The 10 samples include all QC samples/standards with the exception of CCVs and CCBs.

10.3.3 Determine the concentration of the samples and QC items using the procedures of Section 11.

10.3.3.1 If the concentration of a sample is above the linear range of the ICP, the sample digestate must be diluted and reanalyzed.

10.3.3.2 The amount of sample digestate needed to prepare the desired dilution is determined form the following equation:

$$V_{digest} = \frac{Vf_{vol}}{DF}$$

where
Vf_{vol} = final volume of diluted sample (mL)
V_{digest} = volume of sample digestate used to make the dilution (mL)

10.3.3.3 The dilution factor is calculated as follows:

$$DF = \frac{Vf_{vol}}{V_{digest}}$$

where
Vf_{vol} = final volume of diluted sample extract (mL)
V_{digest} = volume of sample extract used to make the dilution (mL)

NOTE: The following examples are based on a final volume of 100mL. It may be more convenient to prepare dilutions at smaller final volumes.

EXAMPLE
A sample digestate is analyzed and one of the target analytes exceeds the linear range of the ICP. 1.0mL of the digestate is added to a 100mL volumetric flask and the extract brought up to volume with reagent water. What is the dilution factor?

$$DF = \frac{100mL}{1.0mL} = 100$$

Dilutions must be prepared in reagent water containing 5% hydrochloric acid and 1% nitric acid by volume.

Some samples may require multiple dilutions; that is, a dilution of a dilution will have to be made. In this case, the final dilution factor is the product of the individual dilutions.

10.4 Dilution QC Check
A dilution is prepared and analyzed on one sample per batch to determine if matrix interferences are present.

10.4.1 Select a sample digestate that contains one or more target analytes at a concentrations greater than 10X the reporting limit.

10.4.2 Dilute the digestate by a factor of 5 (DF=5) and analyze the dilution using the same procedures used for the un-diluted aliquot.

10.4.3 Compare the results of the diluted and un-diluted aliquots of sample digestate.

10.4.4 If the results of the dilution are within ± 10% of the results of the undiluted sample, no matrix interference is present. If the results differ by greater than ± 10%, a matrix interference should be suspected and the sample digestate should be subjected to a post-digestion spike (see section 10.4).

If the concentration of the analyte in the sample is not at least 50 times the instrument detection limit, evaluate the post-digestion spike.

10.5 Post-digestion Spike QC Check
A post-digestion spike is performed on one sample per analytical batch to determine if matrix interferences are present. This post-digestion spike is evaluated if the serial dilution fails or if the analyte concentration is not at least 50 times the instrument detection limit. This should be the same sample selected for dilution in 10.3, above.

10.5.1 Transfer 10mL of a digestate to a suitable vial.

10.5.2 Spike the sample with 0.10mL of ICP Matrix Spike I and 0.10mL of ICP Matrix Spike II. The theoretical concentration of the post digestion spike is the same as the LCS or MS if the volume of spiking solution is discounted.

10.5.3 Analyze the spiked aliquot and an un-spiked aliquot (the un-spiked may have been analyzed previously and does not need to be reanalyzed).

10.5.4 Calculate the percent recovery of the post digestion spike:

$$\%REC = \frac{C_{ps} - C_s}{C_2} \times 100$$

where

Cps = concentration of post digestion spike (ug/L)
Cs = concentration of un-spiked sample (ug/L)
C2 = theoretical concentration of spike (ug/L)
(See 10.2.5.2)

10.5.5 Evaluate the recovery using the following decision matrix. Limits for post digestion spikes are 75-125% recovery.

Result of Post Digestion Spikes	Action
Within 75-125% limits	None
>125% recovery	Repeat analysis. Remake spiking solutions, re-spike, and reanalyze. Reanalyze un-spiked sample
<75% recovery but >50% recovery	1) Dilute and re-spike. Elevate RL accordingly (for all associated samples). 2) Spike and evaluate all associated samples. 3) Spike and evaluate all associated samples by single point MSA 4) Qualify all associated samples
<50% recovery	Dilute digestate and repeat spike. Treat all samples associated with spike in the same manner as the spiked sample (i.e., spike or dilute samples) If recoveries are not 75-125%, analyze all associated samples by single point MSA. Note – high level of target analytes may inhibit spike recovery. Consult the supervisor in events where high levels of targets appear to be interfering

Note: The >50% recovery of the post digestion spike is a benchmark below which samples may be biased high if corrected for spike recovery.

10.5.6 The post digestion spike and the method of standard additions must not be applied to samples analyzed at a dilution that produces a significant negative response. The analyst must use good judgement when evaluating data where the sample response is negative. Where a significant negative response is present, the digestate should be diluted and reanalyzed to determine the extent of the matrix interferences.

10.6 Single Point Method of Standard Additions

Two identical aliquots of the sample digest, Vx, are taken. One aliquot is spiked with a solution of known concentration, Cs. The second aliquot is analyzed un-spiked (the small volume of standard added to the spiked sample should be disregarded). The concentration of both aliquots are measured and the sample concentration, Cx, is calculated:

$$C_x = \frac{S_2 V_s C_s}{(S_1 - S_2) V_x}$$

where

S_1 = absorbance or concentration of the spiked aliquot
S_2 = absorbance or concentration of the un-spiked aliquot
Vs = Volume of spike solution

Example:	Sample concentration (S_2):	523 ug/L.
	Spike solution concentration (C_s):	50,000 ug/L
	Volume of spike solution (V_s):	0.10mL
	Volume of sample aliquots (V_x):	10mL
	Spiked sample concentration (S_1):	951 ug/L

C_x = [(523)*(0.10)*(50,000)]/[(951-523)*10)] = [2,615,000]/[4280] = 611 ug/L

10.7 Determination of Linear Range of the ICP

The linear range must be determined a minimum of once per year. Divisions performing CLP analyses are required to determine and document the linear range quarterly. Documentation of the linear range study must be kept on hand and be available for inspection. A summary of the linear range study must be available to the bench analyst.

10.7.1 Profile and calibrate the ICP as described in Section 10.1

10.7.2 Prepare individual standards at concentrations that are expected to define the linear range of the instrument. Use the concentrations in Table 1 for guidance. The calibration standards and the linear range standards should be matrix matched; that is, they have the same percentage of hydrochloric and nitric acids.

10.7.3 Analyze the standards following the analytical sequence described in Section 10.3. Verify the calibration after every 10 analyses.

10.7.4 Compare the concentration of the linear range standard with its true concentration.

$$PercentDifference = \left| \frac{Ccal - Ctrue}{Ctrue} \right| \otimes 100$$

where
Ccal = concentration determined from analysis
Ctrue = true concentration of the standard

If the percent difference is less than or equal to 5%, the linear range is confirmed at that concentration. If the percent difference is greater than 5%, repeat the analysis with a lower concentration.

The linear range may be extended by analyzing higher standards and evaluating the results against the 5% difference criterion. The linear range of the ICP for an analyte is the highest standard of that analyte that meets this criterion.

11.0 DATA ANALYSIS/CALCULATIONS

11.1 Aqueous and Leachate Samples

Aqueous samples are routinely reported in mg/L while the ICP is routinely calibrated in ug/L. If the results are reported in ug/L, the conversion factor is omitted from the calculation.

11.1.1 The concentration of the target analyte in liquid samples is calculated as follows:

$$Concentration\,(mg/L) = ug/L(from\ printout) \otimes \frac{F}{V} \otimes DF \otimes \frac{1mg}{1000ug}$$

where
F = final volume of the sample digestate (L)-usually 50mL (0.050L)
V = volume of sample digested (L)
DF = dilution factor

11.1.2 The Reporting Limit (RL) of the target analyte in liquid samples is calculated as follows:

$$Concentration(mg/L) = RLqap \otimes \frac{F}{V} \otimes DF \otimes \frac{1mg}{1000ug}$$

where
RLqap = reporting limit from STL LQM (ug/L)
F = final volume of the sample digestate (L)
V= volume of sample digested (L)
DF = dilution factor

The LQM Reporting Limits assumes:
F = 50mL, V = 50mL, and DF = 1

11.2 Soil/Solid Samples

Soils and solids are routinely reported in mg/kg while the ICP is routinely calibrated in ug/L. If the results are reported in ug/kg, the conversion factor is omitted from the calculation.

11.2.1 The concentration of the target analyte in soil and solid samples is calculated as follows:

$$Concentration(mg/kg,dw) = ug/L(from\ printout) \otimes \frac{F}{W \otimes solids} \otimes DF \otimes \frac{1mg}{1000ug}$$

where
F = final volume of the sample digestate (L)
W = volume of sample digested (kg)
DF = dilution factor
solids = decimal equivalent of the percent solids (percent solids/100)
(for example, if the percent solids is 85%, the decimal equivalent is 0.85; if the %solids is 100%, the decimal equivalent is 1.0.)

11.2.2 The Reporting Limit (RL) of the target analyte in soil/solid samples is calculated as follows:

$$Concentration(mg/kg,dw) = RL_{qap} \otimes \frac{0.0010kg}{W \otimes solids} \otimes \frac{F}{0.100L} x\ DF$$

where
RL(qap) = reporting limit from LQM
W = weight of sample digested (kg)
F = final volume of the sample digestate (L)
V = volume of sample digested (L)
DF = dilution factor
solids = decimal equivalent of the percent solids (percent solids/100)

The LQM Reporting Limits assumes F = 0.100L (100mL), DF = 1, W = 0.0010kg (1.0g), and solids = 1.0

12.0 QUALITY ASSURANCE /QUALITY CONTROL

12.1 STL SOP AN02: *Analytical Batching* and the SOP Summary provide guidance on evaluating QC and sample data, including recommended corrective actions.

12.2 The method detection limit (MDL) is determined annually in accordance with STL SOP CA90. The concentrations of the IDL and MDL solutions are given in Section 8 of this SOP.

