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DRAFT MEMORANDUM

To: Sean Sheldrake, EPA
David W. Charters, Ph.D., EPA

From: Jose Gomez-Eyles and Glenn Esler

Date: May 15, 2015

Subject: Passive Sampling Technical Memorandum

Project No.: C167-1509

This memorandum provides the framework for the evaluation of freely dissolved concentrations of certain chemicals of concern (COCs) in sediment porewater using polyethylene (PE) passive sampling devices at locations adjacent to the Arkema site in Portland, Oregon (Site). The primary objective of this assessment is to provide a line of evidence, in addition to those that will be provided by the benthic risk evaluation, to assess whether these COCs have the potential to cause or contribute to benthic invertebrate toxicity. The porewater evaluation will also provide preliminary data to inform future remedy selection and design and provide, in-part, pre-remedial baseline data.

A draft sediment sampling work plan (work plan) was submitted to the U.S. Environmental Protection Agency (EPA) on April 30, 2014. The work plan included an evaluation of certain COCs, consisting of DDX,¹ polychlorinated biphenyls (PCBs), and polychlorinated dibenzo-*p*-dioxins/furans (PCDD/F), in the porewater of surface sediments at the Site (Integral 2014). The information in this memorandum will be incorporated into the revised work plan, which will include general procedures for the laboratory and fieldwork that are discussed in this memorandum (e.g., navigation and positioning, passive sampler preparation, deployment, retrieval, and analysis).

¹Total of 2,4'- and 4,4'-dichloro-diphenyl-dichloroethane (DDD), dichloro-diphenyl-dichloroethene (DDE), and dichloro-diphenyl-trichloroethane (DDT).

BACKGROUND

Empirical benthic toxicity testing with benthic organisms was conducted as part of the Portland Harbor Round 2 and 3 investigations in 2005 and 2007. Toxicity was observed at several stations adjacent to the Site, but correlated poorly with COC concentrations (such as DDx) measured in surface sediments. Total concentrations of hydrophobic organic contaminants (HOCs) have generally been found to be poor predictors of benthic toxicity (USEPA 2012), as they do not provide a measure of the bioavailable contaminant fraction. Freely dissolved porewater concentrations of HOCs have been shown to have a stronger correlation with the bioavailable fraction, which in turn is more closely correlated with adverse impacts to benthos (USEPA 2012). Passive samplers can be used to determine the freely dissolved *in situ* COC concentrations.

DATA QUALITY OBJECTIVES

EPA's seven step data quality objective (DQO) process (USEPA 2006) was followed to systematically generate performance and acceptance criteria for data collected from the Site. Table 1 summarizes the DQOs following EPA's seven step process. The problem that initiated this evaluation (Step 1 of the DQO process) and goals of this study (Step 2 of the DQO process) are discussed below.

Problem Statement

As mentioned above, previous benthic toxicity studies of sediments conducted in 2005 and 2007 for the Portland Harbor Round 2 and 3 investigations (Integral et al. 2011) indicated locations of moderate to high toxicity in select areas of the Site, particularly in the vicinity of the Salt Dock (Figure 1). However, the observed toxicity correlated poorly with concentrations of DDx, PCBs, and PCDD/Fs in surface sediments (Figures 2, 3, and 4). As discussed above, total concentrations of HOCs in sediment are poor predictors of toxicity to benthic invertebrates (USEPA 2012). Differences occur in the bioavailability of HOCs in sediments because of alternate partitioning phases (e.g., black carbon) (USEPA 2012). The true bioavailable concentrations of an HOC can be reasonably estimated by determining the concentration of freely dissolved chemical in sediment porewater using passive samplers (USEPA 2012). This assumption does not imply that exposure occurs only from porewater, rather that the freely dissolved concentration of HOCs in porewater is a better surrogate than the bulk sediment HOC concentration for the bioavailable fraction (USEPA 2012).

As described in the Evaluation of Risk to Benthic Community memorandum (Benthic Risk Memorandum; Integral 2015), high salinity in areas surrounding the Salt Dock likely

affected benthic toxicity test measurements. As also noted in the Benthic Risk Memorandum (Integral 2015), there was a significant reduction in chloride concentrations in shallow groundwater near the salt pads between 2002 and 2009. This reduction occurred after the cessation of operations at the Site and removal of salt from the salt pads, but prior to the installation of the groundwater barrier wall (in 2012), so it is likely that dissolved salts flushing through the shallow groundwater affected the outcome of benthic toxicity testing in the 2005–2007 time frame.

Beginning in late 2012, an upland groundwater source control remedy was implemented that included the installation of a fully penetrating (to bedrock) groundwater barrier wall and a groundwater extraction and treatment system to maintain inward hydraulic gradient behind the wall (ERM 2013). This upland groundwater source control measure has likely mitigated the effects of dissolved salts in groundwater discharging at the bioassay study stations near the Salt Dock, although there may be some dissolved salt working its way through the system. Either way, it is unknown whether non-salt-related toxicity is also present at the stations near the Salt Dock. Dissolved salt influences on toxicity will be eliminated by procedures described in the benthic risk evaluation study, and thereby, freely dissolved COC porewater concentrations measured from the passive sampling study can then be compared to toxicity observed in the benthic bioassays as well as the results of toxicity identification evaluations (TIEs), if conducted.

Goals of the Study

The goals of this study are to:

1. Determine the freely dissolved concentrations of DDx, PCBs, and PCDD/F in surface sediment porewater
2. Compare these measurements with data from the Benthic Risk Evaluation to provide another line of evidence to assess causes of observed toxicity (if any)
3. Provide preliminary data to inform future remedy selection and design (e.g., conventional or reactive capping)
4. Provide some limited data to establish pre-remedial baseline conditions.

These goals are explained in further detail below, and summarized in Table 1 using EPA's seven step DQO process (USEPA 2006).

Additional Line of Evidence for Benthic Risk Evaluation

To meet the first and second goal, freely dissolved porewater concentrations of certain COCs will be measured using PE passive samplers and compared with results from co-

located benthic toxicity tests described in the Benthic Risk Memorandum (Integral 2015). This will provide an additional line of evidence to explain the potential cause of benthic toxicity (if any) observed in the 2015 sediment sampling study at the Site, supplementing information obtained from TIEs, if conducted.

Passive samplers provide an integrated measure of the freely dissolved porewater concentrations over the deployment period. As the fraction of HOCs in porewater is largely controlled by the unchanging sorptive characteristics of the native sediments, it is reasonable to assume any fluctuations in freely dissolved porewater concentrations will be minimal during the deployment period for the HOCs in the sediments. The upland source control measures, specifically the groundwater barrier wall (ERM 2013), will reduce any possible fluctuations in HOCs from groundwater discharge even further.

Future Remedy Selection and Design

To meet the third goal, porewater data obtained from the passive samplers will be used to inform remedy selection and design. As described in the RM11E sampling and analysis plan (SAP), porewater can be used to evaluate monitored natural recovery, the design thickness and efficacy of a conventional cap, the amendment dose of *in situ* treatment (e.g., activated carbon to sequester HOCs), and the relative risks of any remaining HOCs in post-dredging residuals (SEE et al. 2014).

Porewater data can be used to derive partitioning constants (i.e., sediment organic carbon–water partitioning coefficient [K_{oc}]), which can be used to inform models during remedial design (e.g., Reible Cap model). As described in the RM11E SAP, it can also be used to refine equilibrium partitioning models like the one used in the Draft Final Portland Harbor RI Report (Integral et al. 2011) to estimate flux from sediments into the overlying river water. These models usually incorporate generic K_{oc} values that do not provide an accurate representation of partitioning in most sediments (USEPA 2012). By combining bulk sediment HOC and total organic carbon concentrations obtained during the surface sediment chemistry investigation outlined in the work plan with co-located porewater data, K_{oc} will be derived at each passive sampling station.

We do not propose to measure freely dissolved concentrations in the overlying surface water in this study; although measuring such concentrations would enable a more complete parameterization of reactive cap models and better assess diffusive flux from sediments to the water column, it is outside the scope of this effort. Initially, these parameters will be conservatively assumed during remedy design, or if necessary, obtained in a targeted pre-remedial design investigation in the future.

Pre-remedial Site Baseline

To meet the fourth goal, porewater data collected from the passive samplers will be used as one component of a pre-remedial baseline dataset to be used as a reference to assess the effectiveness of the selected remedy at the Site. This will be particularly useful if a remedy aimed at reducing HOC bioavailability using amendments (e.g., activated carbon) is selected, as it will provide a measure of the freely dissolved concentrations of HOCs in the sediment before remedy implementation.

Study Design

For this evaluation, passive samplers will be deployed at 11 locations as shown in Figure 5. Duplicate samplers will be deployed at two locations (Stations SS-21 and SS-6). The duplicate stations were selected in areas with relatively low (Station SS-6) and elevated (Station SS-21) COC concentrations in surface sediment. After the retrieval of the passive samplers, sediment samples will be collected from co-located locations for the benthic toxicity testing and surface sediment chemistry. Sampling locations were co-located with those described in the Benthic Risk Memorandum (Integral 2015) to enable a correlation of porewater data with benthic toxicity responses and surface sediment chemistry under current conditions. The locations selected for benthic toxicity testing included a wide range of benthic responses and surface chemistry characteristics from previous studies to evaluate the correlation between HOC concentrations (primarily DDx) and observed toxicity.

Available surface chemistry data for DDx, PCBs, and PCDD/Fs is summarized in Figures 2 through 4. These data, along with the results of the 2005 and 2007 Round 2 and 3 toxicity tests, were used to guide the selection of locations for benthic toxicity tests and passive sampling. Much of the sampling will be conducted in the vicinity of Docks 1 and 2 because of the presence of relatively high HOC concentrations in these locations (Figures 2 through 4), and in the vicinity of the Salt Dock given the benthic toxicity observed in previous studies as described in the Benthic Risk Memo (Integral 2015). Additional details on the rationale for the location and number of stations is presented in the Benthic Risk Memorandum (Integral 2015).

PASSIVE SAMPLING APPROACH

As recommended by EPA, the passive sampling approach will largely follow the approach described in the RM11E SAP (SEE et al. 2014). General details on the field protocols are provided in the following sections, with the rationale for specific differences between the two approaches highlighted.

Sampler Impregnation

To infer freely dissolved porewater concentrations from concentrations in the passive samplers, it is necessary for the passive sampler to be at equilibrium with sediment porewater. Equilibrium is unlikely to occur for the more hydrophobic organic congeners and isomers. To overcome this problem, performance reference compounds (PRCs) will, therefore, be impregnated into the samplers to correct for nonequilibrium conditions (Apell and Gschwend 2014). PRCs will be impregnated into the PE using an 80:20 methanol-water solution in Maxxam's laboratory in Mississauga, Ontario (Canada). A Work Instruction of this procedure is included in Attachment 1. Three of these samplers will not be taken to the field and will serve as fabrication control blanks. As described in Attachment 1, fabrication control blanks will be extracted and analyzed in triplicate to confirm initial pre-deployment PRC loading concentrations. A list of the PRCs is included in Table 2. These PRCs were selected to cover a wide range of K_{ow} to correct for non-equilibrium conditions (Apell and Gschwend 2014).

Navigation and Diver Passive Sampler Deployment and Retrieval

The impregnated passive samplers will be mounted onto aluminum or steel sampling frames prior to deployment. Each frame will have strips of PRC-impregnated PE that are 30 cm tall by 10 cm wide. Divers will deploy the PE to a target depth of 30 cm below mudline² (bml), where they will be left to equilibrate with the sediment porewater for no less than 60 days.

General details on navigation are described in the 2009 EE/CA field sampling plan (Attachment 2) and are consistent with the equipment and procedures employed to obtain surface sediment samples for chemical analysis and benthic tests. This includes both horizontal and vertical measures of station position. The Standard Operating Procedure (SOP) for Diver-Placement and Retrieval of Passive Samplers developed for the RM11E SAP (Attachment 3) will be used with the following modifications:

1. The passive sampling device (PSD) assembly will be modified to only sample the sediment porewater; therefore, the deployment process will ensure the PE is fully inserted into the sediment to a target depth of 30 cm bml.
2. As site conditions are more amenable to passive sampler deployment than in the RM11E area, a reconnaissance survey is not necessary. However, two PSDs mounted with unimpregnated PE will be deployed and retrieved by the divers at

² The bottom of the sampler will be at 30 cm below mudline and the top of the sampler will be at mudline.

two different locations to ensure the field crew has a clear understanding of the procedures before deployment of the impregnated PSDs commences.

3. No sediment cores will be taken during passive sampler retrieval because a large volume of sediment will be needed for benthic toxicity tests and chemical analysis. A grab sample will therefore be obtained from the same location as the PSD using a power grab or similar sampler following PSD retrieval.
4. PSDs will be deployed in duplicate at only two locations because the risk of losing samplers at the Site is low relative to the RM11E area.

As specified in the Diver-Placement and Retrieval of Passive Samplers SOP, a Dive Operations Plan similar to the plan used in the 2014 RM11E investigation (Attachment 4) will be followed by the divers. After the PSDs are retrieved by the divers, the PE frame will be labeled, wrapped in clean aluminum foil, placed on ice, and transported to the Maxxam laboratory under chain-of-custody protocols.

Post-processing PE Samplers

Once delivered to the Maxxam laboratory, the passive samplers will be processed as described in the RM11E SAP (SEE et al. 2014). First, the sampler will be photographed, and then the PE will be removed from the frame. Next, the PE surface will be wiped and rinsed free of surface particles and coatings. This may include a brief (<1 minute) wiping with a hexane-soaked Kimwipe® (or equivalent) to remove oily or tarry exterior staining. If the PE surface remains wet, the PE surface will be blotted dry with a clean wipe. The strips will then be cut longitudinally into two 5 x 30 cm strips. Strips to be analyzed will be placed into labeled jars. Samples to be archived will be rewrapped in clean aluminum foil envelopes, labeled, rolled, and then inserted into a 1-L clean borosilicate jar. A separate sample label will be affixed to the outside of the jar and wrapped with tape. Each jar will be placed in a gallon Ziploc® bag and stored at -20 °C. The sample labels will note the sample ID, date of sampling, personnel processing the sample, and analyses to be run or archived. A small quantity of laboratory-grade deionized water will be placed into the passive sample jar to prevent dehydration of the polyethylene. The amount of laboratory-grade water added to the sample jar will be recorded by laboratory personnel.

ANALYTICAL PROCEDURES

The analytical procedures for the passive samplers have been developed at Maxxam following EPA methodology for high-resolution gas chromatography and high-resolution mass spectrometry with modifications made for passive sampling devices. The analytical parameters and associated Maxxam SOPs for the passive sampling devices are as follows:

- PCBs congeners by BRL SOP-00408/14 (EPA Methods 1668A/B equivalent)
- Organochlorine pesticides (DDx only) by BRL SOP-00415/5 (EPA 1699 equivalent)
- PCDD/Fs by BRL SOP-00406/12 (EPA Method 8290 equivalent)

The passive samples will be extracted as prescribed in Maxxam SOP BRL SOP-00409/5 (Attachment 5).

Laboratory QA/QC Procedures

There were a number of lessons learned from the analysis of the passive samplers for the RM11E investigation that will be used to enhance this study. The following specific measures will be taken as a result of the issues encountered in the RM11E investigation:

1. All samplers will be impregnated with the same concentration of PRCs to reduce the risk of cross-contamination between samplers.
2. Laboratory equipment will be appropriately decontaminated during sample processing to prevent cross-contamination. The selected laboratory (Maxxam) processes PRC impregnated samplers routinely and already has measures in place to eliminate this risk.
3. PRCs and internal standards will be introduced at the appropriate concentration to ensure analyte to standard ratios are in the optimum range of the calibration. Maxxam conducts this kind of analysis routinely and is, therefore, accustomed to adapting analyses to varying environmental concentrations of target analytes.
4. Method blank and field blank analyses will be scrutinized to assess any signs of sample contamination.
5. Archived samplers will be stored for reanalysis if analytical quality assurance and quality control (QA/QC) is not satisfactory.

QA/QC samples prepared in the laboratory will include method blanks, fabrication blanks, laboratory control spikes, and ongoing precision and recovery (OPR) standards. Details on laboratory QA/QC procedures are described in the following sections.

Method Blank

The purpose of analyzing a method blank (or low density PE [LDPE] blank in Attachment 1) is to demonstrate that the analytical procedures do not result in sample contamination from the laboratory solvents, reagents, or glassware used in processing the samples. The method blanks will consist of a clean strip of PE processed along with the

batch of environmental samples including all manipulations performed on actual samples. The method blank should be placed at the beginning of the analytical sequence (i.e., analyzed before the associated environmental samples). If the method blank concentrations exceed the concentration of the lowest calibration standard (for PCDD/F and DDx analysis) or the minimum levels reported in EPA Method 1668 (for PCB congener analysis), then the source of contamination should be corrected and the associated samples should be reanalyzed.

Fabrication Control Blanks

Fabrication control blanks are PE samplers fabricated concurrently with the field-deployed samplers and retained in storage in the laboratory until they are processed along with the field-deployed samplers. As well as being used to determine pre-deployment PRC concentrations, three fabrication control blanks will be used to account for interferences or contamination incurred from the passive sampler components, storage, processing, and analysis.

Laboratory Control Samples/Ongoing Precision and Recovery Standards

The purpose of analyzing laboratory control samples and OPRs is to demonstrate the accuracy of the analytical method. Laboratory control samples (LCSs) or OPRs will be analyzed at the rate of one per sample batch. LCSs and OPRs consist of laboratory-fortified method blanks. The LCS and OPR analytes and accuracy criteria are listed in Table 3. If the recovery is outside this range, then the analytical process is not being performed adequately for that analyte. If recovery is outside of the specified range, the sample batch must be reprocessed and the LCS or OPR reanalyzed.

Instrument level QC performed by the laboratory and the frequencies for these measures are presented in the applicable laboratory SOPs (Attachment 5).

Field QA/QC Samples

Field QA/QC samples will consist of field blanks and field duplicates. These QA/QC samples are briefly described in the following sections.

Field Blank

The purpose of a field blank is to demonstrate that transport to the field and ambient conditions in the field do not result in contamination of the environmental samples. The field blank will accompany the PSDs from the laboratory to the field, be briefly exposed to air in the field, wrapped in clean aluminum foil, placed on ice, and sent back to the

laboratory under chain-of-custody protocols. The field blank will then be stored in a freezer and analyzed with the remainder of the samplers when they are retrieved from the field.

Field Duplicates

Field duplicates will be deployed and collected at two locations. As discussed above, Stations SS-21 and SS-6 were selected for spatial and concentration variability.

Archived Samples

As previously described, upon receiving the samplers, the Maxxam laboratory will cut each sampler longitudinally and archive half of each strip at $-20\text{ }^{\circ}\text{C}$ in the freezer. Archived samples will be analyzed if:

- Blank contamination is reported
- Other laboratory QC results are obtained that would render the initial analysis suspect or unusable.

Integral will maintain close contact with Maxxam throughout the entire analytical process so any analytical or QC issues encountered are reviewed and addressed immediately to ensure the usability of the results.

Correcting for Nonequilibrium

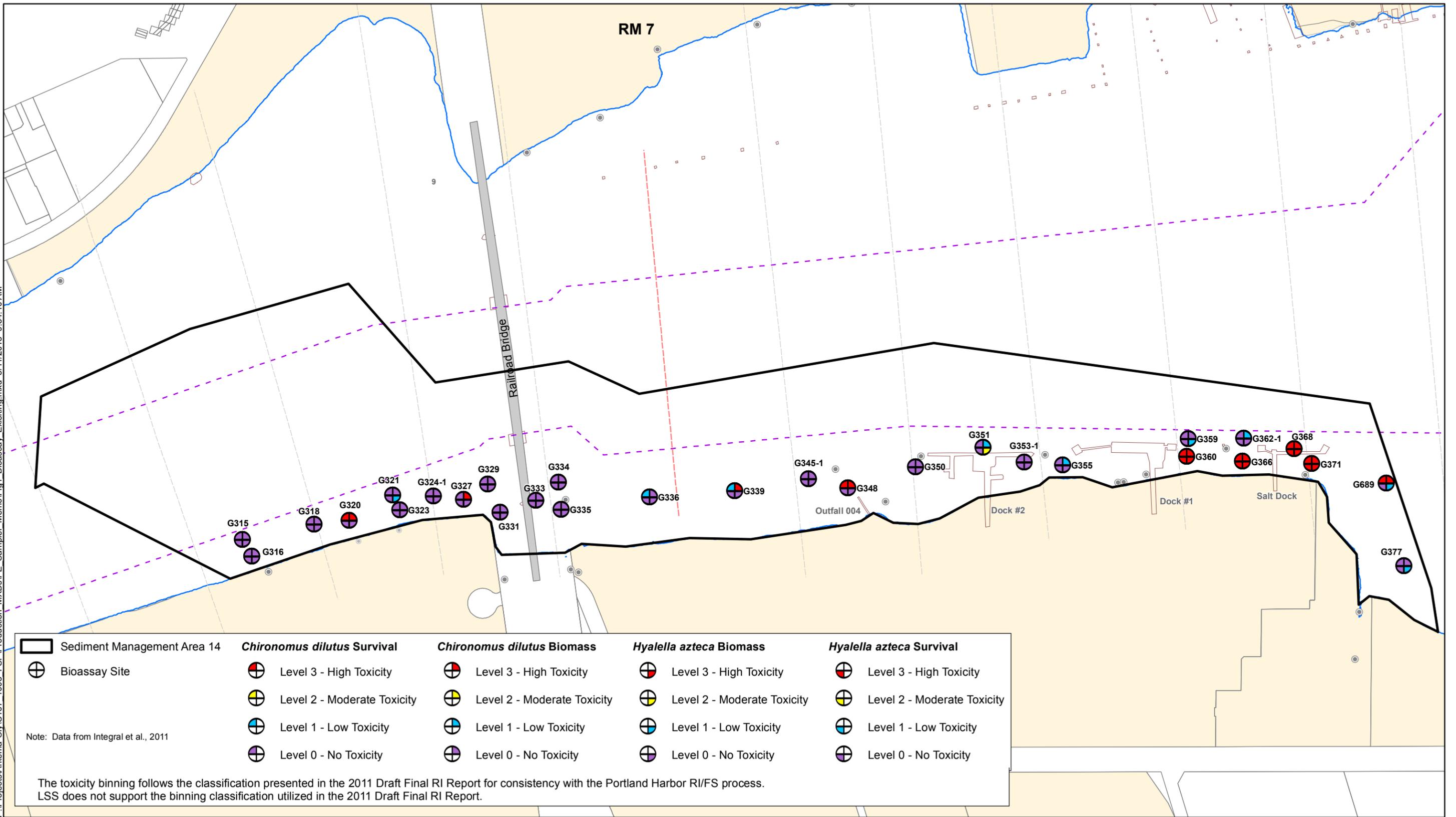
PRC concentrations remaining in the PE sampler after deployment will be used to infer the degree of equilibrium between the sampler and the sediment porewater. PRCs of varying hydrophobicities have been selected, because the rates of mass transfer into and out of the sampler will depend on the hydrophobic properties of each chemical. By calibrating the loss of each PRC against its K_{ow} , the corresponding approach to equilibration for each COC can be calculated. Equilibration will be estimated by plotting PRC loss against PRC K_{ow} and drawing a regression line to correct for non-equilibrium (Apell and Gschwend 2014). PRC corrections for nonequilibrium will be conducted using the graphical user interface developed by Gschwend et al. (2014): If more than 90 percent loss is observed for a PRC, then analytes with a K_{ow} lower than or equal to this PRC will be assumed to be at equilibrium with porewater in that sampler.

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FIGURES

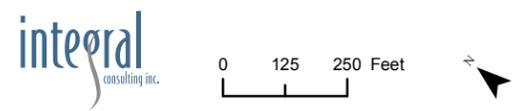
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	<i>Chironomus dilutus</i> Survival	<i>Chironomus dilutus</i> Biomass	<i>Hyalella azteca</i> Biomass	<i>Hyalella azteca</i> Survival
Level 3 - High Toxicity				
Level 2 - Moderate Toxicity				
Level 1 - Low Toxicity				
Level 0 - No Toxicity				

Note: Data from Integral et al., 2011

The toxicity binning follows the classification presented in the 2011 Draft Final RI Report for consistency with the Portland Harbor RI/FS process. LSS does not support the binning classification utilized in the 2011 Draft Final RI Report.



Map Features	
	River Miles
	Navigation Channel
	Docks and Structures
	Bridges
	River Edge 13 ft NAVD
	Upland ECSI Sites (2008)
	Outfall
	Dock Drain
	Roof Drain

Reference: Integral, Windward, Kennedy/Jenks, and Anchor. 2011. Portland Harbor RI/FS Remedial Investigation Report. Draft final. IC11-0001. Prepared for The Lower Willamette Group, Portland, OR. Integral Consulting Inc., Portland, OR; Windward Environmental LLC, Seattle, WA; Kennedy/Jenks Consultants, Portland, OR; and Anchor QEA, LLC, Seattle, WA. August 29, 2011.

Figure 1.
Existing Bioassay Data
Passive Sampling Technical Memorandum

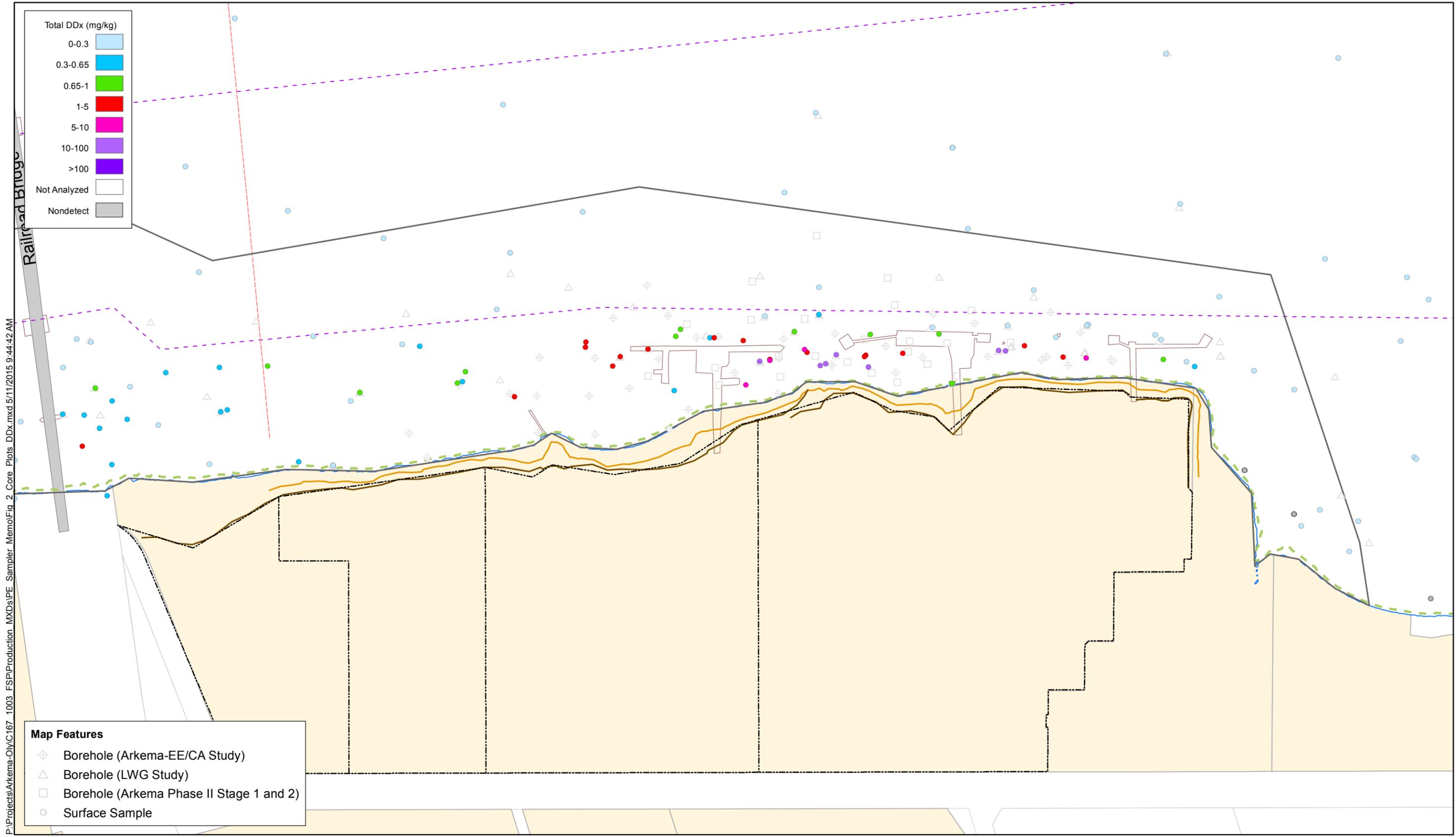
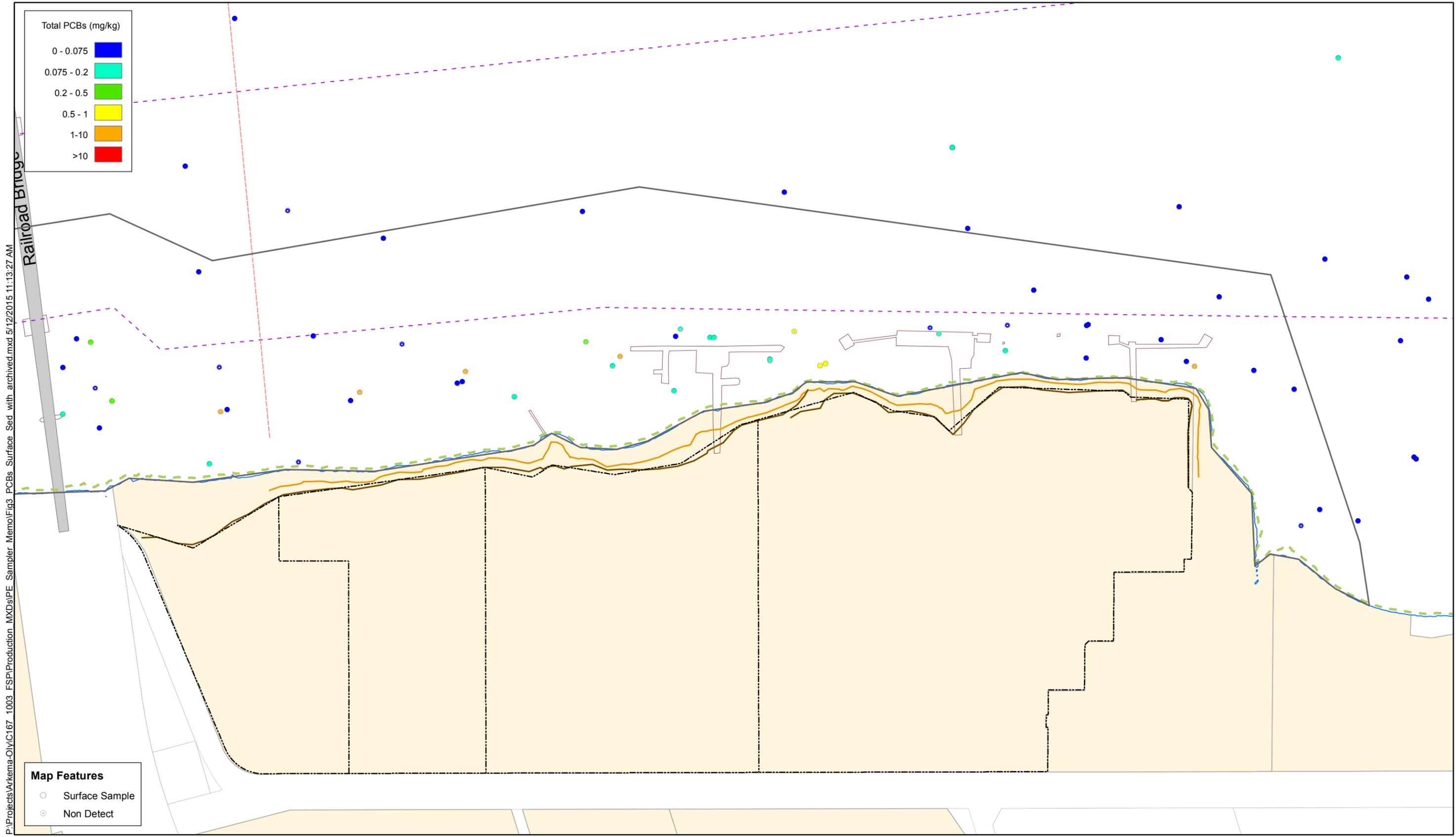


Figure 2.
 Existing DDX Surface Sediment Data
 Passive Sampling Technical Memorandum

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Railroad Bridge

Map Features

- Surface Sample
- Non Detect



Map Features

- Property and Lot Boundary
- Docks and Structures
- - - Navigation Channel
- - - 12 ft Contour
- Ordinary High Water
- Top of Bank
- Sediment Management Area 14

Notes:
 1. Total PCB Aroclors is the sum of all PCB congeners, or the sum of all PCB Aroclors if congeners are not present, using 1/2 the MDL for all undetected results.

Figure 3.
 Existing Total PCB Surface Sediment Data
 Passive Sampling Technical Memorandum

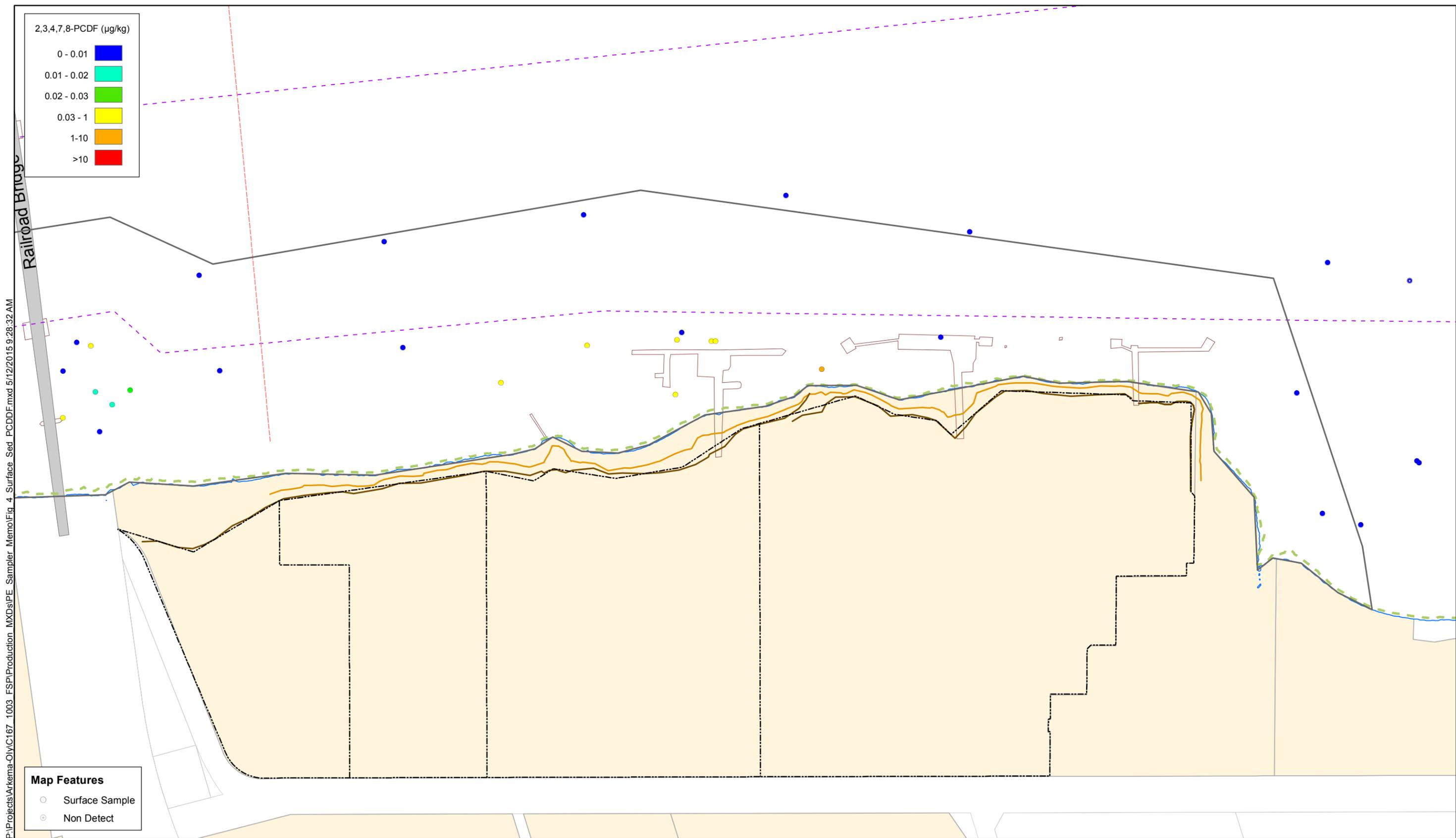


Figure 4.
 Existing 2,3,4,7,8-PCDF Surface Sediment Data
 Passive Sampling Technical Memorandum

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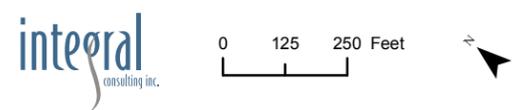
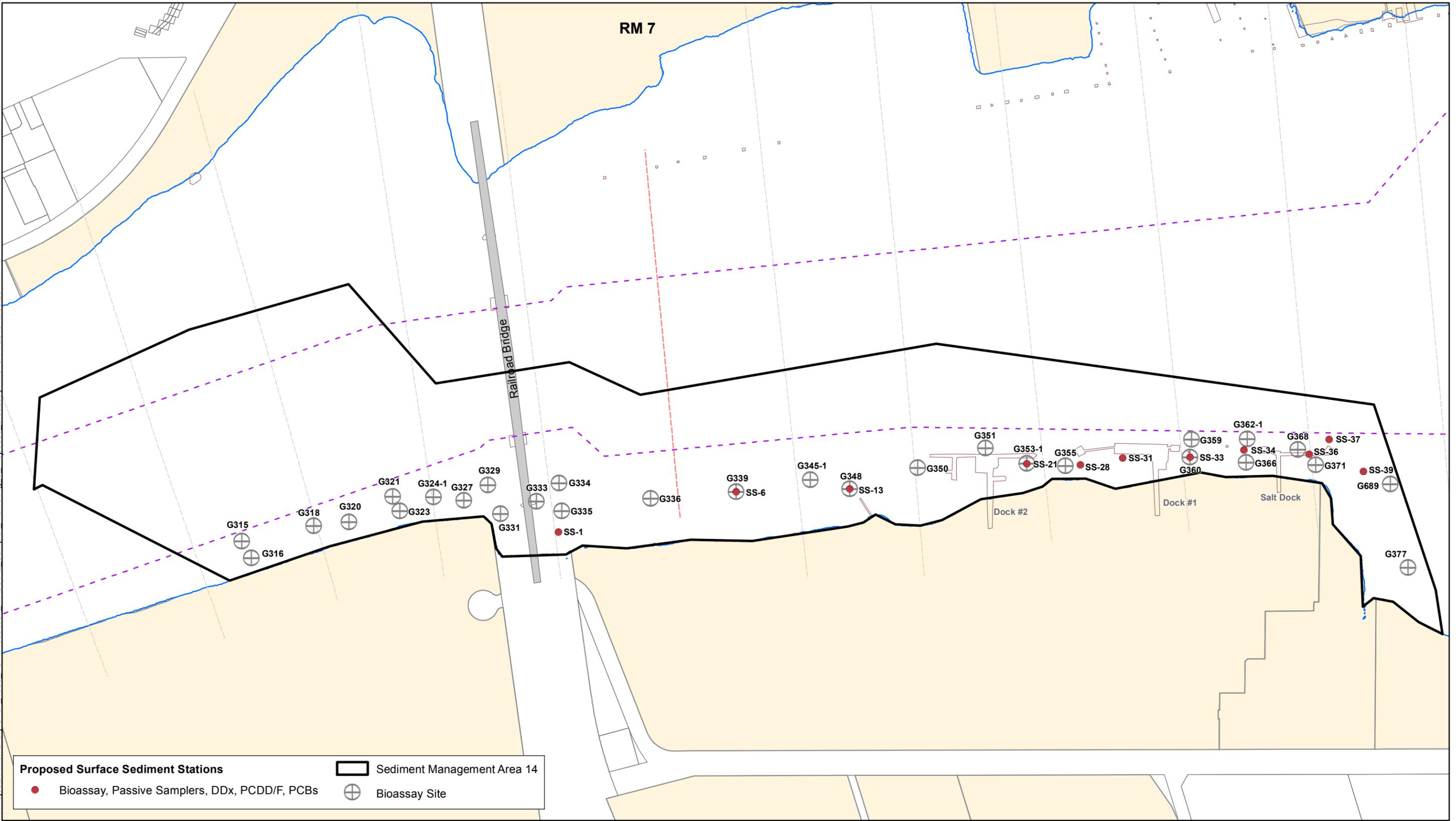