12.3 Determination of the Instrument Detection Limit (IDL)

The difference between the MDL and the IDL is the *digestion step*. The MDL samples are prepared and digested prior to analysis. The IDL is defined as three times the standard deviation of seven replicate analyses analyzed over three non-consecutive days. The concentrations of the IDL and MDL solutions are given in Section 8 of this SOP. See SOP CA91 for the procedures for the determination of the IDL.

12.4 The linear range of the ICP must be determined at least annually. The procedure for the determination is given in Section 10.7 of this SOP. If any calibration regression fit, other than linear, is utilized for the calibration of the ICP (i.e., Curvilinear or Full Fit), the upper limit of the linear range is the concentration of the High Standard.

12.5 Interelement correction factors (IEC) for all elements must be determined annually. Use the manufacturer's guidance for determination of the IECs. The IECs must be verified at the beginning and end of each analytical sequence.

13.0 TROUBLESHOOTING AND PREVENTIVE MAINTENANCE

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
EQUIPMENT ITEM	Service Interval							SERVICE LEVEL
	D	W	M	Q	SA	A	AN	
ICAP								
Pump Tubing	X							Change.
Nebulizer							X	Clean.
Filters			X					Inspect monthly, clean or replace as needed.
Spray Chamber							X	Clean.
Quartz Torch							X	Clean and realign.

D = daily W = Weekly M = monthly Q = Quarterly SA = semi-annually A = annually AN = as needed

14.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

Excess samples, reagents, and digests must be disposed of in accordance with SOP CA70:*Waste Management*.

15.0 REFERENCES

15.1 *Methods for Chemical Analysis of Water and Waste*; U.S EPA Office of Research and Development: Cincinnati, OHIO, March 1983.

15.2 *Test Methods for Evaluating Solid Waste, Third Edition*; U.S. EPA Office of Solid Waste and Emergency Response: Washington, D.C., November 1986.

15.3 *Methods for the Determination of Metals in Environmental Samples*; US EPA Office of Research and Development. Washington, DC.

TABLE 1

Element	Wavelength (nm)	Calibration Conc. (mg/L)	ICV/CCV Conc. (mg/L)	RL Std. Conc. (mg/L)	Linear Range Std. Conc. (mg/L)*	MATRIX SPIKE CONC. (mg/L)	
						Water (mg/L)	Soil (mg/kg)
Aluminum (Al)	308.215	10	1.0/5.0	0.20	800	2.0	200
Antimony (Sb)	206.838	10	1.0/0.50	0.020	10	0.50	50
Arsenic (As)	189.042 193.696	1.0	1.0/0.50	0.010	25	2.0	200
Barium (Ba)	493.409	10	1.0/5.0	0.010	10	2.0	200
Beryllium (Be)	313.042	1.0	1.0/0.50	0.0040	10	0.050	5.0
Boron (B)	249.678	10	1.0/5.0	0.050	100	1.0	100
Cadmium (Cd)	226.502 228.802	1.0	1.0/5.0	0.0050	10	0.050	5.0
Calcium (Ca)	317.933 315.887	10	1.0/5.0	0.50	800	5.0	500
Chromium (Cr)	267.716	10	1.0/5.0	0.010	25	0.20	20
Cobalt (Co)	228.616	1.0	1.0/0.50	0.010	25	0.50	50
Copper (Cu)	324.754	10	1.0/5.0	0.020	50	0.25	25
Iron (Fe)	259.940 271.441	10	1.0/5.0	0.050	800	1.0	100
Lead (Pb)	220.353	1.0	1.0/0.50	0.0050	5	0.50	50
Magnesium (Mg)	279.079	10	1.0/5.0	0.50	1000	5.0	500

TABLE 1

Element	Wavelength (nm)	Calibration Conc. (mg/L)	ICV/CCV Conc. (mg/L)	RL Std. Conc. (mg/L)	Linear Range Std. Conc. (mg/L)*	MATRIX SPIKE CONC. (mg/L)	
						Water (mg/L)	Soil (mg/kg)
Manganese (Mn)	257.610	10	1.0/5.0	0.010	50	0.50	50
Molybdenum (Mo)	202.030	1.0	1.0/0.50	0.010	50	0.50	50
Nickel (Ni)	231.604	5.0	1.0/2.5	0.040	10	0.50	50
Potassium (K)	766.491	20	10/5.0	1.0	50	5.0	500
Selenium (Se)	196.026	10	1.0/5.0	0.010	25	2.0	200
Silver (Ag)	328.068	1.0	1.0/5.0	0.010	5.0	0.050	5.0
Sodium (Na)	588.995 330.231	10	1.0/5.0	0.50	20	5.0	500
Strontium (Sr)	421.552	10	1.0/5.0	0.010	100	0.50	50
Thallium (Tl)	189.042 190.801 377.572	10	1.0/5.0	0.010	30	2.0	200
Tin (Sn)	189.989	10	1.0/5.0	0.050	50	1.0	100
Titanium (W)	334.941	10	1.0/5.0	0.010	10	1.0	100
Vanadium (V)	292.402	10	1.0/5.0	0.010	50	0.50	50
Zinc (Zn)	213.856 206.200+	5.0	1.0/2.5	0.020	20	0.50	50

*For guidance only-instrument sensitivity will vary.

APPENDIX A
SOP SUMMARY

METHOD SUMMARY - ICP ANALYSIS

HOLD/STORAGE

Container	Minimum 250mL plastic bottle with plastic or Teflon-lined lid
Preservative	HNO3 to pH <2 in the field. If dissolved metals are required, filter the samples before preservation.
Storage	Liquids preserved to pH <2 may be stored at room temperature until preparation. Solid samples must be stored at 4C (less than 6C but not frozen) until preparation.
Hold Time	Samples must be analyzed within six months from the time of collection.

SAMPLE PREPARATION

Samples should be prepared with the appropriate matrix-specific procedure.

ANALYTICAL SEQUENCE

Ignite Plasma	Follow instrument manufacturer's guidelines and allow instrument to stabilize for at least 60 minutes.
Profile Instrument	Follow manufacturer's guidelines.
Initial Calibration	Calibrate with a blank and a high standard or a blank and three standards. Verify calibration by reanalyzing highest concentration standard for each element.
Initial Calibration Verification (ICV/ICB)	Analyze an initial calibration verification solution at the beginning of the run. ICV solution must come from a source other than the calibration standard source. Analyze a calibration blank after the ICV.
Continuing Calibration Verification (CCV/CCB)	Analyze a standard with concentrations at or near mid-range levels of the calibration. The CCV should be analyzed every 10 samples and at the end of the analysis run Analyze a continuing calibration blank after every CCV.
Interference Check Solutions	At the beginning and the end of an analysis run, verify the inter-element and background corrections by analyzing the interferent check solutions (ICSA & ICSAB).
Detection limit check solution	At the beginning and the end of an analysis run and verify the accuracy at the RL by analyzing a solution at the SL RL
Serial Dilution	Perform serial dilution (1/5) on a representative sample from each batch..
Post Digestion Spike Recovery.	To check for possible matrix interference, analyze a post digestion spike on a representative sample (minimum of 1 per batch). The post-digestion spike is evaluated if the serial dilution fails or if the analyte concentration in the sample is not at least 50 times the instrument detection limit.

QC Item	Frequency	Criteria	Corrective Action
Initial Calibration	Daily	1 std. and 1 blank	
Initial Calibration: Multi-point-minimum 3 stds and 1 blank	Daily	Correlation ≥0.995	Recalibrate
Highest Standard	Immediately after every calibration	Recoveries within ± 5% of expected values	New initial calibration
Initial Calibration Verification Standard (ICV)	At the beginning of the analysis	SW846 = within ±10% 200.7 = within ± 5%	Recalibrate
Continuing Calibration Verification Standard (CCV)	At the beginning and end of the analysis, and every 10 samples	Within ±10% of the true value, 200.7-NPDES - within ± 5% 200.7-Drinking Water – within ±10%	Terminate the analysis, fix the problem and reanalyze the previous 10 samples.
Calibration Blank (ICB/CCB)	After ICV and every CCV	Absolute value of the calibration blank must be less that the RL/CRDL	Terminate the analysis, correct the problem and reanalyze the previous 10 samples
Interference check standards (ICSA/ICSAB)	At the beginning and end of an analysis run	Determined values must be within ± 20% of the true values. Pay attention to false positives and false negatives for elements not present in the solutions.	Terminate the analysis, correct the problem, recalibrate, and reanalyze all samples since the last ICS that was in control.
Lab control sample	One per batch of twenty samples or less	6010B: STL LQM 200.7: 85-115%	Redigest and reanalyze batch
Preparation blank - SW846	One per batch of twenty samples or less	|result| <RL or result <5% of the analyte level in the sample.	Redigest and reanalyze batch
Preparation blank - 200.7	One per batch of twenty samples or less	|result| <RL or result <10% of the analyte level in the sample	Redigest and reanalyze batch
MS/MSD - SW846	One set per batch of twenty samples or less	STL LQM	Flag and report data
Serial Dilution (1/5 Dilution)	One per batch of twenty samples or less	See section 10.3.4	
Post Digestion Spike	One per batch of twenty samples or less	See section 10.4.5	
Detection Limit Check Solution	At the beginning and end of an analysis run	Recovery +/-50% of the true concentration.	Stop the analysis, fix the problem and reanalyze the affected samples.

APPENDIX B
EXAMPLES OF STANDARD PREPARATION

GENERAL INSTRUCTIONS

All calibration standards must contain 5% hydrochloric acid and 1% nitric acid by volume. The following table lists the volume of each acid needed to prepare the desired final volume of standard.