Figure 5.
Proposed Bioassay and Passive Sampler Locations
Passive Sampling Technical Memorandum

TABLES

Table 1. Data Quality Objectives to Evaluate Sediment Porewater Concentrations

DQO Step	Description
1. State the problem	<p>Empirical benthic toxicity testing with benthic organisms was conducted as part of the Portland Harbor Round 2 and 3 investigations (Figure 1). Toxicity was observed at several stations, but correlated poorly with COC concentrations (such as DDx) measured in surface sediments. Total concentrations of hydrophobic organic contaminants (HOCs) have generally been found to be poor predictors of benthic toxicity (USEPA 2012), as they do not provide a measure of the bioavailable contaminant fraction. Freely dissolved porewater concentrations of HOCs have been shown to correlate more strongly with the bioavailable fraction which in turn is the fraction that correlates well with adverse impacts to benthos (USEPA 2012). Passive samplers can be used to determine these freely dissolved concentrations in the field.</p> <p>Further evaluation of risk to the benthic community will be conducted (see the Evaluation of Risk to Benthic Community memorandum) to assess conditions following implementation of upland source control measures. Co-located passive samplers can provide an additional line of evidence to relate any observed toxicity to freely dissolved COC concentrations, as passive samplers provide an integrated measure of the freely dissolved porewater concentrations over the deployment period.</p> <p>Passive samplers will also provide data that will be useful during the pre-remedial design to (1) evaluate monitored natural recovery, (2) guide the design thickness and assess efficacy of a conventional cap, (3) evaluate the likely levels of <i>in situ</i> treatment (e.g., activated carbon to sequester HOCs), and (4) assess the relative risks of any remaining HOCs in post-dredging residuals. The study will also provide some pre-remedy baseline data that will be useful for assessing remedy effectiveness in the future.</p>
2. Identify the goals of the study	<p>This study has the following goals:</p> <ol style="list-style-type: none"> 1) Determine the freely dissolved concentrations of DDx, PCBs, and PCDD/F in surface sediment porewater 2) Compare these measurements with data from the Benthic Risk Evaluation to provide another line of evidence to assess causes of observed toxicity 3) Provide preliminary data to inform future remedy selection and design (pre-remedial design) 4) Provide some limited data to establish pre-remedial baseline conditions.
3. Identify information inputs	<ol style="list-style-type: none"> 1) Surface sediment analytical data (DDx, PCBs, PCDD/Fs, grain size, and TOC) (sampling and analytical method details are included in the work plan) 2) Freely dissolved porewater concentrations of DDx, PCBs, and PCDD/Fs. Nonequilibrium conditions between the sediment porewater and the passive sampler will be corrected by impregnating the samplers with PRCs and quantifying their loss during deployment. Analytical methods will follow laboratory SOPs. 3) Benthic toxicity data (see Evaluation of Risk to Benthic Community memorandum [Integral 2015])
4. Define the boundaries of the study	<p>The study area is located within Sediment Management Area (SMA) 14 between River Miles 6.8 and 7.6 of the Willamette River in Portland, Oregon. More specifically, the study area is bounded by the navigation channel to the east, the shoreline to the west, the railroad bridge to the north, and the boundary of SMA 14 to the south.</p> <p>Passive samplers will be co-located with benthic toxicity stations. The passive samplers will be deployed and after no less than 60 days, the samplers will be retrieved and a surface sediment sample will be collected for the analysis of bulk sediment chemistry and benthic toxicity. The passive samplers will be deployed in the surface sediment (0–30 cm below mudline).</p>

Table 1. Data Quality Objectives to Evaluate Sediment Porewater Concentrations

DQO Step	Description
5. Develop the analytic approach	<p>Deploy passive samplers to measure freely dissolved porewater concentrations of COCs (particularly DDX). Data from this effort will be compared to benthic toxicity and toxicity identification evaluation (TIE) test results as an additional line of evidence for assessing the cause of toxicity, if observed, in benthic toxicity tests. If there is a statistically significant positive correlation between certain COC porewater concentrations and toxicity, then data will be indicative of a toxic effect caused by that particular COC or group of COCs. If there is no statistically significant positive correlation between COC porewater concentrations and toxicity, then data will be indicative of a toxic effect caused by a factor other than these COCs, which may be identified by TIEs.</p> <p>In addition, if passive sampler data are deemed useful, the data will be utilized in remedy pre-design and to assist in establishing baseline conditions, as described above.</p>
6. Specify performance or acceptable criteria	<p>Passive samplers will be deployed and retrieved after at least 60 days as described in the Diver-Placement and Retrieval of Passive Samplers SOP (Attachment 3), with the modifications described in the text of this memorandum. Passive samplers will then be analyzed for DDX, PCB congeners, and PCDD/F by Maxxam Analytical SOPs. Laboratory control samples (LCSs) or ongoing precision and recovery standards (OPRs) will be analyzed at the rate of one per sample batch. LCSs and OPRs consist of laboratory-fortified method blanks. The LCS and OPR analytes and accuracy criteria are listed in Table 3. If the recovery is outside this range, then the analytical process is not being performed adequately for that analyte. If recovery is outside of the specified range, the sample batch must be reprocessed and the LCS or OPR reanalyzed. Given analytical issues encountered in similar porewater sampling studies, laboratory blanks, fabrication control blanks, and field blanks will be carefully examined. If blank concentrations exceed the concentration of the lowest calibration standard (for TCDD/DF and/or DDX analysis) or the minimum levels reported in EPA Method 1668 (for PCB congener analysis), then the source of contamination will be corrected, and the associated samples will be reanalyzed.</p> <p>Because the freely dissolved fraction is largely controlled by the unchanging sorptive characteristics of the native sediments, it is reasonable to assume any fluctuations in freely dissolved porewater concentrations will be minimal during the deployment period for the HOCs in the sediments. The upland source control measures, specifically the groundwater barrier wall, will reduce any possible fluctuations even further. However, despite the long deployment time (i.e., 60 days or longer), it is likely that many of the more hydrophobic congeners and isomers freely dissolved within the sediment porewater will not be at equilibrium with the passive sampler itself. PRCs will therefore be impregnated into all the samplers to enable correction for nonequilibrium conditions. PRCs covering a wide range of K_{OW} values have been selected to ensure these corrections are possible for all DDX, PCBs, and PCDD/F analytes (Table 3). PRC loss will be plotted against PRC K_{OW} and a regression line will be drawn to correct for nonequilibrium (Apell and Gschwend 2014). PRC corrections for nonequilibrium will be conducted using the graphical user interface developed by Gschwend et al. (2014). If more than 90 percent loss is observed for a PRC, then analytes with a K_{OW} lower than or equal to this PRC will be assumed to be at equilibrium with porewater in that sampler.</p>

Table 1. Data Quality Objectives to Evaluate Sediment Porewater Concentrations

DQO Step	Description
7. Develop the plan for obtaining data	<p>Passive samplers will be impregnated with PRCs as described in the Passive Sampler Preparation SOP (Attachment 1), deployed in surface sediments (0–30 cm below mudline) for at least 60 days, and retrieved as described in the Diver-Placement and Retrieval of Passive Samplers SOP (Attachment 3). The samplers will then be analyzed for DDx, PCBs, and PCDD/Fs. PRC concentrations remaining in the sampler will be used to correct for nonequilibrium conditions. The location and respective rationale for each sampling station is explained in the Benthic Risk Memo (Integral 2015). Briefly, these locations were selected for the following reasons:</p> <ul style="list-style-type: none"> • Assess current benthic toxicity conditions in the vicinity of stations where moderate to high toxicity were observed from previous studies • Assess relationship between toxicity and concentrations of COCs • Assess impacts of salts on toxicity or cause of toxicity in sediment near the Salt Dock • Refine the footprint of the benthic toxicity based on current conditions.

Notes:

DDx = total of 2,4'- and 4,4'-DDD, DDE, and DDT

DQO = data quality objective

EPA = U.S. Environmental Protection Agency

K_{OW} = octanol to water partition coefficient

PCB = polychlorinated biphenyl

PCDD/F = polychlorinated dibenzo-*p*-dioxin/furan

PRC = performance reference compound

QAPP = quality assurance project plan

QA/QC = quality assurance/quality control

Table 2. Performance Reference Compounds

DDx Pesticides

2,4'-DDD 13C12
2,4'-DDE 13C12

PCB Congeners

13C-PCB 32
13C-PCB 70
13C-PCB 127
13C-PCB 128
13C-PCB 170

Polychlorinated Dioxins and Furans

2,3,7,8-TCDD-37CL4
2,3,4,7,8-PeCDF-13C12
1,2,3,4,7,8-HxCDD-13C12
1,2,3,4,7,8-HxCDF-13C12
1,2,3,4,7,8,9-HpCDF-13C12

Notes:

DDE = dichlorodiphenyldichloroethylene
DDD = dichlorodiphenyldichloroethane
HpCDF = heptachlorodibenzofuran
HxCDD = hexachlorodibenzo-*p*-dioxin
HxCDF = hexachlorodibenzo-*p*-dioxin
PeCDF = pentachlorodibenzo-*p*-dioxin
PCB = polychlorinated biphenyl
TCDD = 2,3,7,8-tetrachlorodibenzo-*p*-dioxin

Table 3. Laboratory Control Limits for Matrix Spike and Laboratory Control Samples for Passive Sampler Devices

Analyte	Accuracy		Precision	
	Matrix Spike Recovery (percent)	LCS Recovery (percent)	Type of Duplicate	Control Limit RPD
Organochlorine Pesticides				
2,4'-DDD	40-200	40-200	LD	25
2,4'-DDE	40-200	40-200	LD	25
2,4'-DDT	40-200	40-200	LD	25
4,4'-DDD	40-200	40-200	LD	25
4,4'-DDE	40-200	40-200	LD	25
4,4'-DDT	40-200	40-200	LD	25
PCB Congeners				
PCB 1	50-150	50-150	LD	30
PCB 3	50-150	50-150	LD	30
PCB 4	50-150	50-150	LD	30
PCB 15	50-150	50-150	LD	30
PCB 19	50-150	50-150	LD	30
PCB 37	50-150	50-150	LD	30
PCB 54	50-150	50-150	LD	30
PCB 77- WHO 12	50-150	50-150	LD	30
PCB 81 - WHO 12	50-150	50-150	LD	30
PCB 104	50-150	50-150	LD	30
PCB 105 - WHO 12	50-150	50-150	LD	30
PCB 114 - WHO 12	50-150	50-150	LD	30
PCB 118	50-150	50-150	LD	30
PCB 123 - WHO 12	50-150	50-150	LD	30
PCB 126 - WHO 12	50-150	50-150	LD	30
PCB 155	50-150	50-150	LD	30
PCB 156 - WHO 12	50-150	50-150	LD	30
PCB 157 - WHO 12	50-150	50-150	LD	30
PCB 167 - WHO 12	50-150	50-150	LD	30
PCB 169	50-150	50-150	LD	30
PCB 170	50-150	50-150	LD	30
PCB 188	50-150	50-150	LD	30
PCB 189 - WHO 12	50-150	50-150	LD	30
PCB 202	50-150	50-150	LD	30
PCB 205	50-150	50-150	LD	30
PCB 206	50-150	50-150	LD	30
PCB 208	50-150	50-150	LD	30
PCB 209	50-150	50-150	LD	30
PCB Internal Standards				
PCB 1L	15-150	15-140	LD	30
PCB 3L	15-150	15-140	LD	30
PCB 4L	50-150	30-140	LD	30
PCB 15L	50-150	30-140	LD	30
PCB 19L	50-150	30-140	LD	30
PCB 37L	50-150	30-140	LD	30
PCB 54L	50-150	30-140	LD	30
PCB 77L - WHO 12	50-150	30-140	LD	30
PCB 81L - WHO 12	50-150	30-140	LD	30
PCB 104L	50-150	30-140	LD	30
PCB 105L - WHO 12	50-150	30-140	LD	30
PCB 114L - WHO 12	50-150	30-140	LD	30
PCB 118L	50-150	30-140	LD	30

Table 3. Laboratory Control Limits for Matrix Spike and Laboratory Control Samples for Passive Sampler Devices

Analyte	Accuracy		Precision	
	Matrix Spike Recovery (percent)	LCS Recovery (percent)	Type of Duplicate	Control Limit RPD
PCB 123L - WHO 12	50-150	30-140	LD	30
PCB 126L - WHO 12	50-150	30-140	LD	30
PCB 155L	50-150	30-140	LD	30
PCB 156L - WHO 12	50-150	30-140	LD	30
PCB 157L - WHO 12	50-150	30-140	LD	30
PCB 167L - WHO 12	50-150	30-140	LD	30
PCB 169L	50-150	30-140	LD	30
PCB 170L	50-150	30-140	LD	30
PCB 188L	50-150	30-140	LD	30
PCB 189L - WHO 12	50-150	30-140	LD	30
PCB 202L	50-150	30-140	LD	30
PCB 205L	50-150	30-140	LD	30
PCB 206L	50-150	30-140	LD	30
PCB 208L	50-150	30-140	LD	30
PCB 209L	50-150	30-140	LD	30
PCB 28L Cleanup Standard	50-150	40-125	LD	30
PCB 111L Cleanup Standard	50-150	40-125	LD	30
PCB 178L Cleanup Standard	50-150	40-125	LD	30
Polychlorinated Dioxins and Furans				
2,3,7,8-TCDD	80-140	80-140	LD	25
2,3,7,8-TCDF	80-140	80-140	LD	25
1,2,3,7,8-PeCDD	80-140	80-140	LD	25
1,2,3,7,8-PeCDF	80-140	80-140	LD	25
2,3,4,7,8-PeCDF	80-140	80-140	LD	25
1,2,3,4,7,8-HxCDD	80-140	80-140	LD	25
1,2,3,6,7,8-HxCDD	80-140	80-140	LD	25
1,2,3,7,8,9-HxCDD	80-140	80-140	LD	25
1,2,3,4,7,8-HxCDF	80-140	80-140	LD	25
1,2,3,6,7,8-HxCDF	80-140	80-140	LD	25
1,2,3,7,8,9-HxCDF	80-140	80-140	LD	25
2,3,4,6,7,8-HxCDF	80-140	80-140	LD	25
1,2,3,4,6,7,8-HpCDD	80-140	80-140	LD	25
1,2,3,4,6,7,8-HpCDF	80-140	80-140	LD	25
1,2,3,4,7,8,9-HpCDF	80-140	80-140	LD	25
OCDD	80-140	80-140	LD	25
OCDF	80-140	80-140	LD	25

Notes:

Control limits are updated periodically by the laboratories. Control limits that are in effect at the laboratory at the time of analysis will be used for sample analysis and data validation. These may differ slightly from the control limits shown in this table.

LCS = laboratory control sample
MSD = matrix spike duplicate
NA = not applicable
PCB = polychlorinated biphenyl
RPD = relative percent difference

ATTACHMENT 1

PRC IMPREGNATION WORK

INSTRUCTION

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Campobello

Preparation of LDPE film for passive sampling and loading of PRCs

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Preparation of LDPE film for passive sampling and loading of performance reference compounds (PRC)

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1. Introduction:

Low Density Polyethylene (LDPE) films may be used as passive samplers to estimate the time-weighted average free concentration of lipophilic semi-volatile organic compounds such as PAHs and PCBs in water.

The mechanism of sampling is based on the passive accumulation of the target compounds into the polymer. Small hydrophobic organic compounds dissolved in water diffuse into the LDPE membrane due to the driving force of the partition of the target compounds between the water and the LDPE.

LDPEs are low-density polyethylene films; these may be cut into various shapes according to the needs of the site to be sampled. Disks or rectangular strips are commonly used.

Prior to deployment, the passive samplers need to be first cleaned thoroughly to remove contaminants that can interfere with the analysis or the operation of the analytical instrument. Typically cleaned films are subsequently loaded with Performance Reference Compounds (PRCs). PRCs are, typically, isotopically labeled compounds similar to the target compounds. By measuring the loss of PRCs during deployment of the passive sampler, site-specific environmental factors such as water flow and photolysis degradation are taken into account and used to get a more accurate estimation of the concentration in water. After loading the PRCs, the LDPE films may be stored frozen until they are required for deployment in water.

2. Scope:

This WI covers the preparation (cleaning and PRC-loading) of LDPE passive samplers prior to their submission to the client for deployment. The extraction and analysis of deployed passive samplers are described in a separate SOP specific to the analytical method required.

LDPEs are cleaned up by sequential extraction with different solvents and distilled water. After cleaning, LDPEs are loaded with the PRCs by incubation for a minimum of 48 hr in a methanolic solution.

Depending on the needs of the deployment or the client films may be subjected to a final rinse in water to remove traces of methanol from the film.

Cleaned films are stored either together or separately in pre-cleaned aluminum foil and sealed zipper lock bags. Films are maintained at < 15 °C prior to shipment to the client for deployment. It is important to ensure films are stored separately from any potential sources of volatile contaminants as the films will readily absorb such contaminants from the air.

3. Definitions:

Note: A list with the most common definitions used in Maxxam is compiled in COR WI-00012

Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

Analyte: A target analyte is an environmental compound that is being measured in a chemical test. It is now called the measurand.

Calibration: Operation that, under specified conditions, in a first step, establishes a relation between the quantity values with measurement uncertainties provided by measurement standards and corresponding indications with associated measurement uncertainties and, in a second step, uses this information to establish a relation for obtaining a measurement result from an indication(JCGM/WG2, 2008).

Duplicates: Two separate passive sampler devices deployed at the exact same location and analysed separately using identical procedures.

Fabrication Control: Fabrication Controls occasionally are referred to as Day 0 (zero) Blanks. They are fabricated concurrently with the field-deployed samplers and retained in storage in the lab until they are processed along with the field-deployed samplers. Fabrication Controls account for interferences or contamination incurred from the passive sampler components (i.e. LDPE, triolein...), storage, processing and analysis. Where appropriate, Fabrication Controls are spiked with the PRCs similarly to the field-deployed samplers.