Final Volume of Standard (mL)	Volume of Hydrochloric acid (mL)	Volume of Nitric Acid (mL)
100	5.0	1.0
200	10	2.0
500	25	5.0
1000	50	10

For example, to prepare 500mL of a standard:

- Add 100mL to 200mL of reagent water to a clean 500mL volumetric flask.
- Add 5.0mL of concentrated nitric acid (HNO_3) and 25mL of hydrochloric acid (HCl) to the volumetric flask.
- Add the volumes of the stock standards given in the table to the volumetric flask:
- Dilute to a final volume of 500mL with reagent water. Store the standard at room temperature.

SINGLE POINT CALIBRATION STANDARDS FOR 6010

Calibration Standard 1-Calibration Blank (ICB, CCB)

Add 500mL to 600mL of reagent water to a clean 1-L volumetric flask. Add 10mL of concentrated nitric acid (HNO_3) and 50mL of hydrochloric acid (HCl) to the volumetric flask. Dilute to a final volume of 1.0-L with reagent water. Store the standard at room temperature. Other volumes may be prepared at the discretion of the lab. The nitric acid concentration must be 1% by volume and the hydrochloric acid concentration must be 5% by volume.

Calibration STANDARD 2

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (ml)	Conc. of Cal Std (mg/L)
Silver(Ag)	1000	0.50	500	1.0
Arsenic(As)	1000	0.50		1.0
Molybdenum(Mo)	1000	0.50		1.0
Lead(Pb)	1000	0.50		1.0
Selenium(Se)	1000	5.0		10
Antimony(Sb)	1000	0.50		1.0
Thallium(Tl)	1000	5.0		10

Calibration STANDARD 3

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. of Cal Std (mg/L)
Beryllium(Be)	1000	0.50	500	1.0
Barium(Ba)	1000	5.0		10
Cadmium(Cd)	1000	0.50		1.0
Cobalt(Co)	1000	0.50		1.0
Chromium(Cr)	1000	5.0		10
Copper(Cu)	1000	5.0		10
Manganese(Mn)	1000	5.0		10
Nickel(Ni)	1000	2.5		5.0
Zinc(Zn)	1000	2.5		5.0

Calibration STANDARD 4

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. of Cal Std (mg/L)
Aluminum(Al)	10000	0.50	500	10
Iron(Fe)	10000	0.50		10
Boron(B)	1000	5.0		10
Strontium(Sr)	1000	5.0		10
Titanium (Ti)	1000	5.0		10

Calibration STANDARD 5

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. of Cal Std (mg/L)
Calcium(Ca)	10000	0.50	500	10
Potassium(K)	10000	1.0		20
Magnesium(Mg)	10000	0.50		10
Sodium(Na)	10000	0.50		10
Tin(Sn)	1000	5.0		10
Vanadium(V)	1000	5.0		10

MULTI-POINT INSTRUMENT CALIBRATION-200.7

For all drinking water samples (EPA 200.7) the ICP must be calibrated with a minimum of three standards and a blank. The following standards may be used for this purpose. With the Thermo Jarrell Ash software the Calibration Analysis and Curve-fit programs must be used to be successful with the multi-point calibration of the ICP instruments.

High Standard.

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. of Cal Std (mg/L)
Aluminum (Al)	10000	1.0	1000	10
Antimony (Sb)	1000	1.0		1.0
Arsenic (As)	1000	1.0		1.0
Boron (B)	1000	10		10
Barium (Ba)	1000	10		10
Beryllium (Be)	1000	1.0		1.0
Cadmium (Cd)	1000	1.0		1.0
Calcium (Ca)	10000	1.0		10
Cobalt (Co)	1000	1.0		1.0
Chromium (Cr)	1000	10		10
Copper (Cu)	1000	10		10
Iron (Fe)	10000	1.0		10
Lead (Pb)	1000	1.0		10
Magnesium (Mg)	10000	1.0		10
Manganese (Mn)	1000	10		10
Molybdenum Mo)	1000	1.0		1.0
Nickel (Ni)	1000	5.0		5.0
Potassium (K)	10000	1.0		10
Selenium (Se)	1000	10		10
Silver (Ag)	1000	1.0		1.0
Sodium (Na)	10000	1.0		10
Strontium (Sr)	1000	10		10
Thallium (Tl)	1000	10		10
Tin (Sn)	1000	10		10
Titanium (Ti)	1000	10		10
Vanadium (V)	1000	10		10
Zinc (Zn)	1000	5.0		5.0

Mid-Level Standard- Prepare as the CCV is prepared.

Low-Level Standard- Prepare as the RL/PQL Check Standard.

Initial Calibration Verification (ICV) Solution

Element/Stock	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. of CCV Std (mg/L)
SPEX QC19	(1)	5.0	500	(2)
SPEX QC 7	(1)	5.0		(2)
Tin(Sn)	1000	0.50		1.0
Strontium (Sr)	1000	0.50		1.0
Potassium (K)	10000	0.50		10(3)
Sodium (Na)	10000	0.45		10(3)

(1) SPEX QC19 and SPEX QC7 are solutions containing multiple elements. The concentrations are given on the certificate of analysis.
(2) The final concentrations of the various elements are the same as listed in Table 1. The SPEC QC solutions are diluted by a factor of 100 from the concentration listed on the certificate of analysis.
(3) These concentrations include the contribution from SPEX Solutions QC-7

Continuing Calibration Verification (CCV) Standard

(also used as midpoint of multi-point calibration for EPA 200.7)

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. of CCV Std (mg/L)
Aluminum (Al)	10000	0.50	1000	5.0
Antimony (Sb)	1000	0.50		0.50
Arsenic (As)	1000	0.50		050
Boron (B)	1000	5.0		5.0
Barium (Ba)	1000	5.0		5.0
Beryllium (Be)	1000	0.50		0.50
Cadmium (Cd)	1000	0.50		0.50
Calcium (Ca)	10000	0.50		5.0
Cobalt (Co)	1000	0.50		0.50
Chromium (Cr)	1000	5.0		5.0
Copper (Cu)	1000	5.0		5.0
Iron (Fe)	10000	0.50		5.0
Lead (Pb)	1000	0.50		0.50
Magnesium (Mg)	10000	0.50		5.0
Manganese (Mn)	1000	5.0		5.0
Molybdenum (Mo)	1000	0.50		0.50
Nickel (Ni)	1000	2.5		2.5
Potassium (K)	10000	0.50		5.0
Selenium (Se)	1000	5.0		5.0
Silver (Ag)	1000	0.50		0.50
Sodium (Na)	10000	0.50		5.0
Strontium (Sr)	1000	5.0		5.0
Thallium (Tl)	1000	5.0		5.0
Tin (Sn)	1000	5.0		5.0
Titanium (Ti)	1000	5.0		5.0
Vanadium (V)	1000	5.0		5.0
Zinc (Zn)	1000	2.5		2.5

Reporting Limit (RL) Check Standard

(also used as low point in multi-point calibrations; e.g. EPA 200.7)

Preparation of RL/PQL Stock A-ICP

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. Of Stock Std (mg/L)
Silver (Ag)	1000	0.10	100	1.0
Arsenic (As)	1000	0.10		1.0
Cadmium (Cd)	1000	0.050		0.50
Copper (Cu)	1000	0.20		2.0
Nickel (Ni)	1000	0.40		4.0
Lead (Pb)	1000	0.050		0.50
Selenium (Se)	1000	0.10		1.0
Thallium (Tl)	1000	0.10		1.0

Preparation of RL/PQL Stock B-ICP

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. Of Stock Std (mg/L)
Aluminum (Al)	10000	0.20	100	20
Boron (B)	1000	0.50		5.0
Barium (Ba)	1000	0.10		1.0
Beryllium (Be)	1000	0.040		0.40
Calcium (Ca)	10000	0.50		50
Cobalt (Co)	1000	0.10		1.0
Chromium (Cr)	1000	0.10		1.0
Iron (Fe)	10000	0.050		5.0
Magnesium (Mg)	10000	0.50		50
Manganese (Mn)	1000	0.10		1.0
Molybdenum Mo)	1000	0.10		1.0
Sodium (Na)	10000	0.50		50
Antimony (Sb)	1000	0.20		2.0
Strontium (Sr)	1000	0.10		1.0
Tin (Sn)	1000	0.50		5.0
Titanium (Ti)	1000	0.10		1.0
Vanadium (V)	1000	0.10		1.0
Zinc (Zn)	1000	0.20		2.0

Preparation of RL/PQL Stock C-ICP

Element	Conc. of Stock Std	mL of Stock Std	Final Volume of Cal Std	Conc. Of Stock Std
Potassium(K)	10000	1.0	100	100

Preparation of the RL/PQL Check Solution-ICP

RL/PQL Stock	mL of RL/PQL Stock	Final Volume(mL)
Stock A-ICP	5.0	500
Stock B-ICP	5.0	
Stock C-ICP	5.0	

ICP Interference Check Solutions

Preparation of ICP Interference Check Solution A

Element	Conc. Of Stock(mg/L)	mL of Stock Std	Final Volume(mL)	Conc. (mg/L)
Aluminum (Al)	10000	25	500	500
Calcium (Ca)	10000	25		500
Magnesium (Mg)	10000	25		500
Iron (Fe)	10000	10		200

Preparation of ICP Interference Check Solution AB

Element	Conc. of Stock(mg/L)	mL of Stock	Final Volume (mL)	Conc. of Std (mg/L)
Aluminum (Al)	10000	25	500	500
Calcium (Ca)	10000	25		500
Magnesium (Mg)	10000	25		500
Iron (Fe)	10000	10		200
Silver (Ag)	1000	0.10		0.20
Arsenic (As)	1000	0.050		0.10
Barium (Ba)	1000	0.25		0.50
Beryllium (Be)	1000	0.25		0.50
Cadmium (Cd)	1000	0.50		1.0
Cobalt (Co)	1000	0.25		0.50
Chromium (Cr)	1000	0.25		0.50
Copper (Cu)	1000	0.25		0.50
Manganese (Mn)	1000	0.25		0.50
Nickel (Ni)	1000	0.50		1.0
Lead (Pb)	1000	0.025		0.050
Antimony (Sb)	1000	0.30		0.60
Selenium (Se)	1000	0.025		0.050
Thallium (Tl)	1000	0.050		0.10
Vanadium (V)	1000	0.25		0.50
Zinc (Zn)	1000	0.50		1.0
Molybdenum (Mo)	1000	0.50		1.0
Tin (Sn)	1000	0.50		1.0

ICP Matrix Spiking Solutions

ICP Matrix Spiking Solution 1 is a solution purchased from SPEX. The certificate of analysis will list the concentrations of the analytes. Store this solution at room temperature. Prepare this solution every six months or sooner if needed or required.

Preparation of the ICP Matrix Spiking Solution 2

Element	Conc. of Stock (mg/L)	mL of Stock	Final Volume (mL)	Conc. of Std. (mg/L)
Boron (B)	1000	10	100	100
Calcium (Ca)	10000	5.0		500
Magnesium (Mg)	10000	5.0		500
Molybdenum (Mo)	1000	5.0		50
Potassium (K)	10000	5.0		500
Sodium (Na)	10000	5.0		500
Strontium (Sr)	1000	5.0		50
Tin (Sn)	1000	10		100
Titanium (Ti)	1000	10		100

IDL/MDL Solution

The IDL/MDL solution is used in this procedure for two purposes:

1) To determine the Instrument Detection Limit (IDL) of each target compound on a quarterly basis (SOP CA91); and
2) To determine the Method Detection Limit (MDL) of each target compound on an annual basis (SOP CA90). MDLs should be digested straight and at 1:2 dilutions.

Preparation of IDL/MDL Stock A

Element	Conc. of Stock (mg/L)	mL of Stock	Final Volume (mL)	Conc. of Std. (mg/L)
Silver (Ag)	1000	0.040	100	0.40
Arsenic (As)	1000	0.20		2.0
Barium (Ba)	1000	0.020		0.20
Beryllium (Be)	100	0.050		0.050
Cadmium (Cd)	1000	0.040		0.40
Lead (Pb)	1000	0.10		1.0
Antimony (Sb)	1000	0.20		2.0
Selenium (Se)	1000	0.20		2.0
Thallium (Tl)	1000	0.20		2.0

Preparation of IDL/MDL Stock B

Element	Conc. Of Stock (mg/L)	mL of Stock	Final Volume (mL)	Conc. Of Std. (mg/L)
Cobalt (Co)	1000	0.030	100	0.30
Chromium (Cr)	1000	0.10		1.0
Copper (Cu)	1000	0.10		1.0
Manganese (Mn)	1000	0.020		0.20
Molybdenum (Mo)	1000	0.040		0.40
Nickel (Ni)	1000	0.10		1.0
Tin (Sn)	1000	0.20		2.0
Vanadium (V)	1000	0.060		0.60
Zinc (Zn)	1000	0.10		1.0

Preparation of IDL/MDL Stock C

Element	Conc. of Stock (mg/L)	mL of Stock	Final Volume (mL)	Conc. of Std. (mg/L)
Aluminum (Al)	10000	0.10	100	10
Calcium (Ca)	10000	0.10		10
Iron (Fe)	10000	0.10		10
Magnesium (Mg)	10000	0.10		10
Potassium (K)	10000	0.20		20
Sodium (Na)	10000	0.040		4.0

IDL/MDL Solution

Preparation of IDL/MDL Stock D

Element	Conc. Of Stock (mg/L)	mL of Stock	Final Volume (mL)	Conc. of Std. (mg/L)
Boron(B)	1000	0.40	100	4.0
Strontium (Sr)	1000	0.040		0.40
Titanium (Ti)	1000	0.050		0.50
Sodium (Na)	10000	2.0		200

Preparation of the IDL/MDL Check Solution

IDL/MDL Stock	mL of RL/PQL Stock	Final Volume(mL)
Stock A	5.0	1000
Stock B	5.0	
Stock C	5.0	
Stock D	5.0	

The IDL/MDL Check Solution contains the following elements at the given concentrations:

Element	Concentration(mg/L)
Be	0.00025
Ba, Mn	0.0010
Co	0.0015
Ag, Cd, Mo, Sr	0.0020
Ti	0.0025
V	0.0030
Cr, Cu, Ni, Pb, Zn	0.0050
As, Sb, Se, Sn, Tl	0.010
Na(1), B	0.020
Ca, Fe, Mg	0.050
Al, K	0.10
Na	1.0

(1) If the wavelength for sodium is 588.995, the lower concentration (0.020mg/L) is used for the IDL./MDL check solution. In this case, only stocks A,B, and C are used to make the IDL/MDL Check Solution. IDL/MDL Check Solutions for B, Sr, and Ti are prepared and evaluated separately.

APPENDIX M

Stormwater Runoff and Seep SOP

APPENDIX M Stormwater Runoff and Seep SOP

The following method will be used for collection of storm water samples:

1. Identify the primary storm water drainage route, running from the site to the Mississippi River. Figures 7 and 9 of this FSP present approximate storm water sampling locations for sites R and Q respectively.
2. Collect the sample during a rainfall which results in a discharge. A storm water sample will be collected during three separate storm events (for a total of three samples per site).
3. Use an automated storm water sampler to collect a first flush sample.
4. Remove appropriate sample containers from the transport container, and prepare the sample containers for receiving samples.
5. Fill out a self-adhesive label with the appropriate information and affix it to the appropriate sample container. Place clear polyethylene tape over the completed label to protect it from dirt and water. Sample labels can be prepared prior to sample collection, except for time and date. Labels can be filled in on the date of sample collection and just prior to collecting the sample. Sample containers will be kept cool with their caps on until they are ready to receive samples.
6. Put on a clean pair of disposable gloves.
7. Fill sample containers for the VOC sample, prior to filling other sample containers. Verify that there is no air in the sealed sampled container.
8. Transfer the water from the sampler to sample containers provided by the laboratory.
9. If the sample containers cannot be filled quickly, keep sample containers cool with the cap on until finished. Sample containers will be preserved as described in the QAPP.
10. Return each sample container to its proper transport container. Preserve samples by reducing the temperature within the containers to approximately 4° Celsius, using ice. Samples must not be allowed to freeze.
11. Begin chain-of-custody procedures. A sample chain-of-custody form is included in Appendix F.
12. Record the physical appearance of the storm water observed during sampling in the field notebook.

The owners manual for two automated samplers is provided in this Appendix.

APPENDIX M

Stormwater Runoff and Seep SOP

The following method will be used for collection of seep water samples:

1. Identify the seep location(s) along the riverbank and note location.
2. Remove appropriate sample containers from the transport container, and prepare the sample containers for receiving samples.
3. Fill out a self-adhesive label with the appropriate information and affix it to the appropriate sample container. Place clear polyethylene tape over the completed label to protect it from dirt and water. Sample labels can be prepared prior to sample collection, except for time and date. Labels can be filled in on the date of sample collection and just prior to collecting the sample. Sample containers will be kept cool with their caps on until they are ready to receive samples.
4. Grab sampling procedures and preservation of the collected seep water samples will follow the methods described in the current edition of "Standard Methods for the Examination of Water and Wastewater" (published by the American Public Health Association).
5. Put on a clean pair of disposable gloves.
6. Use a dipping utensil to retrieve a sample.
7. Fill sample containers for the VOC sample, prior to filling other sample containers. Verify that there is no air in the sealed sampled container.
8. Fill remaining sample containers.
9. If the sample containers cannot be filled quickly, keep sample containers cool with the cap on until finished. Sample containers will be preserved as described in the QAPP.
10. Return each sample container to its proper transport container. Preserve samples by reducing the temperature within the containers to approximately 4° Celsius, using ice. Samples must not be allowed to freeze.
11. Begin chain-of-custody procedures. A sample chain-of-custody form is included in Appendix F.
12. Record the physical appearance of the storm water observed during sampling in the field notebook.

Global Water
Stormwater Sampler
SS201

Global Water

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Global Water
Stormwater Sampler
Instruction Manual

Global Stormwater Sampler

Description

The Global Stormwater Sampler is designed specifically to meet the sampling requirements of the Stormwater program. The Global Sampler takes a "first flush" sample in one bottle and a "time weighted" composite sample in the second bottle, to meet the guidelines. It is actually two samplers in one: it consists of two intake tubes, two sampling pumps and two bottles, which eliminates any possiblity of cross contamination between the first flush and the composite sample. The Global Stormwater Sampler is easily set up and installed in any stormwater channel to take and store physical water samples throughout the storm event.

The Global Stormwater Sampler consists of a rugged, rainproof lockable carrying enclosure. Inside the enclosure are two 4000 ml polyethylene sample bottles for first flush and composite samples, two peristaltic sampling pumps, the logic timer/controller, the water sensor, and a rechargeable gel cell battery. Also provided is the rain gauge, two sample pickup hoses and a battery charger. Everything you need is provided for a successful sampling program.

Low Power: The internal rechargeable battery will power the sampler for several months and/or for several storm events.

Overflow Protection: Each sample bottle is equipped with a float switch which automatically turns off the sampler pump if the bottle becomes full. Be sure the electrical leads from the bottle caps are plugged into the jacks on the bottom of the controller housing.

Environmental: The Sampler is not damaged by water or moisture or severe environmental conditions. All parts may be washed with soap and water.

Operating Temperature: 0 to 70 degrees C

Specifications

Sample Size:

First Flush: 4000 ml

Composite: 200 ml at 10 minute intervals, or set by user. 4000 ml composite sample maximum.