Field or Trip Blank: passive sampler used to record any compound interference accumulated in the passive samplers during assembly, storage, transportation, deployment, retrieval and subsequent analysis. Field or Trip Blanks results are used to assess contamination from other sources than the actual water matrix and can be used for background correction to estimate water concentrations. They are transported along with the field-deployed samplers. Trip blanks remain sealed in their shipping containers for the duration. Field Blanks (Field controls) are opened to the atmosphere at each site for the same amount of time in in the same way during both deployment and retrieval but otherwise treated similarly to Trip Blanks.

Holding Time: Elapsed time between sample collection and either sample preparation or analysis, as appropriate. While exceeding the holding time does not necessarily negate the veracity of analytical results, it causes the qualifying or 'flagging' of any data not meeting all of the specified acceptance criteria.

LDPE Blank: Pre-cleaned LDPE passive sampler without PRCs that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples.

Method Detection Limit (MDL): It can also be called Detection Limit (DL). It is defined by US EPA as the minimum concentration of a measurand that can be identified, measured and reported with 99% confidence that is greater than zero; it is determined from analysis of a sample in a given matrix containing the measurand.

Precision: Closeness of agreement between indications or measured quantity values obtained by replicate measurements on the same or similar objects under specified conditions (JCGM/WG2, 2008). It is typically computed as a standard deviation of the test results.

Performance Reference Compounds (PRCs): Deuterated or ¹³C-labeled analogs of the target compounds, spiked into the passive samplers prior to deployment. Loss of PRCs during deployment is used to determine kinetic parameters controlling uptake of target compounds during deployment (not covered by this SOP).

Recovery Control (Spiked LDPE): Quality control LDPE passive sampler, fabricated concurrently with the field deployed samplers and retained in storage in the laboratory until processed along with the field samplers. Recovery Control is pre-spiked with a known mass of analytical standard and used to determine the recovery level of pollutant from passive sampling devices. The Recovery Controls should also be spiked with the PRCs where appropriate.

Reporting Detection Limit (RDL): The lowest concentration that will be reported for a specific method. Typically, the RDL is approximately 10 times the MDL/LOD.

Sensitivity: The capability of an analytical procedure to reliably discriminate between samples having differing concentrations or containing differing amounts of an analyte (NIST260-100, 1993).

Surrogate: A chemical with characteristics similar to those of measurand. Provides analytical response which is distinct from the measurand and not subject to interference. Added to sample prior to sample preparation. Used to assess recovery of measurand.

4. Safety:

General Safety requirements for this WI are provided in the attached critical task analysis (CTA). In addition to the CTA, additional guidance on Maxxam's Environment, Health and Safety (EHS) program is found in various Safe Work Procedures, Safety Policies, and the Corporate Environmental, Health and

Safety Guide (MEHS WI-00013). It is responsibility of the analyst to read and understand the CTA and all corporate SOPs and WIs related with Health and Safety as well as to follow the procedures there described.

The use of personal protective equipment (PPE) is mandatory in all Maxxam labs. It is responsibility of the analyst to ensure that any additional identified hazard controls are used (e.g. nitrile gloves, splash goggles, fume hoods, respirators, etc.).

The toxicity of PRCs (deuterated or ¹³C labeled analogs of target analytes: PAHs, PCBs, DDX, Dioxins, Furans etc.) varies from non-toxic to extremely toxic from compound to compound and it includes carcinogenic and mutagenic effects as well as immunosuppression. Therefore, the exposure to these chemicals should be kept at minimal and the sample preparation should be performed in a fume hood.

Similarly, organic solvents and other reagents used in this WI are potentially toxic and the exposure to them should be kept at minimum.

MSDS for all chemical reagents are available to personnel using this method. Training on the interpretation of MSDS sheets is provided during WHMIS training upon hire. Staff performing this method shall review the associated MSDS sheets for chemicals used in this procedure and ensure they understand the associated hazards and safety controls required to work safely with each chemical.

5. Waste Management:

Disposal of all samples, extracts and reagents must be done in accordance with local, provincial and federal laws and regulations. Waste management, including identification, transport, storage, disposal, etc. must also be done in accordance with Corporate Maxxam's SOPs and WIs:

- MEHS WI-00069: Environmental Waste Management Policy
- CAM SOP-00101: Waste Identification, Registration and Transport
- CAM WI-00018: Waste Disposal

All solvents, reagents and solutions are collected in appropriate disposal containers and stored in the fume hood until final disposal in the waste room.

- Expired standards: disposal in Non-Halogenated Solvent waste drums
- Non-halogenated solvents: disposal in Non-Halogenated Solvent waste drums
- Halogenated solvent: disposal in Mixed-Halogenated Solvent waste drums

6. Storage and shipment conditions:

General guidelines:

- Laboratory and field personnel should wear nitrile or latex gloves whenever handling passive samplers to avoid cross-contamination. Clean forceps should be used for all transfers of cleaned films.
- Passive samplers should not be stored in proximity to other chemicals, particularly volatile chemicals, to avoid cross-contamination.
- LDPE samplers should be wrapped with tissue paper and aluminium foil and placed in a zipper plastic bag.
- Samplers should be stored at minimum of 1-6 °C during shipment and transportation.

6.1 *Storage before deployment*

LDPE passive samplers prepared in the lab (pre-cleaned and/or pre-loaded with PRCs) should be wrapped with tissue paper and aluminium foil, placed in a zipper plastic bag and stored at a maximum temperature of -15 °C for long-term storage. Holding time for non-PRC loaded pre-cleaned LDPE films is indefinite. Holding time for PRC-loaded LDPE films is 1 year.

7. **Glassware Cleaning:**

Follow CAM SOP-00302 Glassware Washing - Trace Organic Department for the general cleaning protocol of laboratory glassware for LDPE films to be processed in the main operations lab. Follow BRL SOP-00006 Air HRMS – ING – SVOC – VOC Labs Glassware Washing for the general cleaning protocol of laboratory glassware for LDPE films to be processed in the HRMS lab.

8. **Apparatus and Materials:**

8.1 *General Labware*

- Class A Volumetric glassware (10mL, 100mL, 200mL, 500mL, 1L) as required for the preparation of PRC solutions and reagents volume measurement
- Hamilton micro syringes, glass air tight (10µL, 25µL, 50µL 100µL, 250µL, 500µL, 1000µL) as required for the preparation of standards, PRC solutions, reagents and spikes volume measurements
- Kimwipes tissue paper
- Stainless steel tongs, pre-cleaned with hexane or methylene chloride
- Bottletop dispensers (various sizes)
- 1L amber glass bottle
- 1L wide mouth glass jars
- Aluminum foil (rinsed or wiped with hexane)
- Zipper plastic bag
- Other suitable labware/suppliers might be necessary

8.2 Apparatus

- Tumbler
- Reciprocal Shaking Water Bath
- Analytical Balance, accurate to 0.0001 g

9. Reagents and standard preparation:

- Dichloromethane, Optima grade (Fisher # D151-4)
- n-Hexane, Optima grade (Fisher # H306-4)
- RODI water, *in-house*
- Methanol, Optima grade (Fisher # A454-4)

10. Preparation of the passive samplers:

10.1 Preparation of LDPEs for deployment: cleaning and PRC loading

- a. Cut samplers from commercial LDPE sheeting at the desired thickness, into the desired dimensions.

Note: LDPE devices are typically cut into discs, squares, rectangles or strips as specified by the client or the deployment conditions.

- b. Place LDPE-s in a 1L amber glass bottle, add DCM until the discs are completely covered, cap the bottle, put the bottle into a tumbler, tumble for 2 hours at 30-60 rpm, discard the DCM.
- c. Add n-Hexane until the discs are completely covered, cap the bottle, put the bottle into a tumbler and tumble for 2 hours at 30-60 rpm, discard the n-Hexane.
- d. Place LDPE-s in the same 1L amber glass bottle, add Methanol until the discs are completely covered, cap the bottle, put the bottle into a tumbler, tumble for 2 hours at 30-60 rpm, discard the Methanol.
- e. Place LDPE-s in the same 1L amber glass bottle, add RODI water until the discs are completely covered, cap the bottle, put the bottle into a tumbler, tumble for 2 hours at 30-60 rpm, discard the RODI water.
- f. Remove LDPE-s from the bottle and wipe them with a tissue paper.
- g. PRC-solution: Prepare the desired volume (typically 800 mL) of Methanol/RODI water mixture- 80/20 (v/v) in 1L wide mouth glass jars and add the appropriate amount of each of PRC spiking solution using a syringe.
The PRC spiking solution is prepared according to the recommendation of Booij, K et al. 2002, Chemosphere. The actual amounts of PRCs and volume(s) of methanolic solution used should be recorded in the worksheet associated with the LDPE lot.
- h. Soak pre-cleaned LDPE-s in PRC solution and place the jars in Reciprocal Shaking Water Bath for a minimum of 2 days at room temperature, 30-40 rpm, or until it is confirmed that sufficient PRC has been loaded into the films.

- At the conclusion of the target PRC loading time one of the laboratory QC films is removed from the loading solution and a sufficient mass of LDPE is cut out to allow for an extracted amount of about 10x RDL after analysis of the film by the appropriate analytical technique. The films remain in the PRC loading solution (without shaking) pending laboratory confirmation that the PRC loading level is >80% of the target. Steps (i) and (j) continue after laboratory confirmation is obtained.
- i. If requested by the client the LDPE-s may be placed in a 1L amber glass bottle with sufficient RODI water until the discs are completely covered, cap the bottle, put the bottle into a tumbler, tumble for 1 hour at 30-60 rpm, to eliminate final traces of methanol from the sorbent. Discard the RODI water.
- j. Remove LDPE-s from the solution and wipe them with a paper tissue.
- k. Wrap LDPE-s in tissue paper and aluminum foil, place inside a zipper plastic bag, and freeze until they are ready for assembly or shipment to the client.
- l. For each passive sampling device set (a group of passive sampling devices deployed together), prepare a minimum of 3 Fabrication Controls (Day-zeros), 1 Field Blank and 1 Trip Blank and 1 – 4 additional control films for lab QC in addition to the samplers required for the client deployment. The client may specify higher numbers of these.

11. Evaluation of the passive samplers after preparation:

Depending on laboratory requirements, up to three entire laboratory QC samplers may be analysed after LDPE preparation is complete according to the standard analytical technique appropriate for the PRCs loaded and/or target measurands of the deployment.

12. Specifications report:

A specification report similar to the one attached to this WI is prepared for each lot of passive samplers prepared with PRCs. Data for this report may be taken from either the three laboratory QC samplers tested subsequent to PRC loading (Step 11) or from the LDPE section found to be within compliance at Step 10.1 (h).

13. Start-Up Procedures:

Not applicable

14. Data Acquisition Procedures:

Not applicable

15. Operating Conditions:

Not applicable

16. Calibration:

Not applicable

17. Performance Optimization:

Passive samplers should be maintained in the PRCs loading solution until >80% of the desired PRC loading level has been attained.

18. Maintenance:

Not applicable

19. Troubleshooting:

Not applicable

20. Attachments:

Example Specification Report to accompany shipment of passive samplers to client.

21. References:

Booij, K., Smedes, F., van Weerlee, E.M. 2002 Chemosphere, 46, 1157-1161.

22. Associated Documents:

No associated documents specified

ATTACHMENT 2

2009 ARKEMA EE/CA FIELD SAMPLING PLAN

**ARKEMA EARLY ACTION
EE/CA WORK PLAN**

Work Plan Addendum

**Appendix A
Field Sampling Plan**

Prepared for
Legacy Site Services LLC
468 Thomas Jones Way
Exton, PA 19341



319 SW Washington Street
Suite 1150
Portland, OR 97204

May 15, 2009

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ACRONYMS AND ABBREVIATIONS

ASTM	American Society for Testing and Materials
CDF	confined disposal facility
COI	constituent of interest
CPT	cone penetration testing
CU	consolidated, undrained triaxial shear stress
DDx	total of 2,4'- and 4,4'-DDD, DDE, DDT
DEQ	Oregon Department of Environmental Quality
DGPS	differential global positioning system
DOT	U.S. Department of Transportation
EE/CA	engineering evaluation and cost analysis
EPA	U.S. Environmental Protection Agency
EVS	Environmental Visual Software
FSP	field sampling plan
GUS	Gregory Undisturbed Sampler
Integral	Integral Consulting Inc.
IRM	interim remedial measure
LSS	Legacy Site Services LLC
NAD	North American Datum
NTCRA	non-time-critical removal action
OVM	organic vapor meter
PCB	polychlorinated biphenyl
PCDD/F	polychlorinated dibenzo- <i>p</i> -dioxin and polychlorinated dibenzofuran
PPE	personal protective equipment
QA	quality assurance
QAPP	quality assurance project plan
RAA	removal action area
SOP	standard operating procedure

SPT	standard penetration testing
SVOC	semivolatile organic compound
TCLP	toxicity characteristic leaching procedure
TZW	transition-zone water
UU	unconsolidated, undrained triaxial shear stress
VOC	volatile organic compound

1 INTRODUCTION

This field sampling plan (FSP) was prepared for the engineering evaluation/cost analysis (EE/CA) non-time-critical removal action (NTCRA) at the Arkema site (Site). This FSP is Appendix A to the EE/CA Work Plan Addendum (Work Plan Addendum). The Work Plan Addendum modifies and updates the May 11, 2007 EPA/Parametrix Arkema Early Action EE/CA Work Plan (EPA/Parametrix Work Plan) pursuant to agreements between the U.S. Environmental Protection Agency (EPA) and Legacy Site Services LLC (LSS), agent for Arkema Inc., between May 2007 and May 4, 2009, and findings by EPA (USEPA 2008). Together, the EPA/Parametrix Work Plan, the Work Plan Addendum, and this and other revised appendices encompass the Final EE/CA Work Plan for the Site.

The Site is located in Portland, Oregon on the northwest bank of the lower Willamette River between approximately river mile 6.9 and 7.6 (Parametrix 2007, Figure 1-1). The upland portion of the Site encompasses approximately 54 acres of land. The in-water portion of the Site is defined as the land below mean high water (18.1 ft City of Portland Datum)^[1]; however, the NTCRA evaluation will include portions of the riverbank to the top of bank, as the riverbank cannot easily be subdivided for construction purposes. The EE/CA NTCRA is primarily focused on the in-water portion of the Site; however, elements of the removal action will be integrated with the upland portion of the Site. The portions of the riverbank (to the top of bank) that are deemed to be recontamination sources or to impact the removal and/or remedial action alternatives may be addressed by the NTCRA, while the remainder of the riverbank may be addressed directly with the Oregon Department of Environmental Quality (DEQ) in accordance with the Agreed Order on Consent dated October 31, 2008. Ultimately, the timing and coordination between the Upland and NTCRA projects will dictate under which program the NTCRA-affected riverbank portions will ultimately be addressed in the field.

This FSP describes the sampling design and rationale to meet the data needs of the removal action characterization activities associated with the EE/CA and, along with the Quality Assurance Project Plan (QAPP; Appendix B), provides specific field methodology and quality assurance procedures that will be followed by Integral Consulting Inc. (Integral) and its subcontractors. Integral is conducting this work under contract to LSS with approval and oversight by EPA and DEQ.

The primary objective of the EE/CA characterization activities is to fill data gaps to further refine the 5 mg/kg preliminary removal action area (RAA) boundary, especially at depth, as cited in the May 23, 2008 Final Decision on Disputes from Dan Opalski, Director, Office of

¹ The in-water portion of the Site below mean low tide is leased from the Oregon Division of State Lands.

Environmental Cleanup (Opalski Decision). The additional characterization falls into two general categories:

- Defining sediment quality characteristics
- Defining sediment physical and engineering characteristics.

The remainder of this FSP is organized as follows:

- Section 2: Data Gaps and Field Investigation Rationale—This section describes the rationale used to fill data gaps at the Site and provides a description of the EE/CA characterization activities.
- Section 3: Field Sampling Methods—This section provides a general description of the field methods that will be employed to fill data gaps at the Site.
- Section 4: References—References cited in this document.
- Attachment A: Standard Operating Procedures—These numbered documents provide specific, detailed information on conducting routine, repetitive field techniques (e.g., split-spoon sampling from a drill rig).
- Attachment B: Field Forms—These field forms will be utilized to record data in the field.

2 DATA GAPS AND FIELD INVESTIGATION RATIONALE

This section identifies data needs and presents approaches to fill data gaps for the removal action technologies and alternatives presented in the EE/CA EPA/Parametrix Work Plan and Work Plan Addendum (Parametrix 2007; Integral 2008), and as clarified by the Opalski Decision. The data needs for removal action technology groups are summarized in Table 2-1. The proposed investigation activities described in this FSP are intended to support the analysis and selection of removal action alternatives during the EE/CA, to identify a preferred removal action alternative, and in part to support engineering analyses during the design phase of the Arkema NTCRA.

2.1 DATA GAPS

The following sections address data gaps identified to complete the EE/CA.

2.1.1 Removal Action Technologies and Alternatives

Table 2-1 presents the sampling and analysis methods that will be considered for each potential removal and/or remedial action technology for the Site. Table 2-2 presents the sampling and analysis methods that may be considered for each potential disposal alternative. A checkmark (✓) indicates that sufficient data are available and that no additional data are needed for the sampling or analysis method. An "X" indicates that available data are insufficient and that additional data are needed for the sampling or analysis method.

These methods are discussed in more detail in the following sections.

2.1.2 Nature and Extent of Contamination

Although extensive sediment data have been gathered over portions of the Site, especially in the area of Arkema Docks 1 and 2 (Figure 2-1), additional data are needed for completion of the EE/CA. Sediment data are limited in certain portions of the study area, and additional sediment chemistry data are needed (predominantly vertically) to refine the RAA boundary limits at depth. Additional borings will also be used to further confirm the 5 mg/kg RAA boundary laterally. Currently sufficient data exist, including recent Round 3b Lower Willamette Group sampling data, upstream of Dock 1 to support the evaluation of recontamination caused by resuspension and redeposition of nearby upstream sediments into the RAA. Sediment quality data are generally less abundant with depth, as determined in part by the Environmental Visual Software (EVS) Drill Guide, resulting in greater statistical uncertainty about levels of contamination at different depth intervals between the sediment surface and bedrock within the 5 mg/kg total of 2,4'- and 4,4'-DDD, DDE, DDT (DDx) preliminary RAA. Therefore, in

accordance with the Opalski Decision, much of the EE/CA characterization is focused on and designed to provide higher confidence in the definition of the base of the RAA within the RAA boundary. In addition, some ancillary sediment chemistry data are also needed for other non-site-specific analytes (e.g., dioxin/furan congeners and polychlorinated biphenyls [PCBs]) to obtain a better understanding of these river-wide constituents of interest (COIs) within the Arkema RAA for sediment management and handling.

2.1.3 Sediment Physical and Engineering Characteristics

A suite of physical tests is proposed to evaluate sediment properties pertinent to dredging and capping technologies, dredged material behavior in a disposal site, potential short-term impacts at the dredge and disposal sites, capacity of existing sediments to provide foundation support for capping material, and the viability of sheet pile wall construction or other technology for nearshore containment. The tests discussed below will be required to evaluate these technologies.

2.1.3.1 Index Properties

Grain Size

Grain size provides information on site geologic character and engineering properties and behavior of sediment proposed for capping, dredging, or nearshore containment. Sediment grain-size information is available for most surface sediments previously collected from the Site. Fewer grain-size data are available for the subsurface sediments within the 5 mg/kg DDx preliminary RAA boundary.

Atterberg Limits

Atterberg limits, which include the liquid limit, plastic limit, and plasticity index, are used to define plasticity characteristics of cohesive sediments and are useful index parameters for sediment characterization, engineering behavior, and shear strength correlations. Limited Atterberg limit data are available from historical studies within the preliminary RAA boundary. Selected fine-grained surface and subsurface sediments collected for grain size will also be analyzed for Atterberg limits.