Size: 9" L X 17" W X 22" H

Weight: 22 # (Shipping Weight 24#)

Materials:

Enclosure: Expanded UV protected PVC
Bottles: 4000 ml polyethylene
Sample Tubing: Polyethylene

Sample Pumps:

Flow Rate: 1000 ml per minute at 4 ft. head
Type: Peristaltic
Maximum Lift: 22'

Logic Timer/Controller: CMOS Solid State (fully potted in epoxy).

Water Level Sensor: Solid State with a 15' cable.

Sample Hoses: Two 15' nylon reinforced 1/4" ID polyethylene flexible tubing sections with intake strainers. Hoses may be extended, as required, using standard 1/4" tubing and fittings.

Battery: Rechargeable2 AH Gel Cell

Battery Life: The battery will power the sampler for a minimum of four months including five 24-hr. storm events before recharging is required.

Sampler Operation

The Global Stormwater Sampler is shipped fully assembled and tested. Remove everything from the box and straighten out the hoses.

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1. *Set the Sampler in an upright position.* (It will not work if it is on its side.)

2. Be sure the water sensor is plugged into its jack on the lower right side of the control panel.

2. Check to be sure the two float switches in the bottle cap are properly connected. Plug the lead from the bottle cap into the socket on the bottom of the controller housing.

The Global Stormwater Sampler is controlled by the water sensor. Plug the sensor into the jack on the lower right side of the control panel. The water sensor can be used to trigger the sampler based on rainfall *or* raise in water level in the storm drain. For rainfall triggering, position the water sensor in the inner tube of the rain gauge. Adjust the height of the two sensor electrodes to the amount of rainfall you want before samples are taken. (For example, if you want 0.1" rain before samples are taken, adjust the sensor so the bottom to the electrodes is opposite the 0.1" marking on the inner cylinder.) See separate instruction sheet for rain gauge installation and operation. For triggering based on water level, position and secure the water sensor in the channel at a point of depth where you want the sampler to start operation.

After the water sensor touches the water (in either the rain gauge or storm drain) the sampler pump is activated. The first flush will run until the bottle is full and then the float switch in the bottle cap will turn off the Sampler. Normally, the composite sampler side is set (by the user—it is not set in the factory) to take a 200 ml sample every 10 minutes until the composite sample bottle is full. The sample size and sampler interval are fully adjustable by using the knobs on the upper right side of the control panel.

Open the Sampler enclosure and remove the battery charger. The battery is installed in the controller enclosure. On the right side of the controller enclosure, find the on-off toggle switch. Push the switch up, for ON. This turns on the battery power to the Sampler. Press the push button on the right side to activate the right side sampler pump. Press the left side button to activate the left side pump. Use these buttons to verify system operation, to take manual samples, and to remove sample water from the hoses after a storm event.

If the pumps grind slowly, this is an indication that it is time to recharge the battery. Also, before any extended use, it is a good idea to recharge the battery. Plug the charger into the charger socket, on the left side. *Then* plug the charger into the wall socket. Charge for 12 hours for a full recharge.

The sample size is approximate and varies with vertical distance between the water and the Sampler. For precise sample size, you may want to verify sample size and adjust for your specific installation.

After the storm, remove the sample bottles and take the samples to your lab for analysis. Run the sampler pump to remove old water from the lines and then install a clean empty bottle. Be sure to plug the lead from the bottle cap into the socket on the bottom of the controller housing. The battery is good for several storms between recharging.

Maintenance

The Global Stormwater Sampler should require no maintenance for several years except routine cleaning with soap and water, and battery recharging.

Warranty

The Global Stormwater Sampler is warranted to be free of defects for one year after purchase. If you have a problem, please call the factory for return authorization and then ship the unit prepaid. We will repair or replace the unit, and return it to you freight prepaid.

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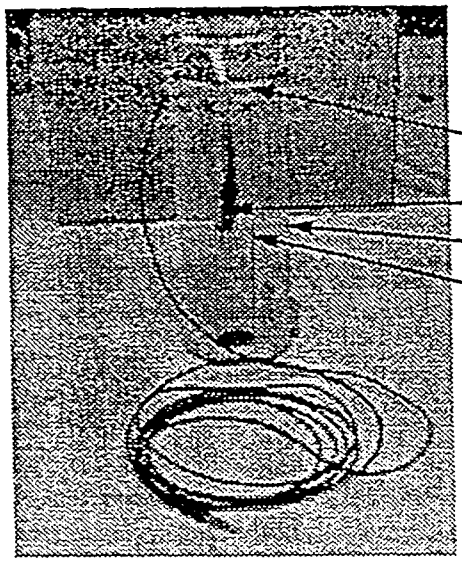
Rain Gauge Installation and Operation

The Rain Gauge is a precision weather instrument. With minimal care it should provide years of satisfactory service. Guard against extremely rough usage. Wash periodically with mild soap or detergent and warm water, using a household bottle brush. Do not use solvents or abrasives to clean the gauge and do not wash the gauge in your dishwasher. Do not allow accumulated water to freeze in the gauge.



Installation:
Mount the gauge on a post that you walk past each day so you will be reminded to read and empty the gauge daily. Ideally the post should be a 4" x 4," or use 2-2 x 4" nailed together. Where possible do not mount near buildings or trees that would prevent rainfall from reaching the gauge. The gauge should be mounted so the top of the gauge is level and is about 6" higher than the top of the post.

Operation:
The top funnel catches the rain and delivers it to the measuring tube. The measuring tube has a capacity of 1.00 inch. Rainfalls of less than one inch can be read directly from the measuring tube. Stand the measuring tube on a level surface. Read the amount to the nearest 100th of an inch. Record the rainfall in your log and discard the rain water.

If rainfall exceeds 1 inch, the excess flows into the outer cylinder. To measure, empty the measuring tube containing the first 1.00 inch. Place in the funnel into the measuring tube, then carefully pour the excess rainwater until the outer cylinder is empty. Then record the amount measured in your log. Be sure to count the first inch of rain water that was in the measuring tube. In fact it's a good idea to measure precipitation from heavy rains twice to insure accuracy. Just use an empty can or pan to receive the measured rain water and measure again.

In colder weather use only the outer cylinder to catch hail, sleet, or snow. Melt the snow indoors. Then, using the measuring tube, measure the moisture content of the snow. You may also use the outer cylinder to get a measure of moisture of accumulated snow by pressing the cylinder into a level area of snow then melting the captured snow. Also, you may add a known amount of hot water to speed up the melting process. Then measure the resultant water and subtract the amount of water you added.

Daily Log:
Whenever possible, take your readings at the same time each day. Record your readings on the daily log. Use the date on which you take the reading even though much or all of the rain may have fallen the preceding day, after you had already taken your daily reading. Enter your reading in hundredths of an inch (.01, .31, 1.01. 3.01). If the rainfall is less than 0.1 enter "T" for trace in your daily precipitation log.

Stormwater Sampler Rain Gauge Daily Log

1. Try to record precipitation each day at the same time.
2. Record precipitation to the nearest 1/100 of an inch. (.01, .31. 1.31, etc.)
3. If precipitation is less than .01, record "T" for Trace.
4. Use the remarks column to list any unusual weather.

	Jan.	Feb.	Mar.	Apr	May	June	July	Aug.	Sept	Oct.	Nov.	Dec.	Remarks
1													
2													
3													
4													
5													
6													
7													
8													
9													
10													
11													
12													
13													
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31													
Total													

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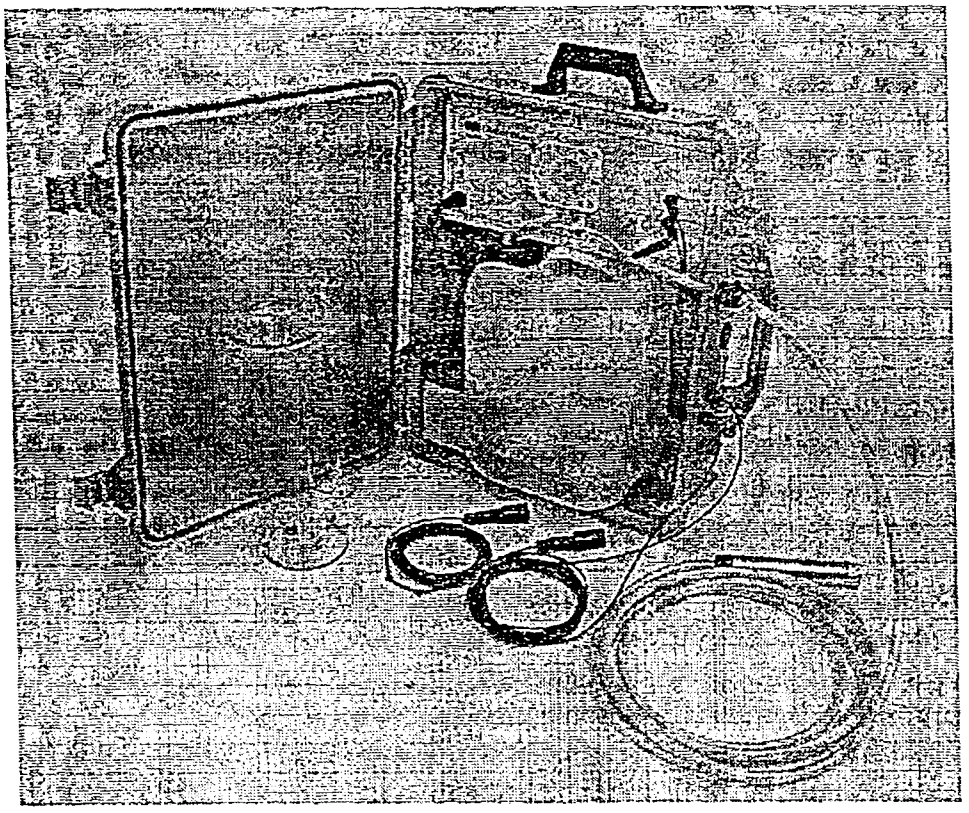
SS101 Stormwater Sampler

User's Manual



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Accessories	A-2
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Specifications

Sample Size: Approximately 2.5 liters.