Specific Gravity

The specific gravity of sediment samples is used to determine weight-volume relationships of sediment, which are used for unit weights and void ratio calculations. Limited data for specific gravity in sediment are available between the docks and nearshore (Portland Harbor Remedial Investigation sampling locations only). Selected samples will be analyzed in support of the remedial alternative selection.

Moisture/Bulk Density

Moisture content is used to determine the initial *in situ* void ratio of the sediment, to estimate short-term bulking (or increase in volume) during dredging activities, and to correlate with other geotechnical parameters. There have been no direct measurements in site sediments for moisture content or bulk density. Selected samples will be analyzed in support of the remedial alternative selection.

2.1.3.2 Subsurface Information and Advanced Geotechnical Parameters

In addition to index property testing, more advanced testing will be performed to estimate subsurface information and geotechnical parameters such as shear strength, stress history, compressibility, and hydraulic conductivity of the *in situ* material. These parameters are needed to support the analysis and design of the various removal action technologies under consideration for the Site. Analysis and design of sediment caps involves the evaluation of long-term stability and integrity, based upon physical and chemical parameters expected at the Site. Parameters to be evaluated during the design of a cap include chemical isolation, cap thickness, cap materials, cap armoring, shear strength and consolidation characteristics of underlying sediments, bioturbation, cap erosion and scour, vessel prop wash, slope stability, and settlement/consolidation (USACE 1998; USEPA 1998). Physical characteristics and shear strength parameters are also needed to assess the stability of proposed dredge cuts and potential impacts to adjacent shorelines and structures. Geotechnical parameters will also be needed to assess the suitability of the Site subsurface materials to support a nearshore confined disposal facility (CDF) and other structures that may be necessary during remedial construction. The geotechnical tests required to support evaluation of these removal action technologies are described below. None of these tests has been conducted previously on site sediments.

Shear Strength Testing

Shear strength test results are used to assess bearing capacity, slope stability, and earth pressures for analysis and design of removal action technologies such as *in situ* capping, CDFs, and dredging. Drained and undrained shear strength parameters will be used during design. These parameters will be assessed using a variety of approaches and include the use of unconsolidated, undrained (UU) and consolidated, undrained (CU) triaxial shear tests. In addition, shear strength will also be assessed based on the results of standard penetration testing (SPT), cone penetration testing (CPT), and index property testing, in conjunction with published correlations and engineering judgment.

In addition to the shear strength testing on sediment samples, the unconfined compressive strength of rock samples will be tested by performing point load index tests and unconfined compressive strength tests. These tests will be performed to assess the “rippability” and bearing characteristics of the underlying bedrock. These characteristics may become important

in the assessment of constructability and feasibility of sheet pile structures such as CDF containment structures.

Consolidation Testing

Consolidation tests are performed to determine the compressibility and stress history parameters. These parameters are used for assessment of consolidation behavior of sediment deposits under loading conditions associated with capping materials and assessment of the shear strength of cohesive materials. An understanding of the consolidation of underlying sediment is important in evaluating the effective (or minimum) thickness of a cap (USACE 1998). The effective thickness of a cap is reduced by the consolidation in the underlying sediment. Vertical loads for cap consolidation testing and analyses are determined on the basis of the anticipated cap configuration and thickness (modified EM-1110-2-5027). Additionally, stress history parameters are useful in assessing the in-situ strength of the cohesive material. The use of strength data is explained in more detail under Shear Strength Testing.

Hydraulic Conductivity

Hydraulic conductivity testing will be conducted to assess the permeability of lower cohesive strata within the RAA boundary, which may serve as a key-in feature for nearshore CDF options considered during the EE/CA.

2.1.4 Upland Disposal of Dredged Material

In order to identify the appropriate type of upland disposal options for the dredged sediments, a waste determination analysis must be conducted. The waste determination analysis involves evaluating the source of the waste and the waste characteristics, including toxicity characteristic leaching procedure (TCLP) testing. For example, for assessing disposal options at offsite landfills, the waste would have to be evaluated per the Oregon Administrative Rules prior to disposal at a Subtitle D landfill.

Additionally, landfill-specific criteria such as the presence of free liquids and other permit required testing (e.g., total petroleum hydrocarbons, asbestos) will apply. These criteria are specific to the landfill selected to receive the dredged sediments. Therefore, other offsite landfill-specific testing may be performed to evaluate disposal options for any dredged material.

2.1.5 Hydrogeologic Characteristics

Groundwater characteristics have been evaluated for upland soils and in-water sediments, including the transition zone between sediments and overlying water (Integral 2007). Upland groundwater zones and their characteristics (including hydraulic gradient) are summarized in Section 3.2.2.3 of the Final EE/CA Work Plan (Parametrix 2007; Integral 2008). As stated in the

Final EE/CA Work Plan, the quality of some of the transition-zone water (TZW) data is considered to be unusable for the purpose of evaluating recontamination potential for chlorinated pesticides because of the collection method (i.e., unfiltered, turbid water samples from Trident probes). Other TZW data, including peepers samples (a sample device that uses a semi-permeable membrane) and filtered Trident probe samples, are more likely to be representative of water moving through the sediment prior to discharge at the sediment surface. These latter data will be used to evaluate the potential for long-term release and sediment or cap recontamination at the sediment interface for the EE/CA. No additional TZW data collection is proposed in this FSP.

Transition-zone groundwater seepage rates were measured as part of the recent Portland Harbor remedial investigation groundwater study, as described in Section 3.2.2.1 of the Final EE/CA Work Plan (Parametrix 2007; Integral 2008). The information from these studies, and other relevant site data, will be used in calculations and modeling to estimate long-term contaminant release or loss associated with placement of an isolation cap and to assist in the evaluation of hydraulic containment technologies. An understanding of groundwater advection in the sediments is important in evaluating the effective (or minimum) thickness of a cap. This information will also be beneficial in evaluating hydraulic containment alternatives for the Site.

Additional information is also needed to understand the depth to basalt bedrock and low-permeability horizons within the in-water portion of the Site. No other hydrogeologic data are required in support of the EE/CA.

2.1.6 Debris Survey, Dock Encumbrances, and Utilities

The nature and extent of debris within the project site RAA will need to be considered in the development and evaluation of sediment capping, dredging, and hydraulic containment technologies. Accordingly, a reconnaissance survey of the project area will be conducted to estimate the quantity and nature of surface debris. In addition, boring logs will be reviewed to identify subsurface debris encountered during both historical and proposed site investigations. This information will be compiled for consideration during the EE/CA and also will be useful for inclusion in the final design documents and remedial construction contract.

2.2 REMOVAL ACTION CHARACTERIZATION ACTIVITIES

This section summarizes the rationale for removal action sampling and analytical methods that will be employed in support of the EE/CA. Future sampling methods that may be necessary for the removal action, but are beyond the scope of this FSP, are also noted below.

2.2.1 Nature and Extent of Contamination

This section presents the sampling design and rationale for the EE/CA characterization to evaluate sediment characteristics at the Site. Additional information on sediment characteristics is required per the Opalski Decision to further refine the horizontal and vertical extent of the 5 mg/kg DDx preliminary RAA boundary. For the vertical boundary definition, the Opalski decision specifically states: *“the EE/CA shall proceed with analyses that considers the implications of dredging to a range of concentrations vertically, with that range to include at least the SLVs and the approximate 5 ppm concentration suggested by LSS’ mass-based analysis.”* The proposed investigations are designed to fill data gaps identified by conventional data gap analysis and by the Drill Guide to adequately define the base of the removal action within the RAA boundary, and to provide a baseline for monitoring remedial activities.

2.2.1.1 Rationale

Surface and subsurface samples will be collected and analyzed to support delineation of the 5 mg/kg RAA boundary in accordance with the Opalski Decision and development of removal action alternatives. Sampling locations have been selected to characterize sediment in areas identified by conventional data gap analysis and identified by the Drill Guide¹ to provide a higher statistical certainty in the 5 mg/kg RAA boundary contour.

2.2.1.2 Sampling Strategy

A total of 37 sediment chemistry boreholes are proposed (WB-30 through WB-66; Figure 2-1) and will be completed to basalt (or refusal) to evaluate the horizontal and vertical extent of COIs within and adjacent to the 5 mg/kg DDx RAA boundary. Samples will be collected for chemical analyses and/or archived at all proposed sampling locations. The proposed sampling, analysis, and archiving plan and rationale for each borehole location is summarized in Table 2-3. Proposed sediment samples are distributed at representative locations within the vicinity of the preliminary RAA boundary to measure the vertical and horizontal extent of DDx and other chemicals. In addition to characterizing the broader Site conditions, this sampling will focus on the perimeter of the 5 mg/kg preliminary RAA Boundary contour where the majority of DDx mass is located. Selected samples will be archived for possible subsequent analysis, depending on the analytical results from samples collected at nearby boreholes (Table 2-3; Figure 2-1).

In some locations, sediment chemistry cores will be near geotechnical borehole locations. In general, the installation sequence for the sediment chemistry and geotechnical boreholes does not matter. However in the area immediately downstream of Dock 2, sediment chemistry cores WB-49, WB-50, and WB-51 will be installed prior to the CPT boreholes (CPT-1 and CPT-3). If

¹ A description of EVS Drill Guide methodology is presented in Section 8.2 of the Work Plan Addendum (Integral 2008).

the geotechnical engineer determines that the sediment lithology in the Dock 2 area is substantially different² than the sediment lithology near Dock 1 then one of the collocated geotechnical boreholes (SPT) may be moved to this downstream location.

Sediment quality samples will be collected using a barge-mounted hollow-stem auger drill rig (or equivalent) advanced to basalt or refusal. Samples will be collected continuously at 2- to 3-ft intervals in accordance with Table 2-3 for the entire length of the borehole, using a variety of samplers, depending on the sample location and bottom conditions. Sampling equipment may include split-spoon samplers, Gregory Undisturbed Sampler (GUS) or Osterberg sampler, and/or Shelby tubes.

2.2.1.3 Analytical Strategy

The rationale, analytes, and laboratory methods for the sediment samples are detailed in Table 2-3 and the QAPP (Appendix B). Additional samples may be analyzed based on field observations, including visual observation, odor, and presence of volatile chemicals (e.g., using a photoionization detector). A portion of each sample interval will be archived for possible future chemical analysis. The analytes are grouped into standard and expanded lists.

Most samples will be analyzed for the standard analyte list, which includes the following:

- Conventional analytes (grain size, total solids, and total organic carbon) by American Society for Testing and Materials (ASTM) Method D-422, EPA Method 160.3 modified, and EPA Method SW846-9060A, respectively
- DDx by EPA Method SW846-8081A.

Other samples, as identified in Table 2-3, will be analyzed for an expanded analyte list to better characterize the nature and extent of river-wide COIs inside and adjacent to the preliminary RAA. The expanded analyte list includes the following:

- Standard analyte list (described above)
- Semi-volatile organic compounds (SVOCs) by EPA Method SW846-8270C
- PCB Aroclors by EPA Method SW846-8082
- Volatile organic compounds (VOCs) by EPA Method SW846-8260B
- Organochlorine pesticides by EPA Method SW846-8081A
- Polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran (PCDD/Fs) by EPA Method 1613B.

² For the purposes of the geotechnical evaluation.

2.2.2 Physical and Engineering Characteristics

2.2.2.1 Rationale

A testing program will be performed to determine the sediment index properties and geotechnical engineering parameters within and adjacent to the RAA boundary. The physical characteristics of sediments are important in the evaluation of dredging, capping, and containment technologies, dredged material transport and disposal, dredged material behavior in a disposal site, potential short-term impacts at the dredge and disposal sites, and the capacity of the sediments to support capping materials.

2.2.2.2 Geotechnical Investigation Sampling Strategy

The geotechnical investigation program will consist of three mud-rotary sediment borings and 13 CPT explorations to evaluate geotechnical properties and subsurface conditions within and adjacent to the RAA boundary (Figure 2-1). CPTs were selected because they are an effective exploratory technique that can be used to collect continuous soil type and property data. Mud-rotary drilling was selected because the drilling mud used for mud-rotary drilling prevents soil heave in the borehole. Heave can obscure the results of SPT.

The CPT measures tip resistance, sleeve friction, and pore pressure essentially continuously to the total depth of the borehole. These three parameters are used to estimate the soil behavior type, which typically correlates well with stratigraphy obtained from drilling and sampling in a collocated mud-rotary borehole. CPT parameters will also be correlated with other important soil parameters used in geotechnical analysis and design, such as sediment shear strength. No sediment samples are collected with the CPT.

The three mud-rotary boreholes (identified as SPT on Figure 2-1) will be collocated with three of the CPTs (identified as CPT on Figure 2-1) to allow development of site-specific correlations between CPT parameters and parameters based on sampling and laboratory testing. The collocated explorations were selected strategically based on existing subsurface information such that correlations for both cohesive and granular soils can be established.

All geotechnical explorations will be advanced to bedrock refusal. Based on existing basalt surface information for the site, bedrock will be encountered at relatively shallow depths. The sediment cover between the shoreline and the existing docks is on the order of 20 to 40 ft. The sediment cover in the channel is only on the order of 2 to 10 ft. Sediment cover is important for the feasibility of installing sheet pile structures.

In the mud-rotary boreholes, SPTs will be performed in the boreholes continuously or at 2.5-ft intervals for the first 20 ft of drilling and at 5-ft intervals thereafter. The SPT is an *in situ* testing technique that is used to estimate soil density of granular material and consistency of cohesive material. Correlations of SPT results with soil parameters are used in geotechnical analysis and

design. Disturbed split spoon samples will be collected for visual soil/sediment classification during SPT. Laboratory testing, consisting of index property testing for soil/sediment classification, will be conducted on selected split spoon samples (refer to Geotechnical Testing Strategy below).

Relatively undisturbed, thin-wall tube samples (Shelby tubes) will also be collected in the mud-rotary boreholes, for advanced laboratory testing (consolidation and shear strength testing) and index property testing on selected samples. Shelby tubes will be collected using a piston sampler (Osterberg Sampler or GUS) to ensure proper sample recovery and minimization of sample disturbance. Shelby tubes will be handled with utmost care so as to minimize further sample disturbance after retrieval. Sample disturbance can obscure the results of advanced geotechnical testing, including shear strength and consolidation parameters.

The preferred sequence for borehole installation is to install CPTs first where a CPT borehole is collocated with a mud-rotary borehole (see CPT -9, CPT-10, and CPT-13 on Figure 2-1). If the CPT is performed first, the stratigraphy at that location is already known prior to mud-rotary drilling, and the Shelby tube sampling depths can be targeted more easily. Shelby tubes will only be collected in cohesive material (i.e., silt and clay). Based on existing subsurface information, relatively thick deposits of cohesive material are expected to be encountered in borings SPT-1 and SPT-3. Shelby tube sampling will, therefore, likely be focused on these two locations. More than one borehole may be required at the mud-rotary locations to allow for undisturbed sampling and/or to provide enough sediment for all proposed tests.

In one of the mud-rotary boreholes (SPT-1; Figure 2-1), rock coring will be performed to 20 ft below the bedrock contact elevation to determine the quality of the rock. The constructability of certain structures may depend on the “rippability” of the bedrock at the site; therefore, unconfined compressive strength and point load index testing of rock samples will be conducted (see Section 2.2.2.3).

The proposed rationale, test parameters, and laboratory methods for each geotechnical boring is presented in Table 2-4 and the QAPP (Appendix B).

2.2.2.3 Geotechnical Testing Strategy

The selection of samples for geotechnical testing will be determined on the basis of observed lithology, as required to characterize the observed range of lithologies and associated geotechnical conditions critical to the selection, evaluation, and design of candidate removal action technologies (Table 2-1). Target sample intervals in the SPT borehole will be determined in the field based on the interpretation of the collocated CPT explorations, which will be advanced prior to the SPT geotechnical boring. The geotechnical testing program will include the following parameters:

- Grain-size analysis by ASTM-D422

- Atterberg limits by ASTM-D4318
- Specific gravity by ASTM-D854
- Moisture content by ASTM-D2216
- Organic content by ASTM-D2974.
- Consolidation by ASTM D 2435 (Method B)
- UU triaxial shear stress by ASTM-D2850
- CU triaxial shear stress by ASTM-D4767
- Unconfined compressive strength (rock) by ASTM D-7012
- Point load index (rock) by ASTM-D5731
- Hydraulic conductivity by ASTM-D5084.

2.2.3 Waste Disposal Evaluation

2.2.3.1 Rationale

Representative large-volume samples are required for disposal design requirements (USEPA/USACE 1998). The assessment of offsite landfill disposal will be performed with landfill-specific acceptance criteria including hazardous waste determinations (i.e., TCLP).

2.2.3.2 Sampling Strategy

Two large-volume samples will be composited from each of seven boreholes located between Dock 1 and Dock 2 (WB-35, WB-36, WB-37, WB-39, WB-41, WB-42, and WB-43; Table 2-3). These areas are within or immediately downstream of the highest DDx concentrations in sediments within the RAA boundary. The composite sample analyses will provide data for sediment that could require disposal as part of the removal action. Figure 2-1 presents the proposed boring locations for each composite sample. Table 2-3 presents the compositing intervals for each large-volume sample. A total of 14 composite samples will be collected—two from each borehole.

2.2.3.3 Analytical Strategy

A representative sample of the composite sediment described above will be analyzed for hazardous waste determination and used to assess landfill disposal options. Composite sediment samples will be analyzed for the following:

- TCLP for standard TCLP VOCs, SVOCs, metals, pesticides, and herbicides (42 individual chemicals using EPA SW-846 methods)

- Asbestos (EPA Method 600/R-93-116).

Additional testing associated with disposal at a solid waste landfill may also be performed. These analyses may include:

- PCB Aroclors by EPA Method SW846-8082
- PCDD/Fs.

2.2.4 Debris Survey, Dock Encumbrances, and Utilities

There are two large docks at the Site within the RAA boundary area, both of which have been out of service since 2001. The docks are primarily timber construction (but each includes four large concrete dolphins), supported by a dense network of timber, steel, and concrete pilings. Three stormwater outfall structures extend into the preliminary RAA boundary. The dock and outfall structures will likely be removed as part of the removal action, as their presence will impact the feasibility of sediment capping or dredging. The site characterization program will include a survey of these structures to verify their condition and catalogue the type and quantity of construction materials. A historical review will be conducted to determine the extent of building and demolition debris in the area currently occupied by the docks and outfalls. In addition, the removal of large obstructions, such as the existing docks, that could affect the implementability of in-water removal and/or remedial actions will be evaluated in the EE/CA.

2.2.5 Future Sampling

The following sections briefly describe future sampling of surface water, groundwater, TZW, and biota. Although the sampling is not part of this FSP, a brief description of the objectives for sampling these media is presented below. The timing and details of these sampling activities will be submitted as addenda to this FSP and the QAPP after the EE/CA as specified below.

2.2.5.1 Water Quality/Chemical Mobility Testing During Dredging and Disposal

Representative sediment from areas that could be dredged will be collected in the future to assess chemical mobility during sediment dredging and disposal. This will consist primarily of elutriate testing (dredging elutriate testing and effluent elutriate testing) on representative dredged material to provide an assessment of contaminant mobility during dredging and disposal operations. However, this sampling will be delayed until after the removal area/removal action is selected so that it is better understood which specific tests, models, and sample locations are required. The water quality and chemical mobility testing will be conducted during the EE/CA design phase.

2.2.5.2 Surface Water

Future sampling of surface water will be conducted to provide baseline conditions and post-removal action monitoring to determine if there are any significant impacts during and after the in-water removal action. In addition, existing and future surface water sample data will provide information on potential Site recontamination from upstream water. The pre- and post-removal action surface water sampling will be included as an element of the removal action work plan. Pre-removal action sampling will be implemented prior to removal action activities.