Sample Pump:

Flow Rate: 1,000 ml per minute at 4 ft. head.
Type: Peristaltic
Maximum Lift: 22'

Size: 9" L x 17" W x 22" H

Operating Temperature: 0 to 70 deg. C

Weight: 22 lbs. (Shipping Weight 24 lbs.)

Materials:

Enclosure: Expanded UV protected PVC
Bottle: 4000 ml polyethylene
Sample Tubing: Polyethylene

Logic Timer/Controller: CMOS Solid State (fully potted in epoxy).

Water Sensors: Solid State with a 15' cable.

Sample Hose: 15' nylon reinforced 1/4" ID polyethylene flexible tubing sections with intake strainers. Hoses may be extended, as required, using standard 1/4" tubing and fittings to a maximum of 50'

Battery: Rechargeable 5 AH Gel Cell. Battery charger included.

Battery Life: The battery will power the sampler for a minimum of four months including five 24-hr. storm events before recharging is required.

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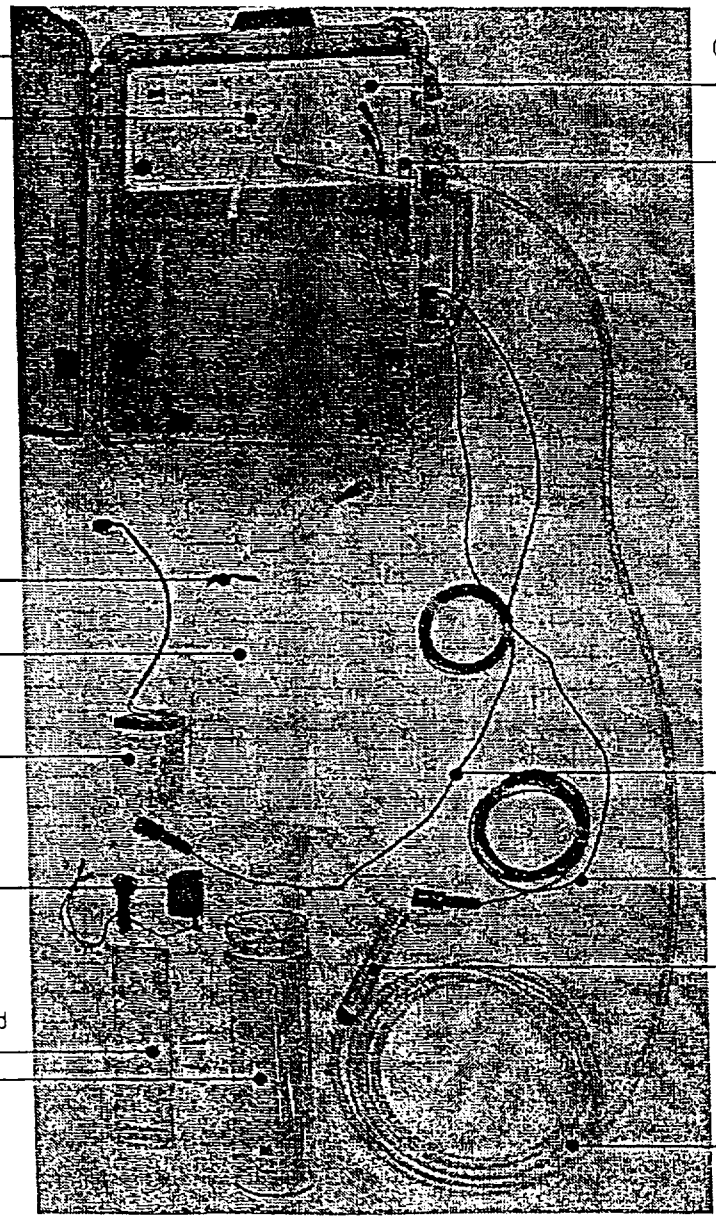
Product Description

The Global Water SS101 Stormwater Sampler is easily installed near any storm water channel and can store water samples throughout a storm event. The Sampler takes a discrete sample in one bottle based on rainfall accumulation and/or rise in storm water level.

The Global Water SS101 Stormwater Sampler consists the following parts to ensure a successful sampling program:



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Installation

Sampling Location

To meet specific permitting requirements, sampling locations may need to be established and certified by a licensed professional- refer to your permitting requirements prior to establishing a sampling program. An appropriate sampling location will most likely be:

- close to a storm water discharge channel or stream,
- situated so the rain gauge is away from trees and buildings, and
- removed from public areas.

Georgia's NPDES Permit Sampling Location Requirements

The Permit discusses sampling location requirements for the following construction projects:

- For all sites and common developments other than linear construction projects, all waters into which storm water flows, or all storm water channels, or a combination thereof must be sampled.
- For linear construction projects, all perennial and intermittent streams and other water bodies shown on a current 7.5 minute USGS topographic map and all other field verified streams, storm water channels, and water bodies must be sampled. However, representative streams, water bodies, and storm water channels may be sampled.

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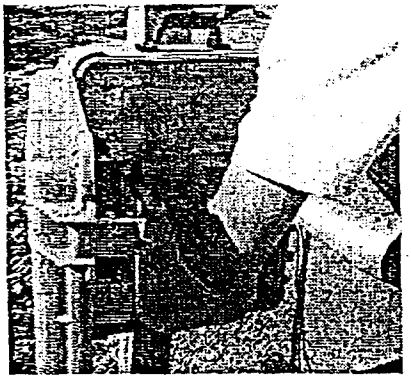
Sampling Unit

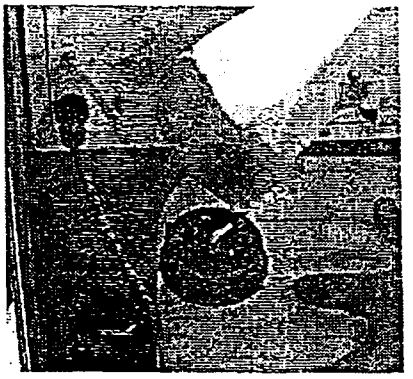
The sampler should be placed upright (it will not work if placed on its back or side) within 15 feet from both the rain and water sensors (see installation instructions below). The battery lead should be securely fastened to the appropriate connection.

To secure the sample bottle:

1) tighten the bottle cap,
2) place bottle into the sampler enclosure,
3) insert end of peristaltic pump hose into hole in bottle cap, and
4) plug the lead from the bottle cap into the "Bottle SW" socket on the control panel.



Place sample bottle into the carrying enclosure.



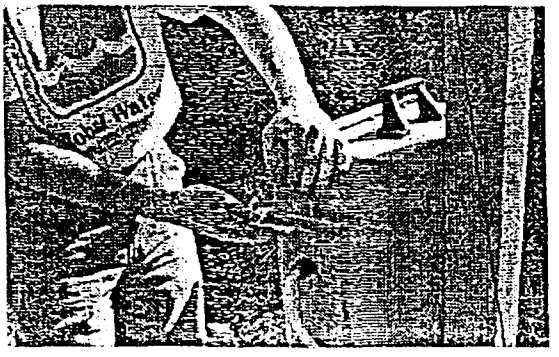
Insert end of peristaltic pump hose into the hole in bottle cap.

Plug the lead from bottle cap into "Bottle SW" socket.

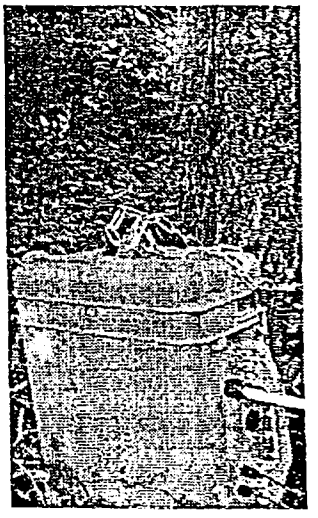
The sampling unit can be secured from vandalism and strong winds by one of the following methods:

- mount unit on post and lock closed,
- lock closed and chain rugged handle to a solid structure (such as a tree, post, or building), or
- enclose and lock unit in a steel electrical box.

The sampling unit can be mounted onto a post.



Lock the carrying enclosure closed to ensure security.



The sampling unit can be chained to a solid structure.

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Rain Gauge

Mount the Global Water Rain Gauge on a post. Ideally, the post should be 4" x 4". Install or use an existing post that is located conveniently for daily readings. Do not mount the rain gauge near buildings or trees that may prevent rainfall from reaching the gauge.

The Rain Gauge should be mounted near eye-level. The top of the rain gauge should be higher than the top of the post. To install the rain gauge:

1) screw the mounting bracket onto the post, making sure the bracket is level,
2) insert the measuring tube into the rain gauge,
3) slide the rain gauge into the mounting bracket,
4) insert the rain sensor to desired rainfall depth (see installation instructions below), and
5) place the top funnel on the unit.

Install a 4" x 4" post that is located conveniently for daily readings.

Screw the mounting bracket onto the post, making sure the bracket is level.

Slide the rain gauge into the mounting bracket.

Georgia's NPDES Permit Sampling Requirements

According to the Permit, runoff must be sampled for the following events:

- First rainfall event greater than or equal to 0.5 inches in 24 hours;
- Any rainfall event greater than or equal to 1.0 inches in 24 hours (but only one event per month needs to be sampled until final stabilization);
- Any rainfall event greater than or over 2.0 inches in 24 hours until final stabilization;
- One rainfall event greater than or equal to 0.5 inches in 24 hours after final stabilization; and
- If Best Management Practices have not been properly designed, installed or maintained in accordance with the Permit, any rainfall event greater than or equal to 0.5 inches in 24 hours.

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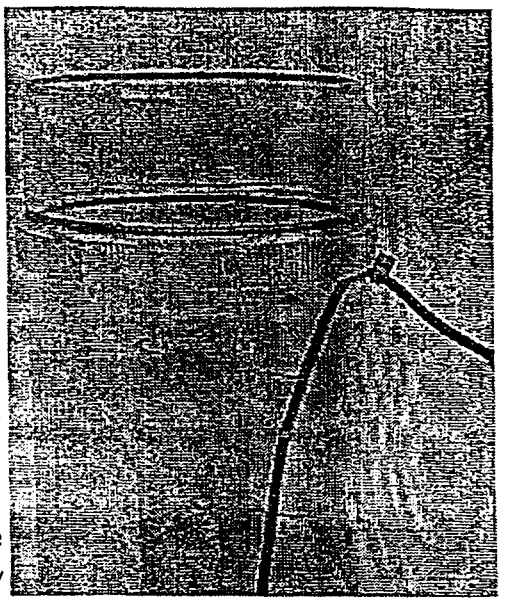
Rain Sensor

The rain sensor is used to trigger a sample for specific amounts of rainfall accumulation. Based on your application's requirements, insert the tip of the rain sensor into the rain gauge at a specified rainfall accumulation (0.1 to 0.6, 1.0, or 2.0 inches). Securely hook the rain sensor's cable into the groove in the cylinder and place a tie wrap (provided on the cable) outside the groove to secure the installation. Place the Rain Gauge funnel over the cylinder. Insert the rain sensor's plug into the "Rain Sensor" socket on the control panel.



Hook the sensor's cable into the Rain Gauge's groove, securing a tie wrap outside the groove.

To trigger a sample when rainfall from 0.1 to 0.6 inch accumulates, insert the sensor at an appropriate depth into the measuring tube (inside cylinder). To trigger a sample when rainfall accumulates at 1.0 or 2.0 inches, insert the sensor at the appropriate depth in the outer cylinder. For your reference, 0.5" is clearly marked on the inside measuring tube, and 1.0" and 2.0" are clearly marked on the outside cylinder.

To trigger a sample when rainfall at 0.5 inch accumulates, insert the sensor into the measuring tube (inside cylinder) at the depth as marked.

To trigger a sample when rainfall accumulates at 1.0 inch, insert the sensor in the outer cylinder at the depth as marked.

To trigger a sample when rainfall accumulates at 2.0 inch, insert the sensor in the outer cylinder at the depth as marked.

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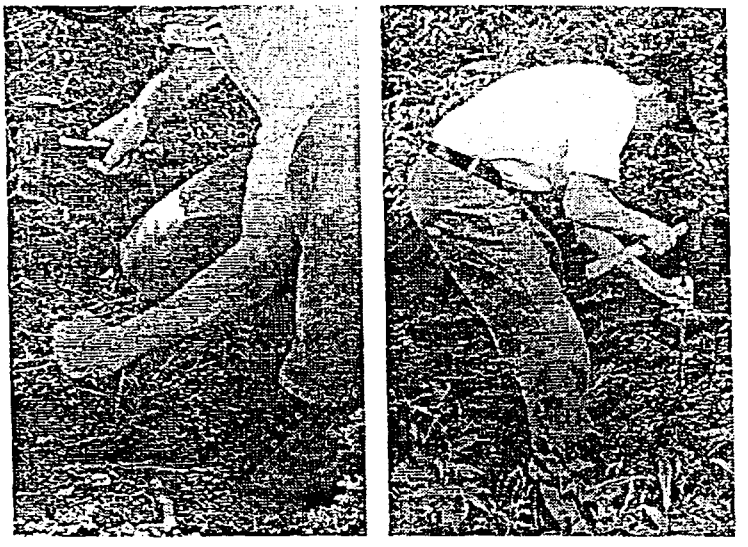
Pickup Hose and Water Sensor

The water sensor and pickup hose should be installed in a storm water discharge channel or stream that is appropriate for your sampling program. The water sensor and pickup hose can be installed in the following manner:

1) Securely insert a piece of rebar or similar mounting material into the center of the storm water discharge channel or stream. The material should extend from the bottom of the channel at a distance appropriate for sensor installation (see step 2). Avoid installation where water may pool.

2a) In a dry channel, fasten the water sensor and the end of the pickup hose onto the mounting material using tie wraps, electrical tape, or hose clamps. Ideally, the pickup strainer should be placed at 1/2 the depth of flow during a storm event. The water sensor should be tied just above the debris strainer, in order to trigger a sample after the sample intake is submerged. The water sensor and pickup hose should be situated to avoid contact with the channel bottom.



Securely insert a piece of mounting material into the center of the channel.

2b) In a stream, fasten the end of the pickup hose onto the mounting material using tie wraps or hose clamps. The pickup strainer should be submerged under water and should be situated to avoid contact with the channel bottom. For stream sampling (as opposed to dry channel sampling) only the rain sensor will be used to trigger a sample.

3) For dry channel sampling, plug water sensor into "Water Sensor" socket on the control panel. For stream sampling, the bypass plug must be installed in the "Water Sensor" socket.

In a dry channel, the water sensor should be tied just above the debris strainer.

In a stream, the pickup strainer should be submerged under water.

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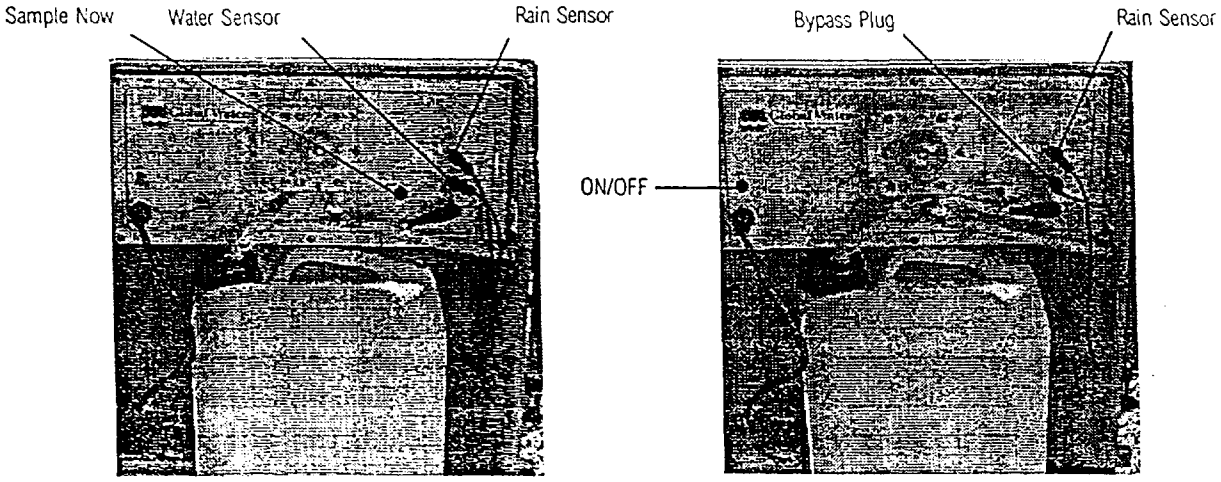
Operation

Sampler

Verify that the sampling unit, rain gauge, water and rain sensors, and sampling pickup hose are installed correctly (see previous section). The Global Water SS101 Stormwater Sampler will function only if the battery plug is securely fastened into the appropriate socket on the control panel, the bottle plug is inserted into the "Bottle SW" socket, and either:

- both the rain sensor and water sensor are plugged into the appropriate sockets on the control panel (i.e., both sensors must be submerged to trigger a sample), or
- the rain sensor or water sensor is plugged into its appropriate socket and the bypass plug is inserted into the remaining socket (i.e., only the sensor that is plugged in must be submerged in order to trigger a sample).



Sampler with both sensors used to trigger a sample

Sampler with one sensor used to trigger a sample (bypass plug in use).

Turn the sampling unit ON (switch is on the control panel) and verify that the sampler is operating using the "Sample Now" switch. The "Sample Now" switch can also be used to take manual samples. If the "Sample Now" switch does not run the pump, verify that the unit was installed and set up correctly (see above) and that the battery is recharged (see Maintenance section). If the unit still does not sample, refer to the Trouble Shooting section. The unit must be ON to take automatic samples.

The sampler will take approximately a 2.5 L sample. The sampler has a backflush function that will clear the pickup hose and pickup strainer after a sample is complete. The float switch in the bottle cap will turn off the sampler before the sample bottle overflows. After a storm, remove the sample bottle or transfer the sample to a small bottle for lab or turbidity meter analysis. Then, install an empty, clean bottle.

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RAIN GAUGE

The top funnel of the Rain Gauge catches the rain and delivers it to the measuring tube. When over one inch of rain falls before the gauge is emptied, water will spill out of the measuring tube into the outer cylinder.

Rainfall of less than one inch can be read directly from the measuring tube by standing the measuring tube on a level surface and reading the amount to the nearest 100th of an inch. This measurement can then be recorded in a rainfall log (sample log provided). For rainfall over one inch, empty the measuring tube containing the first 1.00 inch of rain. Using the top funnel, carefully pour water from the outer cylinder into the measuring tube (if there is more than one inch of rain in the outer cylinder, pour out the measuring tube and repeat). Measure and record the total amount of rainfall, being sure to count the first inch of rain that was in the measuring tube.

Place the measuring tube on a level surface and read the rainfall amount to the nearest 100th of an inch.

Georgia's NPDES Permit Sampling Requirements

As required by the Permit, samples from automatic samplers must be collected no later than the next business day after their accumulation. Rainfall must be measured and recorded every 24 hours. We recommend establishing a convenient time each day to check and collect (if necessary) samples and record rainfall.