2.2.5.3 Groundwater and Transition-Zone Water

Future sampling of groundwater and TZW will be required to verify the effectiveness of the Upland Source Control interim remedial measures (IRMs). The future sampling necessary for the NTCRA will depend on the selected removal action. The purpose of the sampling for the Upland Source Control IRMs will be to monitor groundwater conditions upland (upgradient) of the planned cutoff wall and in the shoreline area immediately downgradient of the planned groundwater cutoff wall. The timing and details of this sampling activity will be developed in coordination with the Upland Source Control IRMs and the selected removal action. Post-removal action TZW monitoring will be included as an element of the removal action work plan.

2.2.5.4 Biota

Future biota sampling will be needed for several objectives including, but not limited to, 1) identifying baseline conditions in biota before the removal action; 2) assessing the short term impacts of the removal action on biota contaminant levels; and 3) assessing the long-term effectiveness of the removal action. The details of this sampling activity will be developed in coordination with the selected removal action. Baseline and post-removal action biota monitoring will be included as an element of the removal action work plan.

3 FIELD SAMPLING METHODS

This section presents the field sampling methods to be used by Integral and its subcontractors for the RAA characterization. In general, field sampling methods will follow the standard operating procedures (SOPs) listed in Attachment A. Attachment B contains field forms and examples of chain-of-custody forms, sample labels, custody seals, and logbooks. All sampling will be conducted in accordance with the quality assurance (QA) procedures outlined in the QAPP. Safety guidelines are presented in the site health and safety plan. General guidelines for conducting the field work are described in the following sections.

3.1 HORIZONTAL AND VERTICAL CONTROL METHODS

3.1.1 Utility Survey

Prior to commencing field activities, a utility survey will be conducted to identify all known in-water utilities within the study area. Arkema representatives will be contacted regarding the locations of the private utilities in the study area, including stormwater outfalls and other utilities associated with former plant operations. The Oregon Utility Notification Center (1-800-332-2344) will be contacted to locate public utilities in the study area. If proposed sample locations interfere with utilities, alternate locations will be determined in consultation with the LSS Project Team, as designated in the Final EE/CA Work Plan.

3.1.2 Surface Debris Survey

A visual surface debris survey will be conducted to catalogue and identify the locations of outfalls, pilings, concrete, and other debris within the preliminary RAA boundary. The purpose of the survey is to identify any debris or structures that could affect the implementation of the Final EE/CA Work Plan and potential in-water removal and/or remedial actions.

The survey will be conducted during a low river stage when the riverbank and sediments are most visible. The debris survey in the in-water portion of the Site will be conducted using a small boat equipped with a differential global positioning system (DGPS) unit with an accuracy of approximately ± 1 to 2 meters. The riverbank area will be surveyed using a DGPS unit after blackberries and other vegetation are removed. The DGPS unit will be used in accordance with SOP 1.

The DGPS beacon will be located directly on top of the structure or debris and the horizontal location of the debris will be recorded in latitude and longitude (North American Datum [NAD] 1983) in the field and converted to state plane coordinates (Oregon North, International Feet). Dense areas of debris will be mapped as areas rather than discrete points. Each structure or

piece of debris will be photodocumented and a description (e.g., type of debris, size) will be recorded in the field logbook.

3.1.3 Sample Locations

The horizontal coordinates of each sample station are specified in Tables 2-3 and 2-4. The barge will be guided to the station locations using a DGPS unit with an accuracy of approximately ± 1 meters. The DGPS beacon will be positioned where the drilling will occur (i.e., moon pool). The horizontal location of the station will be recorded in latitude and longitude (NAD 1983) in the field and converted to state plane coordinates (Oregon North, International Feet). Navigation and positioning will follow guidelines in SOP 1.

The mudline elevation at each station will be calculated using a staff gauge attached to one of the docks prior to the field effort (location to be determined). Prior to commencing work, the elevation of the staff gauge will be surveyed relative to the NAVD88 benchmark by an Oregon licensed professional land surveyor. The mudline depth from the water surface will be measured with a sounding device (e.g., weight tied to the end of a fiberglass tape measure) to the nearest 0.1 ft. The water surface elevation will be determined from the staff gauge. The mudline elevation will be calculated as the staff gauge elevation of the river minus the depth to mudline in feet.

The following parameters will be documented in the field logbook at every sample location:

- Horizontal location using a DGPS unit
- Depth to mudline from river level
- River level measured on surveyed tide staff gauge on Arkema dock (measurement must be made within 0.5 hour of the mudline measurement)
- Time and date.

3.2 SAMPLING METHODS

Sampling during this field effort will consist of surface and subsurface sediment sampling and large volume river water samples to be used for dredge material water quality tests.

3.2.1 Sediment Boreholes

3.2.1.1 General Guidelines

A hollow-stem auger (or equivalent) drill rig positioned on a barge will be used to complete the sediment boreholes for sediment quality sampling. The boreholes will be drilled through a moon pool (or equivalent access location) on the barge. Samples will be collected continuously

as detailed in Table 2-3 to bedrock or refusal using a split spoon sampler or a GUS or Osterberg Sampler equipped with a stainless-steel or aluminum Shelby tube. A large-volume split-spoon sampler may also be used for sampling. All chemistry samples that are not identified for analysis will be archived at the analytical laboratory. The drilling and sampling procedures will follow SOP 3, except for the use of conductor casing on selected boreholes, as described below.

A mud-rotary (or equivalent) drill rig positioned on a barge will be used to complete the SPT geotechnical investigation boreholes. The SPT boreholes will be drilled through a moon pool (or equivalent access location) on the barge. SPTs will be performed in the boreholes continuously or at 2.5-ft intervals for the first 20 ft of drilling and at 5-ft intervals thereafter to bedrock or refusal. A GUS or Osterberg Sampler equipped with a stainless-steel or aluminum Shelby tube, or a large-volume split-spoon sampler may be used for sampling. The drilling and sampling procedures will follow SOP 3, except for the use of conductor casing on selected boreholes, as described below.

A CPT (or equivalent) rig positioned on a barge will be used to complete the CPT geotechnical explorations. The CPT explorations will be performed through a moon pool (or equivalent access location) on the barge. CPTs will be performed continuously to bedrock or refusal. The CPT procedures will follow SOP 3, except for the use of conductor casing on selected boreholes, as described below.

Target depths for geotechnical sampling (relatively undisturbed Shelby tube samples) will be based on the lithology observed at the collocated CPT exploration. The preferred sequence for geotechnical explorations is to install CPTs first where a CPT borehole is collocated with a mud-rotary borehole (see CPT -9, CPT-10, and CPT-13 on Figure 2-1). If the CPT is performed first, the stratigraphy at that location is already known prior to mud-rotary drilling, and the Shelby tube sampling depths can be targeted more easily. Shelby tubes will only be collected in cohesive material (i.e., silt and clay). Based on existing subsurface information, relatively thick deposits of cohesive material are expected to be encountered in borings SPT-1 and SPT-3. Shelby tube sampling will, therefore, likely be focused on these two locations. More than one borehole may be required at the mud-rotary locations to allow for undisturbed sampling and/or to provide enough sediment for all proposed tests.

The mudline elevation at each station will be calculated using a tide staff gauge attached to one of the docks, as described in Section 3.1.3. The tide staff gauge will be monitored periodically during drilling activities and adjustments to sample intervals will be made as necessary based on river stage.

3.2.1.2 Conductor Casing

Conductor casing will be employed for all boreholes to recover the majority of the sediment cuttings. Steel conductor casing will be chosen with an inside diameter that is slightly larger

than the outside diameter of the hollow-stem auger (i.e., approximately 1 to 2 in.) so that the majority of the cuttings are extruded to the top of the casing on the barge deck. The conductor casing will be pushed approximately 2 ft into the sediment and will be securely attached to the barge deck using a clamping mechanism so it does not drop when drilling commences.

To contain the sediment cuttings as they surface during drilling activities, the top of the conductor casing will protrude through a 4-ft by 8-ft sheet of ¾-in. plywood that has a 2-in. by 6-in. frame attached. The sediment cuttings will be shoveled into properly labeled, U.S. Department of Transportation (DOT)-approved, 55-gallon steel drums and handled according to specifications in Section 3.8. Care will be taken to minimize any spilling of the sediment. The conductor casing will be retrieved after the augers are retrieved and the borehole has been grouted.

When the borehole is at depth and the augers are ready to be removed from the conductor casing, the augers will be rotated rapidly to bring as much sediment to the top of the conductor casing as possible.

Conductor casing will not be used for CPT boreholes which do not require the removal of sediment during explorations.

3.2.1.3 Logging and Sampling

Sediments from each borehole will be continuously collected and logged by a licensed geologist using ASTM (2000) guidelines, as described in SOP 4. Lithologic logging will include observations of bioturbation, where observed. Each sediment sample that is collected for potential chemical analysis will be processed in accordance with SOP 3. In addition, each sample will be screened for VOCs using an organic vapor meter (OVM) prior to mixing, in accordance with SOP 12. Each sediment sample for potential chemical analysis will be processed (i.e., mixed and composited) in accordance with SOP 2 (Attachment A). After processing³, samples will be placed in the appropriate containers listed in Table 3-1 and labeled in accordance with Sections 3.3 and 3.5 and SOP 5. Samples for potential chemical analysis will be immediately placed in a cooler with ice for preservation. Additional QA guidelines, including sample handling and the collection of duplicate and rinsate blank samples, are presented in the QAPP. Sediment samples collected for the geotechnical investigation will not require mixing nor will they require preservation on ice for shipment.

The large-volume sediment sample for the waste disposal characterization will require the collection of composite samples from seven boreholes (Section 2.2.3). An equal volume of representative sediment will be collected from each composite interval subinterval (approximately 2 ft) and mixed in a large stainless-steel pot using a power mixer or equivalent

³ With the exception of samples collected for VOCs.

device. All materials contacting the sediment will be decontaminated in accordance with Section 3.7 and SOP 9.

3.2.1.4 Borehole Abandonment

The boreholes will be abandoned with a high-solids bentonite grout, mixed according to the manufacturer's specifications, and placed inside the augers through a tremie pipe as the augers are withdrawn. Once the borehole is grouted, the augers will be brought to the barge deck, and any residual sediment left on the augers will be transferred to properly labeled, DOT-approved, 55-gallon drums. The conductor casing (if used) and augers will be decontaminated using a hot pressure-washer in accordance with Section 3.7 and SOP 9.

3.3 SAMPLE IDENTIFICATION

Sediment samples will be assigned an individual sample identification number in the following manner:

- ARK-WB-##-depth

Where:

ARK = Arkema

WB = Boring

= Station number

Depth (e.g., 021 = 0 to 2 ft below mud surface).

Sediment sample processing will occur on the barge as described in the following sections. Sample processing methods are intended to result in high-quality samples that meet the program's QA objectives. Guidelines for sample handling and storage are presented in the QAPP. All samples will be placed immediately in a cooler with ice to preserve them at $4\pm 2^{\circ}\text{C}$ and will be kept at this temperature at all times. All samples will be labeled and identified in accordance with SOP 5.

Field QC samples (i.e., equipment rinsates and field blanks) will be assigned an individual sample identification number in the following manner:

- ARK-EB-## (Equipment Blank - Sample Number starting at 01).

Duplicate sediment samples delivered to the laboratory will be given a blind sample identification (to be determined) that will correspond to the numbering system described above.

3.4 SEDIMENT PROCESSING

Compositing will be performed within individual locations to ensure that adequate sediment is available for the required analyses.⁴ Power Grab and split-spoon samples not used for analysis will be managed in accordance with applicable investigation-derived waste requirements as described in SOP 11.

Sediment composite samples will be processed according to the following step-by-step procedure and SOPs 2 and 3:

1. Screen a representative subsample of all sediment samples collected for volatile organics using an OVM following procedures in SOP 12. Do not composite or homogenize the sample before screening.
2. Transfer sediment from split-spoon to a clean, stainless-steel bowl and cover with aluminum foil.
3. Stir the composite sample until the sample is of uniform color and texture. If any material (e.g., shells, rocks) has to be removed from the sample, note it in the field logbook or on the sample description sheet.
4. Fill jars for physical and chemical analyses.
5. Seal each glass container in a plastic bag in case of breakage. Place in ice chest and pack samples to minimize the chances of breaking.
6. Decontaminate the equipment as described in Section 3.7 and SOP 9.
7. Collect excess sediment from the composite and dispose of as investigation-derived waste, as discussed in Section 3.8 and SOP 11.

3.5 SAMPLE CONTAINERS AND LABELS

Guidelines for sample handling and storage are presented in the QAPP. All samples will be placed immediately in a cooler with ice to preserve them at $4\pm 2^{\circ}\text{C}$ and will be kept at this temperature at all times. All samples will be labeled and identified in accordance with SOP 5.

3.5.1 Sampling Handling Procedures

The following sections describe documentation with sampling and handling procedures. Details are outlined in SOP 6.

⁴ Compositing and homogenizing is not appropriate for the analysis of volatile organics. Discrete samples will be collected only for analysis of volatile organics in soil and sediments.

3.5.1.1 Sample Labels

Sample containers will be clearly labeled with waterproof black ink at the time of sampling. Sample labels will contain the following information:

- Sample identification numbers
- Sample date
- Sample time
- Preservation used, if any (this information will also be included on the chain-of-custody form)
- Initials of sampling personnel.

The sample label will be attached to the sample container prior to, or just after, the container is filled and the lid secured. As an added measure of security, the finished label will be covered with clear packaging tape to protect the ink from moisture and to tightly secure the label to the sample container. Information on the sample label must match the information on the chain-of-custody form and in the site logbook for each sample.

3.5.1.2 Custody Seal

Custody seals will be used on sample shipping containers (coolers) that will either be shipped or sent by messenger to the laboratory as described in SOP 7. Custody seals will be attached to the lid and body of the coolers to detect any tampering during shipment. The custody seals will be signed and dated by the sampler or sample shipper. Custody seals are not required for samples delivered by hand directly to the lab unless left unattended.

3.5.1.3 Sample Summary Log

Sample summary logs will be maintained by the field team leader and used to keep track of all phases of the sampling and analysis process for all individual samples. The sample summary logs will include sample collection date(s), sample delivery date(s), the date(s) analytical results are received, laboratory sample delivery group, and laboratory work order number. The sample summary logs will also identify blind sample numbers given to the laboratory with corresponding numbering in the field.

3.5.1.4 Sample Custody/Tracking Procedures

The samples collected must be traceable from the time they are collected until their derived data are used in the final report. In general, the following provisions apply to sample handling and are described in SOPs 6 and 7:

- The field team leader, or sampler, will be responsible for the care and custody of the samples collected until they are properly transferred or dispatched to the laboratory.
- All appropriate documentation forms will be used, including sample labels, chain-of-custody forms, sample logs, and any other appropriate forms. Documentation will be completed neatly using waterproof black ink.
- When transferring possession of samples, the individuals relinquishing and receiving them will sign, date, and note the time on the chain-of-custody form. Containers shipped by common carrier will have the chain-of-custody form enclosed in a watertight container (e.g., plastic resealable bag) and placed in the container prior to sealing.
- Samples will be packaged properly according to the current DOT requirements and promptly dispatched to the laboratory for analysis. Sample containers will be packed in coolers (or other shipping containers) with a low-density packing material, such as bubble wrap, and Blue Ice® or its equivalent. The coolers will be securely sealed.
- Each cooler will be accompanied by its own chain-of-custody form identifying its contents. A copy of the chain-of-custody form will be retained by the field team leader for inclusion in project records.
- For coolers shipped via express delivery service, custody seals will be affixed to the outside of the coolers (shipping containers). The field team leader, sampler, or shipper will sign and date the custody seals.
- All samples will be shipped via express delivery for overnight delivery or hand delivered to the laboratory.

3.6 FIELD DOCUMENTATION PROCEDURES

The primary methods of documentation that will be used for this project include site logbook, photo logs, sample log forms, field change request forms, and sample tracking forms. A description of each of these documentation methods is provided in the following sections. Example field forms are presented in Attachment B.

3.6.1 Field Logbooks

Field logbooks will be used to document all field sampling activities performed at the project site, as described in SOP 8. The logbooks will contain the date, time, and description of all field activities performed; names of personnel; weather conditions; the names of visitors to the Site; areas where photographs were taken; and any other data pertinent to the project. The site logbooks will also contain all sample collection and identification information and (if appropriate) a drawing of each area sampled, along with the exact location (coordinates) of where the sample was collected. The sampling information will be transferred to sample log forms when the sampler returns to the site office. The logbook is the official, legal record of site

activities, and will serve as the key to sample designations and locations. It will include the date, time, river stage, depth to mudline, horizontal DGPS coordinates, site/sample location, sample identification number, sample matrix, how the sample was collected, any comments, and the sampler's name. In addition, the logbook will document deviations from the project plans and health and safety tailgate meeting minutes.

Requirements for logbooks include the following:

- Logbooks will be sturdy, weatherproof, and bound, with consecutively numbered pages. If multiple logbooks are used, they will be numbered sequentially.
- Entries will be made legibly with waterproof, black (or dark) permanent ink.
- Removal of any pages, even if illegible, will be prohibited. Any mistakes will be crossed out with a single line, initialed, and dated.
- Unbiased, accurate language will be used.
- Entries will be made while activities are in progress or as soon afterward as possible (the time of the observation will be noted and the time that the notation is made will be noted if significantly later than the observation time).
- Each consecutive day's first entry will be made on a new, blank page. Each page of the field logbook will be numbered, dated, and signed by the author.
- The date will appear at the top of each page. The time, based on a 24-hour clock (e.g., 0900 for 9:00 a.m. and 2100 for 9:00 p.m.), also will appear for each entry.
- Blank pages, if any, will be marked "page intentionally left blank."

An example of the field logbook can be found in Attachment B.

3.6.2 Photo Documentation

Digital photographs will be taken at sampling locations and of selected samples. These photos will help to identify the sampling locations and will provide an accurate visual record of the material being sampled. All photographs taken will be identified in the field logbooks (preferably in a separate section of the book set aside for that purpose). Photographic logs will contain, at a minimum, the file number, date, time, initials of the photographer, and a description of the image in the photograph.

3.6.3 Sample Collection Information Form

Sampling logs and collection forms will be used to document site and sample characteristic data, which should agree with the information recorded in the site logbooks. Field personnel are required to fill out one sample log form for each sample collected. A copy of these forms will be stored in the field office or field files, with the original stored in the project file. A copy

of these forms will also be included in the final data report and other documents, as appropriate. At a minimum, the log for each sample will contain the sample number, the date and time of sample collection, and a description of the sampling site, as well as the physical characteristics of the sample, the planned analysis, and the initials of the sampler. Example field forms are located in Attachment B.

3.6.4 Field Change

The field team leader will be responsible for all environmental sampling activities, and will occasionally be required to adjust the field program to accommodate site-specific needs after consultation with the project manager and/or QA manager. The field team leader will notify the project manager of any significant field changes. The project manager will immediately notify EPA for approval (verbal or written) of any significant field changes. This notification/approval will typically occur via e-mail or telephone, to avoid suspension of field work. The project manager and/or field team leader will follow up these conversations with an e-mail and field change request form that summarizes the approved changes for EPA signature. When it becomes necessary to modify a program or task, the changes will be documented in the field logbook.

3.6.5 Sample Tracking Forms

Sample tracking is an important aspect of field investigation activities, as it documents the proper handling and integrity of the samples. Sample tracking forms for the project will include chain-of-custody forms, sample labels, custody seals, and sample summary logs. Example forms are located in Attachment B.

3.6.6 Chain-of-custody Form

The chain-of-custody form is used to document the history of each sample and its handling from its collection through all transfers of custody until it reaches the analytical laboratory. Internal laboratory records will document custody of the sample from the time it is received in the lab through its final disposition. The chain-of-custody form will be filled out after the samples have been collected and will be double-checked prior to the transport of the samples to the laboratory. At a minimum, the chain-of-custody form will contain the following information and follow procedures described in SOP 7:

- Name of project
- Names of sampling personnel
- Sample identification numbers
- Collection date and time

- Number and type of containers per sample
- Sample matrix
- Sample preservation, if any
- Analysis requested.

The completed chain-of-custody form will be placed in a large capacity Ziploc® bag and secured to the sample transport container. If coolers are used to transport samples, the chain-of-custody form will be taped to the underside of the cooler lid.

3.7 DECONTAMINATION PROCEDURES

Equipment decontamination will be performed using procedures outlined below and in SOP 9. Site personnel will perform decontamination of all equipment prior to removal from the Site and between sample locations. All decontamination fluids will be containerized in properly labeled, DOT-approved, 55-gallon drums. If any solvents or acids are utilized during the decontamination process, they will be containerized in separate, properly labeled 5-gallon containers. Investigation-derived wastes will be handled in accordance with Section 3.8.

The hollow-stem augers, drill rods, and conductor casing will be decontaminated with a hot water pressure washer.

All non-disposable components of the sediment coring equipment (e.g., split spoons), or other equipment used to collect sediment samples that contacts the sediments, will be decontaminated as follows:

- Potable water rinse
- Alconox™/Liquinox™ detergent wash
- Potable water rinse
- Solvent rinse (if visible contamination is observed)⁵
- Deionized water rinse
- Air dry.

As specified in SOP 10 and the QAPP, rinsate blank samples will be collected once per sampling type (e.g., Power Grab sampling) to document the level of decontamination of sampling equipment. Two equipment rinsate blanks will be collected from the first two cores and will be expedited to the extent practicable (given the number of parameters and low-level methods required) to determine the effectiveness of the procedure. In the event contamination is

⁵ Solvent rinse will include the use of clean paper towels to remove water followed by a hexane rinse. The hexane solvent rinse is only required if visible non-aqueous phase liquid is observed on the sampling equipment.

detected in the rinsate blanks, a field change to the decontamination procedure would be implemented as outlined in Section 3.6.4.

All disposable personal protection equipment (PPE) and liquids generated as a result of decontamination processes will be containerized and handled as investigation-derived wastes, as discussed in Section 3.8 and SOP 11.

3.8 INVESTIGATION-DERIVED WASTES

The primary waste streams to be generated during this project and the proposed storage/disposal methods are described below. LSS is responsible for the proper characterization and disposal of investigation-derived waste streams.

3.8.1 Sediment Cuttings and Excess/Rejected Sediment Samples

Sediment cuttings from drilling activities will be placed in properly labeled, DOT-approved, 55-gallon drums on the barge deck. The drums will be lifted onto one of the docks at the end of the field event, staged on site, and characterized for offsite disposal in accordance with state and federal regulations.

Sediment samples that are rejected and/or determined to be in excess of what is required to conduct analytical sampling will be containerized in 55-gallon drums and managed as described in SOP 11.

3.8.2 Decontamination Wastewaters

Liquid wastes (i.e., decontamination waters) will be potentially contaminated with Site chemicals, including DDx. The presence of any of these constituents in the wastewaters is expected to be diluted; therefore, the wastewaters are not expected to be classified as hazardous waste. Decontamination waters will be containerized in 55-gallon drums as described in SOP 11. The drums will be lifted onto one of the docks at the end of the field event, staged on site, and characterized for offsite disposal in accordance with state and federal regulations.

For solvents (e.g., methanol and hexane), decontamination activities will be conducted so as to minimize the potential for spills/releases of wastewaters. Spent decontamination solvents must be stored in leak-proof container(s) with secured lid(s). The lid will remain closed except when the container is being used for decontamination activities. It is anticipated that liquid wastes will be placed in 5-gallon buckets or similar containers for characterization and offsite disposal.

3.8.3 Personal Protective Equipment/Miscellaneous Debris

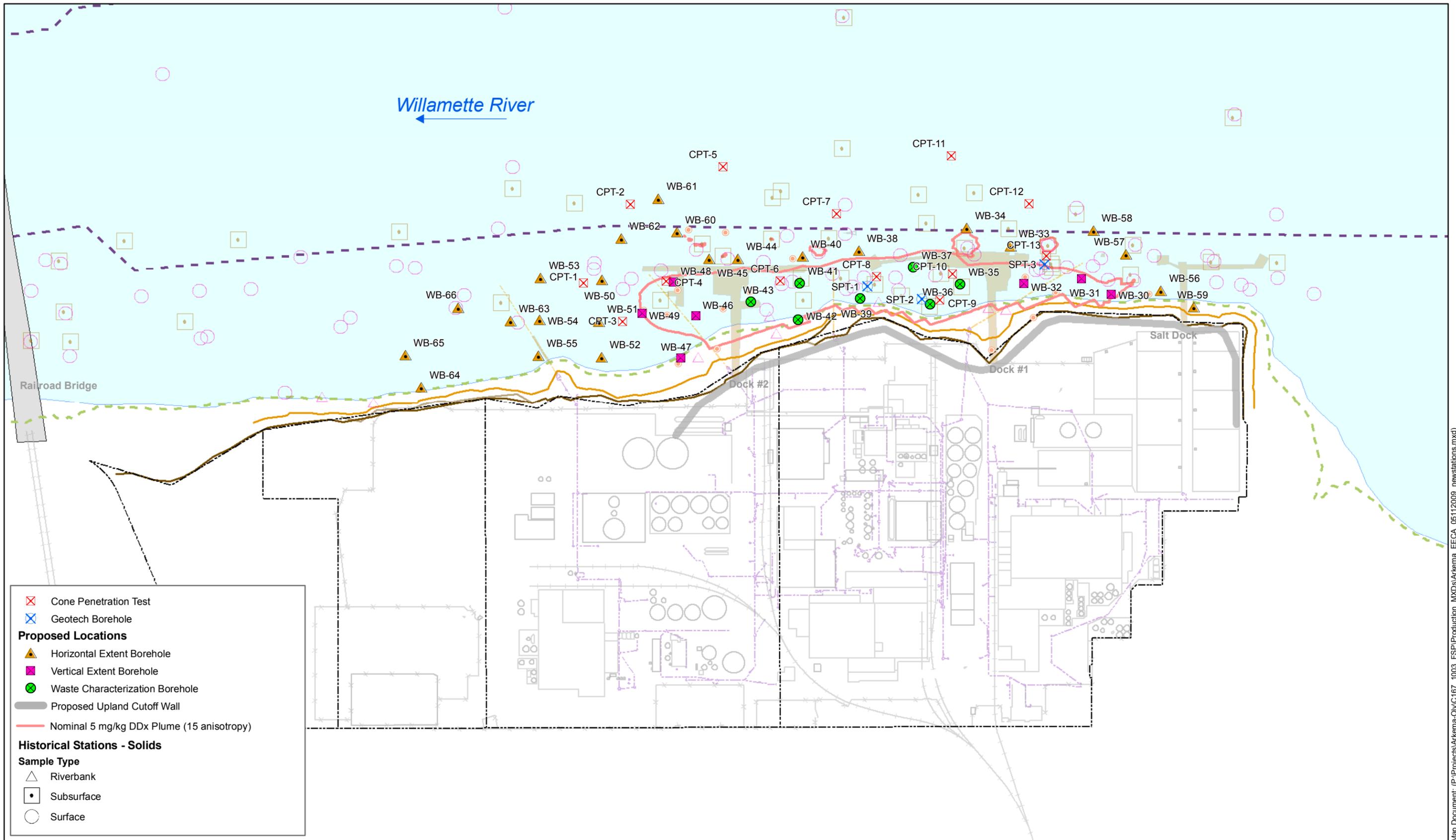
Sediment sampling activities will generate PPE and miscellaneous debris. Gross contamination will be removed from these items, and the items will be placed in plastic bags. Interim storage of these materials in plastic bags is acceptable. The bags will be disposed of at a solid waste facility dumpster at the end of each day.

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FIGURES



✕ Cone Penetration Test
✕ Geotech Borehole
Proposed Locations
▲ Horizontal Extent Borehole
■ Vertical Extent Borehole
● Waste Characterization Borehole
 Proposed Upland Cutoff Wall
 Nominal 5 mg/kg DDX Plume (15 anisotropy)

Historical Stations - Solids
Sample Type
 Riverbank
 Subsurface
 Surface

FEATURE SOURCES:
 Bathymetric Information: Multibeam bathymetric survey conducted by David Evans and Associates, Inc. from February 6 - March 6, 2004. Contours were derived from a Digital Terrain Model (DTM) based on a three-foot grid of multibeam data.
 Vertical Datum: North American Vertical Datum of 1988 (NAVD88).
 Horizontal Datum: North American Datum of 1983 - 91 adjusted (NAD83/91), State Plane Coordinate System (SPCS), Oregon North Zone.
 Units: International Feet.
 Basemap: Basemap features updated in 2006 by David Evans and Associates. Ordinary high water line, top of bank, and other site features surveyed in April 2006. Most buildings and structures on the Arkema site have been demolished or removed.
 OHW and Top of Slope lines were created from the April 2006 DEA survey, the +12ft contour line was derived from the combined lidar/bathymetry grid.
 Lot Lines: Created by importing pdf file from ERM, georeferencing to CAD lines (RMS error = 2.3042) and heads-up digitizing the lot lines.

 E-Sewer-L	 River
 Storm Drain	 Property and Lot Boundaries
 12ft Contour	 Docks and Structures 2005
 Bridges	 Ordinary High Water
 Navigation Channel	 Top of Bank

0 100 200 400 Feet

Figure 2-1
Arkema EE/CA
Proposed Sediment
Sampling Locations

Map Document: (P:\Projects\Arkema-O\167_1003_FS\P\Production_MXD\Arkema_EECA_05112009_newstations.mxd)
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TABLES

Table 2-1. Sampling/Analysis Methods – Potential Remedial Action Technologies^a

Sampling/Analysis Tools	Monitored Natural Recovery	Thin-Layer Placement	Isolation Cap	Sediment Dredging/Disposal – Characterization	Hydraulic Containment
Sediment Samples					
Chemical Analyses (COIs, Conventional ^b)	X	X	X	X	--
Physical Analyses (Grain Size)	X	X	X	X	--
Geotechnical Analyses					
Grain Size	--	--	X	X	X
Standard Penetration Test	--	--	X	X	X
Atterberg Limits	--	--	X	X	X
Specific Gravity	--	--	X	X	X
Moisture Content	--	--	X	X	X
Consolidation	--	--	X	X	X
Shear Strength ^c	--	--	X	X	X
Unconfined Compressive Strength (Rock)	--	--	--	X	X
Point Load Index (Rock)	--	--	X	X	X
Hydraulic Conductivity	X	X	X	--	X
Debris Survey	--	X	X	--	X

Notes:

- ^a Once the final RAA boundary is established, several factors pertaining to the area will be examined in the EE/CA report, including constructability, short-term impact, recontamination potential, permanence of the removal action, and proposed institutional controls.
- ^c May include *in situ* vane shear, cone penetration testing, and/or laboratory shear strength testing.
- ^d Suite of conventional and chemical analyses including anions/cations, TOC, COIs.
- ^e The ATT is required by Oregon for all applicable pesticide wastes in determining its acceptability into a Subtitle D Landfill.

- ✓ Sufficient data are available and no additional data and evaluation are needed for the sampling or analysis tool.
- X Insufficient data are available and additional data and evaluation are needed for the sampling or analysis tool.

-- Data not required for the EE/CA.
ATT – aquatic toxicity test
COI – constituent of interest

EE/CA – engineering evaluation/cost analysis
RAA – remedial action area
TOC – total organic carbon

Table 2-2. Sampling/Analysis Methods – Potential Disposal Alternatives^{a,b}

Sampling/Analysis Tools	Onsite Disposal		Offsite Disposal
	Nearshore CDF	Onsite Landfill	Subtitle C/D Landfill
Sediment Boreholes			
<i>Chemical Analyses (COIs, TOC)</i>	X	X	X
<i>Index Parameters</i>			
Grain Size	X	X	X
SPT	X	X	X
Atterberg Limits	X	X	X
Specific Gravity	X	X	X
Moisture Content	X	X	X
<i>Geotechnical Tests</i>			
Consolidation	X	--	--
Shear Strength ^c	X	--	--
Permeability	X	--	--
Unconfined Compressive Strength (Rock)	X	--	--
Point Load Index (Rock)	X	--	--
<i>Waste Characterization</i>			
RCRA Characteristic/TCLP	--	X	X
ATT	--	X	X

Notes:

^a Once the final RAA boundary is established, several factors pertaining to the area will be examined in the EE/CA report including constructability, short-term impact, recontamination potential, permanence of the removal action, and proposed institutional controls.

^b Chemical analyses that include an evaluation of the leachability of sediment will be conducted on representative composite samples prior to disposal.

^c Includes *in situ* vane shear, cone penetration testing, and/or laboratory shear strength testing.

X – Additional data required for this sampling/analysis tool.

-- Data not required for the EE/CA.

ATT – aquatic toxicity test

CDF – contained disposal facility

COI – constituent of interest

EE/CA – engineering evaluation/cost analysis

RAA – remedial action area

RCRA – Resource Conservation and Recovery Act

SPT - standard penetration test

TCLP – toxicity characteristic leaching procedure

TOC – total organic carbon

Table 2-3. Proposed Sediment Chemistry Boreholes, Analyses, and Rationale^a

Station No.	Proposed X Coordinate	Proposed Y Coordinate	Estimated Sediment Thickness (ft) ^b	Proposed Chemistry Sample Intervals and Parameters ^c	Borehole Rationale
WB-30	7628292.80	701945.99	40	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on samples from 8 - 10' bgs interval and below. ^d	Inside horizontal extent of nominal 5 ppm DDx plume, placed to define vertical extent.
WB-31	7628273.94	702029.99	25	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on samples from 8 - 10' bgs interval and below. ^d	Inside horizontal extent of nominal 5 ppm DDx plume, placed to define vertical extent.
WB-32	7628169.37	702134.57	25	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on samples from 10 - 12' bgs interval and below. ^d	Inside horizontal extent of nominal 5 ppm DDx plume, placed to define vertical extent.
WB-33	7628219.08	702223.72	10	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on all samples if WB-34 shows DDx > 5 ppm at any interval.	Outside horizontal extent of nominal 5 ppm DDx plume, placed based on Drill Guide analysis to refine horizontal extent if indicated by WB-34. If location is within horizontal RAA, data will also be used to help define vertical extent in that location.
WB-34	7628183.08	702340.30	5	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on all samples.	Outside horizontal extent of nominal 5 ppm DDx plume, placed based on Drill Guide analysis to refine horizontal extent. If location is within horizontal RAA, data will also be used to help define vertical extent in that location.
WB-35	7628063.08	702259.72	40	Sample and archive every 2' interval from sediment surface to 20' bgs, and every 3' interval from 20' bgs to bedrock. Composite and archive one sample using samples from 2' intervals from 0 - 10' bgs and from 10 - 20' bgs. Analyze as follows: Standard analysis for each 3' interval from 20' to bedrock. Expanded analysis + Asb on composite samples from 0 - 10' and 10 - 20'. ^d	Inside horizontal extent of nominal 5 ppm DDx plume, placed to define vertical extent and for waste characterization.
WB-36	7627973.93	702285.44	35	Sample and archive every 2' interval from sediment surface to 22' bgs, and every 3' interval from 22' bgs to bedrock. Composite and archive one sample using samples from 2' intervals from 0 - 10' bgs and from 10 - 22' bgs. Analyze as follows: Standard analysis for each 3' interval from 22' to bedrock. Expanded analysis + Asb on composite samples from 0 - 10' and 10 - 22'. ^d	Inside horizontal extent of nominal 5 ppm DDx plume, placed to define vertical extent and for waste characterization.
WB-37	7628018.50	702379.73	25	Sample and archive every 2' interval from sediment surface to 14' bgs, and every 3' interval from 14' bgs to bedrock. Composite and archive one sample using samples from 2' intervals from 0 - 6' bgs and from 6 - 14' bgs. Analyze as follows: Standard analysis for each 3' interval from 14' to bedrock. Expanded analysis + Asb on composite samples from 0 - 6' and 6 - 14'. ^d	Inside horizontal extent of nominal 5 ppm DDx plume, placed to define vertical extent and for waste characterization.
WB-38	7627960.21	702515.16	5	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on all samples if WB-40 shows DDx > 5 ppm at any interval.	Outside horizontal extent of nominal 5 ppm DDx plume, placed based on Drill Guide analysis to refine horizontal extent if indicated by WB-40. If location is within horizontal RAA, data will also be used to help define vertical extent in that location.
WB-39	7627869.35	702432.87	35	Sample and archive every 2' interval from sediment surface to 18' bgs, and every 3' interval from 18' bgs to bedrock. Composite and archive one sample using samples from 2' intervals from 0 - 8' bgs and from 8 - 18' bgs. Analyze as follows: Standard analysis for each 3' interval from 18' to bedrock. Expanded analysis + Asb on composite samples from 0 - 8' and 8 - 18'. ^d	Inside horizontal extent of nominal 5 ppm DDx plume, placed to define vertical extent and for waste characterization.

Table 2-3. Proposed Sediment Chemistry Boreholes, Analyses, and Rationale^a

Station No.	Proposed X Coordinate	Proposed Y Coordinate	Estimated Sediment Thickness (ft) ^b	Proposed Chemistry Sample Intervals and Parameters ^c	Borehole Rationale
WB-40	7627855.64	702616.31	5	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on all samples.	Outside horizontal extent of nominal 5 ppm DDx plume, placed based on Drill Guide analysis to refine horizontal extent. If location is within horizontal RAA, data will also be used to help define vertical extent in that location.
WB-41	7627799.06	702576.88	20	Sample and archive every 2' interval from sediment surface to 14' bgs, and every 3' interval from 14' bgs to bedrock. Composite and archive one sample using samples from 2' intervals from 0 - 6' bgs and from 6 - 14' bgs. Analyze as follows: Standard analysis for each 3' interval from 14' to bedrock. Expanded analysis + Asb on composite samples from 0 - 6' and 6 - 14'. ^d	Inside horizontal extent of nominal 5 ppm DDx plume, placed to define vertical extent and for waste characterization.
WB-42	7627725.34	702520.30	35	Sample and archive every 2' interval from sediment surface to 14' bgs, and every 3' interval from 14' bgs to bedrock. Composite and archive one sample using samples from 2' intervals from 0 - 6' bgs and from 6 - 14' bgs. Analyze as follows: Standard analysis for each 3' interval from 14' to bedrock. Expanded analysis + Asb on composite samples from 0 - 6' and 6 - 14'. ^d	Inside horizontal extent of nominal 5 ppm DDx plume, placed to define vertical extent and for waste characterization.
WB-43	7627682.48	702642.03	20	Sample and archive every 2' interval from sediment surface to 18' bgs, and every 3' interval from 18' bgs to bedrock. Composite and archive one sample using samples from 2' intervals from 0 - 8' bgs and from 8 - 18' bgs. Analyze as follows: Standard analysis for each 3' interval from 18' to bedrock. Expanded analysis + Asb on composite samples from 0 - 8' and 8 - 18'. ^d	Inside horizontal extent of nominal 5 ppm DDx plume, placed to define vertical extent and for waste characterization.
WB-44	7627744.20	702739.74	10	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on all samples if WB-40 or WB-45 show DDx > 5 ppm at any interval.	Outside horizontal extent of nominal 5 ppm DDx plume, placed based on Drill Guide analysis to refine horizontal extent if indicated by WB-40 or WB-45. If location is within horizontal RAA, data will also be used to help define vertical extent in that location.
WB-45	7627696.20	702796.32	5	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on all samples.	Outside horizontal extent of nominal 5 ppm DDx plume, placed based on Drill Guide analysis to refine horizontal extent. If location is within horizontal RAA, data will also be used to help define vertical extent in that location.
WB-46	7627564.19	702727.74	20	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on samples from 8 - 10' bgs interval and below. ^d	Inside horizontal extent of nominal 5 ppm DDx plume, placed to define vertical extent.
WB-47	7627456.19	702688.31	30	Sample and archive every 2' interval from sediment surface to bedrock. Standard on all samples.	Between horizontal extent of nominal 5 ppm DDx plume and shoreline, placed to define horizontal and vertical extent.
WB-48	7627593.34	702827.18	15	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on samples from 2 - 4' bgs interval and below. ^d	Inside horizontal extent of nominal 5 ppm DDx plume, placed to define vertical extent.
WB-49	7627480.19	702837.46	25	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on samples from 6 - 8' bgs interval and below. ^d	Inside horizontal extent of nominal 5 ppm DDx plume, placed to define vertical extent.
WB-50	7627478.47	702972.90	15	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on all samples.	Outside horizontal extent of nominal 5 ppm DDx plume, placed based on Drill Guide analysis to refine horizontal extent. If location is within horizontal RAA, data will also be used to help define vertical extent in that location.