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Maintenance

Sampler

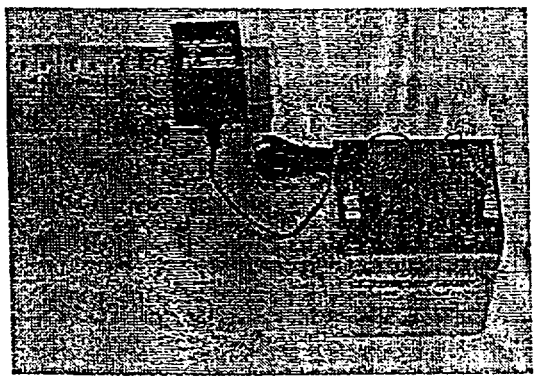
The Global Water SS101 Stormwater Sampler requires minimal maintenance. The sampler enclosure is rain-proof and rugged. Prevent exposure to extremely rough usage. Routinely wipe the carrying case and control panel face, rinse the pickup hose and debris strainer, and wash the sample bottle with mild soap and warm water. Additional plastic and glass sample bottles, norprene tubing for the sampler pump, bottle caps/float switches, removeable debris strainers, sensors, and pickup hose can be purchased from Global Water (see Accessories section).

Rain Gauge

The sampler's Rain Gauge requires minimal maintenance. Wash the Rain Gauge periodically with mild soap and warm water using a household bottle brush. Do not use solvents or abrasives to clean the gauge and do not wash the gauge in a dishwasher. Do not allow accumulated water to freeze in the gauge and avoid extremely rough usage.

Battery

The battery will last without requiring recharging through several storm events. If the pump grinds slowly, this is an indication that the battery requires recharging. We recommend fully recharging batteries approximately once per month. In addition, the battery should be recharged before any extended use. To recharge the battery, unfasten it from the control panel, slide it out of the carrying case, and unhook the cord from the battery terminals. Then, fasten the battery charger's disconnects onto the battery terminals and plug the charger into a wall socket. Full recharge will take about 12 hours. Additional batteries and battery chargers are available from Global Water (see Accessories section).



To recharge the battery, fasten the charger's disconnects onto the battery terminals and plug the charger into a wall socket.

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Troubleshooting

If your Global Water SS101 Stormwater Sampler does not seem to be functioning properly:

- Refer to the manual for proper setup, check all connections and power supplies. Manuals and additional technical information can be viewed on Global Water's web page (www.globalw.com).

- Call Global Water for technical support at (800) 876-1172 or (916) 638-3429 (many problems can be solved over the phone). You can also fax [(916) 638-3270] or e-mail (globalw@globalw.com) Global Water a detailed description of problems relating to your product.

- If your equipment needs to be returned to the factory for any reason, please call Global Water to obtain a RMA number (Return Material Authorization). Do not return items without a RMA number displayed clearly on the outside of the package.

- When contacting Global Water for technical support, please have the following information accessible:

  Product name and model number
  Unit serial number
  Purchase Order Number (if applicable)
  Global Water invoice number
  Detailed description of problems relating to the product

Global Water Warranty

Our goal is to provide you with the finest water instrumentation at a reasonable price. Our products are always fully supported and 100% guaranteed.

Global Water warrants that its products are free from defects in material and workmanship under normal use and service for a period of one year from date of shipment from factory. Global Water's obligations under this warranty are limited to, at Global Water's option: (i) replacing, or (ii) repairing any products determined to be defective. In no case shall Global Water's liability exceed the product's original purchase price. This warranty does not apply to any equipment that has been repaired or altered by anyone but Global Water, or which has been subjected to misuse, negligence, or accident. It is expressly agreed that this warranty will be in lieu of all warranties of fitness and in lieu of the warranty merchantability.

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Regulations Overview

Construction Site Storm Water Sampling:
Georgia's National Pollutant Discharge Elimination System (NPDES) Permit[1]

Georgia's Department of Natural Resources General Permit No. GAR100000 - Authorization to Discharge Under the National Pollutant Discharge Elimination System, Storm Water Discharges Associated with Construction Activity became effective August 1, 2000. The permit strongly encourages the use of automated water sampling equipment.

Although it can be used for a variety of applications, the Global Water SS101 Stormwater Sampler was specifically designed to meet Permit No. GAR100000's storm water sampling requirements. The Permit requires that storm water samples[2] be taken at construction sites between 5 and 250 acres, as well as at smaller sites that are part of a common development, within 45 minutes following either:

- the collection of a specified amount of rainfall after storm water runoff begins; or
- the beginning of storm water runoff after the collection of a specified amount of rainfall.

The Permit also requires that samples be taken at the following frequency[3]:

- the first rainfall event greater than or equal to 0.5 inches in 24 hours;
- any rainfall event greater than or equal to 1.0 inch in 24 hours (but only one 1.0 inch event per month needs to be sampled until final stabilization);
- any rainfall event greater than or over 2.0 inches in 24 hours until final stabilization;
- one rainfall event greater than or equal to 0.5 inches in 24 hours after final stabilization; and
- any rainfall event greater than or equal to 0.5 inches in 24 hour if Best Management Practices have not been properly designed, installed or maintained in accordance with the Permit.

In addition, rainfall must be measured and recorded once every 24 hours. The SS101 uses a rain gauge that was developed and is manufactured to United States Weather Bureau specifications.

To meet the Permit's sampling requirements, the Global Water SS101 uses two sensors to start an automatic sample: the rain sensor and the water sensor. The sensors can also be used to trigger samples independently. The rain sensor is positioned in a rain gauge and can trigger a sample at 0.5, 1.0, and 2.0 inch rainfall events. The water sensor is positioned in a storm water runoff channel where it will trigger a sample when runoff begins.

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[1] This information is presented for general application overview only and should not be considered a replacement for fully reading and understanding Permit No. GAR100000 -Authorization to Discharge Under the National Pollutant Discharge Elimination System, Storm Water Discharges Associated with Construction Activity.

[2] Storm water discharge sampling locations are identified for each site in a Comprehensive Monitoring Program, prepared and certified by a professional licensed by the State of Georgia.

[3] Based on average rainfall in Georgia, it appears that there will be about 12-18 qualifying rainfall events per year.

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Accessories

Part Name	Part Number	Unit
Removeable Battery	BAT003	Each
Battery Charger	GB011	Each
1 Gallon Glass Sample Bottle	GL066	Each
Bottle Cap/Float Switch	SS003	Each
Rain Gauge	SS005	Each
Pickup Hose	SS017	Per/ft.
Removeable Sample Pickup	SS025	Each
Norprene Peristaltic Pump Tubing	SS060	Each
Rain and Water Sensors with 15' Cable	SS063	Each
2.5 Gallon Plastic Sample Bottle	WS001	Each

Please contact Global Water or visit our website (www.globalw.com) for unit prices.

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Stormwater Sampler Rain Gauge Daily Log

1. Try to record precipitation each day at the same time.
2. Record precipitation to the nearest 1/100 of an inch. (.01, .31. 1.31, etc.)
3. If precipitation is less than .01, record "T" for Trace.
4. Use the remarks column to list any unusual weather.

	Jan.	Feb.	Mar.	Apr	May	June	July	Aug.	Sept	Oct.	Nov.	Dec.	Remarks
1													
2													
3													
4													
5													
6													
7													
8													
9													
10													
11													
12													
13													
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24													
25													
26													
27													
28													
29													
30													
31													
Total													

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APPENDIX N Groundwater Sampling Log

URS Corporation

GROUNDWATER SAMPLING FORM

Well No. _____

Well Type: ☐Monitor ☐Extraction

☐Other_____

Job Name _____

Job Number _____

Recorded by _____

Well Material: ☐PVC ☐St. Steel ☐Other _____

Date _____ Time_____

Sampled by _____

WELL PURGING

PURGE VOLUME

Casing Diameter (D in inches):

☐2-inch ☐4-inch ☐6-inch ☐Other_____

Total Depth of Well (TD in feet BTOC):_____

Water Leve Depth (WL in feet BTOC): _____

Number of Well Volumes to be Purged (# Vols)

☐ 3 ☐ 4 ☐ 5 ☐ 10 ☐ Other _____

PURGE METHOD

☐Bailer - Type:_____

☐Submersible ☐Centrifugal ☐Bladder; Pump No:_____

☐Other - Type: _____

PUMP INTAKE SETTING

☐Near Bottom ☐Near Top ☐Other _____

Depth in feet (BTOC): _____ Screen Interval in Feet (BTOC) from _____ to _____

PURGE VOLUME CALCULATION:

(---------- - ----------) x ----------^{2} x ---------- x 0.0408 = ---------- gallons

TD (feet) WL (feet) D (inches) # Vols Calculated Purge Volume

PURGE TIME

_____ Start _____ Stop _____ Elapsed

PURGE RATE

Initial _____ gpm Final _____ gpm

FIELD PARAMETER MEASUREMENT

Minutes Since Pruging Began	pH	Cond. (umhos/em)	☐° C T ☐° F	Other:_____

Minutes Since Pruging Began	pH	Cond. (umhos/em)	☐°C T ☐° F	Other:_____
Meter Nos.				

Observations During Purging (Well Condition, Turbidity, Color, Odor):_____

Discharge Water Disposal: ☐Sanitary Sewer ☐Storm Sewer ☐Drummed & retained on-site ☐Other _____

WELL SAMPLING

SAMPLING METHOD

☐ Bailer - Type: _____

☐Submersible ☐Centrifugal ☐Bladder; Pump No:____

☐Same as Above

☐Grab - Type: _____

☐Other- Type: _____

SAMPLING DISTRIBUTION

Sample Series: _____

Sample No.	Volume/Cont.	Analysis Requested	Preservatives	Lab	Comments

QUALITY CONTROL SAMPLES

Duplicate Samples

Type	Sample No.

Blank Samples

Type	Sample No.

Other Samples

Type	Sample No.