Table 2-3. Proposed Sediment Chemistry Boreholes, Analyses, and Rationale^a

Station No.	Proposed X Coordinate	Proposed Y Coordinate	Estimated Sediment Thickness (ft) ^b	Proposed Chemistry Sample Intervals and Parameters ^c	Borehole Rationale
WB-51	7627391.04	702909.47	25	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on all samples if WB-50 shows DDx > 5 ppm at any interval.	Outside horizontal extent of nominal 5 ppm DDx plume, placed based on Drill Guide analysis to refine horizontal extent if indicated by WB-50. If location is within horizontal RAA, data will also be used to help define vertical extent in that location.
WB-52	7627325.89	702846.04	30	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on all samples if WB-51 shows DDx > 5 ppm at any interval.	Outside horizontal extent of nominal 5 ppm DDx plume, placed based on Drill Guide analysis to refine horizontal extent if indicated by WB-51. If location is within horizontal RAA, data will also be used to help define vertical extent in that location.
WB-53	7627380.75	703096.33	15	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on all samples.	Outside horizontal extent of nominal 5 ppm DDx plume, placed based on Drill Guide analysis to refine horizontal extent. If location is within horizontal RAA, data will also be used to help define vertical extent in that location.
WB-54	7627296.75	703029.47	25	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on all samples if WB-53 or WB-63 show DDx > 5 ppm at any interval.	Outside horizontal extent of nominal 5 ppm DDx plume, placed based on Drill Guide analysis to refine horizontal extent if indicated by WB-53 or WB-63. If location is within horizontal RAA, data will also be used to help define vertical extent in that location.
WB-55	7627224.75	702972.90	30	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on all samples if WB-54 shows DDx > 5 ppm at any interval.	Outside horizontal extent of nominal 5 ppm DDx plume, placed based on Drill Guide analysis to refine horizontal extent if indicated by WB-54. If location is within horizontal RAA, data will also be used to help define vertical extent in that location.
WB-56	7628380.23	701855.13	35	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on all samples.	Outside horizontal extent of nominal 5 ppm DDx plume, placed based on Drill Guide analysis to refine horizontal extent. If location is within horizontal RAA, data will also be used to help define vertical extent in that location.
WB-57	7628393.95	701983.71	15	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on all samples.	Outside horizontal extent of nominal 5 ppm DDx plume, placed based on Drill Guide analysis to refine horizontal extent. If location is within horizontal RAA, data will also be used to help define vertical extent in that location.
WB-58	7628387.09	702086.57	10	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on all samples.	Outside horizontal extent of nominal 5 ppm DDx plume, placed based on Drill Guide analysis to refine horizontal extent. If location is within horizontal RAA, data will also be used to help define vertical extent in that location.
WB-59	7628402.28	701762.98	35	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on all samples if WB-56 shows DDx > 5 ppm at any interval.	Outside horizontal extent of nominal 5 ppm DDx plume, placed based on Drill Guide analysis to refine horizontal extent if indicated by WB-56. If location is within horizontal RAA, data will also be used to help define vertical extent in that location.
WB-60	7627695.64	702903.53	10	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on all samples.	Outside horizontal extent of nominal 5 ppm DDx plume, placed based on Drill Guide analysis to refine horizontal extent. If location is within horizontal RAA, data will also be used to help define vertical extent in that location.

Table 2-3. Proposed Sediment Chemistry Boreholes, Analyses, and Rationale^a

Station No.	Proposed X Coordinate	Proposed Y Coordinate	Estimated Sediment Thickness (ft) ^b	Proposed Chemistry Sample Intervals and Parameters ^c	Borehole Rationale
WB-61	7627730.35	702995.27	20	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on all samples if WB-60 or WB-62 show DDx > 5 ppm at any interval.	Outside horizontal extent of nominal 5 ppm DDx plume, placed based on Drill Guide analysis to refine horizontal extent if indicated by WB-60 or WB-62. If location is within horizontal RAA, data will also be used to help define vertical extent in that location.
WB-62	7627591.50	703002.71	15	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on all samples if WB-50 or WB-60 show DDx > 5 ppm at any interval.	Outside horizontal extent of nominal 5 ppm DDx plume, placed based on Drill Guide analysis to refine horizontal extent if indicated by WB-50 or WB-60. If location is within horizontal RAA, data will also be used to help define vertical extent in that location.
WB-63	7627246.85	703084.53	30	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on all samples.	Outside horizontal extent of nominal 5 ppm DDx plume, placed based on Drill Guide analysis to refine horizontal extent. If location is within horizontal RAA, data will also be used to help define vertical extent in that location.
WB-64	7626969.15	703151.48	30	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on all samples if WB-65 shows DDx > 5 ppm at any interval.	Outside horizontal extent of nominal 5 ppm DDx plume, placed based on Drill Guide analysis to refine horizontal extent if indicated by WB-65. If location is within horizontal RAA, data will also be used to help define vertical extent in that location.
WB-65	7627006.34	703235.78	30	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on all samples.	Outside horizontal extent of nominal 5 ppm DDx plume, placed based on Drill Guide analysis to refine horizontal extent. If location is within horizontal RAA, data will also be used to help define vertical extent in that location.
WB-66	7627186.51	703210.09	30	Sample and archive every 2' interval from sediment surface to bedrock. Standard analysis on all samples.	Outside horizontal extent of nominal 5 ppm DDx plume, placed based on Drill Guide analysis to refine horizontal extent. If location is within horizontal RAA, data will also be used to help define vertical extent in that location.

Notes:

^a Separate boreholes will be advanced for geotechnical sampling (see Table 2-4).

^b Sediment thicknesses are estimated based on nearby historical sample stations.

^c Cores will be divided into 2' sections to bedrock or refusal, except for the surface sample that will be collected from 0 - 1'. Composite samples representing the whole length of the 2 - 3' core segments will be collected, mixed to homogeneity (as is possible), and analyzed. In addition, if any field indications of contamination within core sections are noted, discrete samples will be obtained from that portion of core segments that show staining, have odors, show "hits" on a field instrument, etc. All samples that are not analyzed will be archived for possible future analysis.

^d DDx analysis in 2' samples above designated depth interval is not required as it is assumed the upper sediments are within the RAA boundary and will be evaluated in the EE/CA.

Analytes:

Chemistry Standard Analyte List = DDx, conventionals (grain size, total solids, TOC).

Expanded Analyte List = Standard List + SVOCs, PCBs, Dioxins/Furans (D/F), VOCs; full suite of organochlorine pesticides.

Asb = Asbestos

bgs - below ground/sediment surface

DDx - total of 2,4'- and 4,4'-DDD, DDE, and DDT

EE/CA - engineering evaluation/cost analysis

PCB - polychlorinated biphenyl

RAA - removal action area

SVOC - semivolatile organic compound

TOC - total organic carbon

VOC - volatile organic compound

Table 2-4. Proposed Geotechnical Explorations, Analyses, and Rationale

Station No. ^a	Proposed X Coordinate	Proposed Y Coordinate	Estimated Sediment Thickness (ft) ^b	Proposed Geotechnical Parameters	Borehole Rationale
CPT-1	7627443.59	703002.76	20	CPT-tip resistance, sleeve friction, and pore pressure.	Geotechnical evaluation for EE/CA including sheet pile structure & CDF feasibility.
CPT-2	7627675.20	703040.27	10	CPT-tip resistance, sleeve friction, and pore pressure.	Geotechnical evaluation for EE/CA including sheet pile structure & CDF feasibility.
CPT-3	7627431.88	702862.93	25	CPT-tip resistance, sleeve friction, and pore pressure.	Geotechnical evaluation for EE/CA including sheet pile structure & CDF feasibility.
CPT-4	7627583.38	702843.54	20	CPT-tip resistance, sleeve friction, and pore pressure.	Geotechnical evaluation for EE/CA including sheet pile structure & CDF feasibility.
CPT-5	7627902.10	702919.88	10	CPT-tip resistance, sleeve friction, and pore pressure.	Geotechnical evaluation for EE/CA including sheet pile structure & CDF feasibility.
CPT-6	7627771.95	702619.08	20	CPT-tip resistance, sleeve friction, and pore pressure.	Geotechnical evaluation for EE/CA including sheet pile structure & CDF feasibility.
CPT-7	7627997.09	702618.77	5	CPT-tip resistance, sleeve friction, and pore pressure.	Geotechnical evaluation for EE/CA including sheet pile structure & CDF feasibility.
CPT-8	7627939.33	702436.36	25	CPT-tip resistance, sleeve friction, and pore pressure.	Geotechnical evaluation for EE/CA including sheet pile structure & CDF feasibility.
CPT-9	7627998.35	702273.97	35	CPT-tip resistance, sleeve friction, and pore pressure.	Geotechnical evaluation for EE/CA including sheet pile structure & CDF feasibility.
CPT-10	7628070.62	702291.73	30	CPT-tip resistance, sleeve friction, and pore pressure.	Geotechnical evaluation for EE/CA including sheet pile structure & CDF feasibility.
CPT-11	7628300.58	702488.28	10	CPT-tip resistance, sleeve friction, and pore pressure.	Geotechnical evaluation for EE/CA including sheet pile structure & CDF feasibility.
CPT-12	7628334.82	702256.31	10	CPT-tip resistance, sleeve friction, and pore pressure.	Geotechnical evaluation for EE/CA including sheet pile structure & CDF feasibility.
CPT-13	7628260.78	702136.63	20	CPT-tip resistance, sleeve friction, and pore pressure.	Geotechnical evaluation for EE/CA including sheet pile structure & CDF feasibility.
SPT-1	7627905.47	702438.77	25	Various geotechnical tests. See FSP text. ^c	Geotechnical evaluation for EE/CA. Collocated with CPT-8 for development of site-specific correlations of CPT parameters with design soil parameters. Rock coring to 20 ft below bedrock contact to determine rock quality.

Table 2-4. Proposed Geotechnical Explorations, Analyses, and Rationale

Station No. ^a	Proposed X Coordinate	Proposed Y Coordinate	Estimated Sediment Thickness (ft) ^b	Proposed Geotechnical Parameters	Borehole Rationale
SPT-2	7627970.42	702309.76	35	Various geotechnical tests. See FSP text. ^c	Geotechnical evaluation for EE/CA. Collocated with CPT-9 for development of site-specific correlations of CPT parameters with design soil parameters.
SPT-3	7628241.09	702126.03	20	Various geotechnical tests. See FSP text. ^c	Geotechnical evaluation for EE/CA. Collocated with CPT-13 for development of site-specific correlations of CPT parameters with design soil parameters.

Notes:

^a SPT borings will be advanced with mud-rotary equipment. CPTs will be performed with CPT equipment.

^b Sediment thicknesses were estimated based on nearby historical sample stations.

^c Geotechnical tests will be assigned based on conditions encountered during the field program.

CDF - confined disposal facility

CPT - cone penetration testing

EE/CA - engineering evaluation/cost analysis

FSP - field sampling plan

SPT - standard penetration testing

Table 3-1. Sample Containers and Preservation Requirements

Analysis	Laboratory	Container		Preservation	Holding Time
		Type	Size		
Sediment Quality Characteristics					
Grain size	TestAmerica Tacoma or Burlington	WMG	16 oz.	4 ± 2°C	6 months
Total organic carbon	TestAmerica Tacoma	WMG	8 oz.	4 ± 2°C	28 days
Semivolatile organic compounds	TestAmerica Tacoma	WMG	inc.	4 ± 2°C	14 days/40 days ^a
PCBs	TestAmerica Tacoma	WMG	inc.	4 ± 2°C	14 days/40 days ^a
Total solids	TestAmerica Tacoma	WMG	inc.	4 ± 2°C	6 months
Volatile organic compounds	TestAmerica Tacoma	WMG with Septa	2 oz.	No headspace, 4 ± 2°C Do not freeze	14 days
Organochlorine pesticides	TestAmerica Burlington or Knoxville	WMG	8 oz.	4 ± 2°C	14 days/40 days ^a
Chlorinated dioxins/furans	TestAmerica West Sacramento	WMG	8 oz.	4 ± 2°C	1 year
Archive	TestAmerica Tacoma	WMG	16 oz. ^b	Deep frozen (-20°C)	TBD
Physical and Engineering Characteristics					
Subsurface Sediments					
<i>Physical Characteristics</i>					
Grain size	Kleinfelder	WMG	16 oz. ^c	4 ± 2°C	6 months
Atterberg limits	Kleinfelder	WMG		4 ± 2°C	--
Specific gravity	Kleinfelder	WMG		4 ± 2°C	--
Moisture content/density	Kleinfelder	WMG		4 ± 2°C	--
<i>Engineering Characteristics</i>					
Consolidation	Kleinfelder	Sealed Shelby Tube	--	4 ± 2°C	--
Unconsolidated undrained triaxial shear stress	Kleinfelder	Sealed Shelby Tube	--	4 ± 2°C	--
Consolidated undrained triaxial shear stress	Kleinfelder	Sealed Shelby Tube	--	4 ± 2°C	--
Hydraulic conductivity	Kleinfelder	Sealed Shelby Tube	--	4 ± 2°C	--
Torvane shear strength testing	Kleinfelder	Sealed Shelby Tube	--	4 ± 2°C	--
Unconfirmed compressive strength (Rock)	Kleinfelder Redmond	TBD	--	NA	--
Point load index (Rock)	Kleinfelder Redmond	TBD	--	NA	--

Table 3-1. Sample Containers and Preservation Requirements

Analysis	Laboratory	Container		Preservation	Holding Time
		Type	Size		
Sediments for Waste Characterization					
Toxicity Characteristic Leaching Procedure					
TCLP testing ^d	TestAmerica Tacoma	WMG	8 oz.	4 ± 2°C	14 days
Asbestos					
Asbestos	TBD	WMG	8 oz.	--	180 days
Field Blanks					
Total organic carbon	TestAmerica Tacoma	HDPE	250 mL	4 ± 2°C; H ₂ SO ₄ to pH < 2	28 days
Organochlorine pesticides	TestAmerica Burlington or Knoxville	AG	2 x 1 L	4 ± 2°C	7 days/40 days ^e
PCB Aroclors	TestAmerica Tacoma	AG	1 L	4 ± 2°C	7 days/40 days ^e
Semivolatile organic compounds	TestAmerica Tacoma	AG	2 x 1 L	4 ± 2°C	7 days/40 days ^e
Volatile organic compounds	TestAmerica Tacoma	VOA vial	3 x 40 oz. w/ septum	No headspace; HCl to pH < 2; 4 ± 2°C	14 days
Chlorinated dioxins/furans	TestAmerica West Sacramento	AG	2 x 1 L	4 ± 2°C in the dark	1 year

Notes:

^a Holding time is 14 days to extraction and extracts must be analyzed within 40 days from extraction.

^b Two 16 oz jars will be collected for sample intervals chosen for archive.

^c One 16 oz. jar will be collected for all physical characteristics.

^d For standard TCLP VOCs, SVOCs, metals, pesticides, and herbicides (42 individual chemicals) using EPA SW-846 methods.

^e The holding time is 7 days from collection to extraction and 40 days from extraction to analysis.

AG - amber glass

HDPE - high density polyethylene

NA - not applicable

PCB - polychlorinated biphenyl

SVOC - semivolatile organic compound

TBD - to be determined

TCLP - toxicity characteristic leaching procedure

VOA - volatile organic analysis

VOC - volatile organic compound

WMG - wide mouth glass

ATTACHMENT A

STANDARD OPERATING PROCEDURES

STANDARD OPERATING PROCEDURE SOP-1: NAVIGATION AND POSITIONING

Scope and Application

Accurate station positioning is required to help ensure quality and consistency in collecting samples and in data interpretation and analysis. Station positioning must be both absolutely accurate in that it correctly defines a position by latitude and longitude, and relatively accurate in that the position must be repeatable, allowing a user to reoccupy a station location (e.g., long-term monitoring programs).

This SOP describes the most commonly used station positioning method, Differential Global Positioning System (DGPS). Integral owns the following DGPS hardware and software systems for station positioning at many of their field efforts.

- Trimble Pathfinder™ Pro XRS system (TSC1 handheld unit, GPS receiver and GPS antenna)
- Trimble GeoXT
- Trimble Pathfinder Office (Version 4.0)
- Trimble TerraSync Professional (Version 3.05)
- ESRI ArcPad 7.1

The Trimble DGPS offers post-processing sub-meter accuracy often required for documenting sampling station locations and for relocating previously sampled stations. A thorough and comprehensive discussion of the Trimble DGPS is provided in attachments to this SOP.

Summary of Method

Global positioning system (GPS) navigation is used to navigate and position the sampler at the desired location. GPS is a satellite-based system that receives positioning data at 1-second intervals from multiple satellites at known positions in space. Standard GPS is calculated to an accuracy of about ± 50 m.

A higher accuracy of approximately 2 m may be obtained by applying differential corrections to the standard GPS positioning data using DGPS. These differential corrections are applied by sending GPS differential corrections to the GPS receiver via radio transmission. If the sampling location is near the coastal United States, the U.S. Coast Guard generates differential corrections that are transmitted via radio link to the

GPS receiver. If a Coast Guard station is out of range of the sampling area, then a receiver may be set up at a known (i.e., surveyed) reference point on land or real-time satellite differential signals can be purchased from a private company (e.g., OmniSTAR).

With the Trimble GeoXT and Pro XRS systems, GPS data can be gathered to sub-meter accuracy using a choice of differential correction sources (i.e., free beacon differential signals [e.g., Coast Guard or U.S. Forest Service beacons] or OmniSTAR) without establishing a reference station. Correction of data is required to gain sub-meter accuracy. Free beacon or base station signals allow differential corrections to be performed after data collection by using a nearby beacon or base station logging data files. (Note: Station must be within 150 km (93.2 miles) of the data collection location.) For satellite-based signals, a built-in virtual base station allows for real-time data correction, eliminating the need for post-processing data in some cases. However, post-processing data corrections can obtain accuracies in the range of 30–50 cm. These accuracies are for the horizontal (northing and easting) component only. The vertical component (elevation) accuracy ranges from sub meter to three times larger than the horizontal accuracy.

The GPS receiver transmits differentially corrected positioning data to the computer and displays it on the screen using an integrated navigation software package (e.g., HYPACK, TerraSync). The computer data are typically displayed and recorded in World Geodetic System of 1984 (WGS-1984) geographic coordinates (latitude/longitude). However, the integrated navigation system can display and record information in other datums (e.g., UTM, NAD83, etc.). The integrated navigation system, acting as a data manager, displays the sampler's position relative to a target station location in plan view on a video screen. The resulting pictorial screen presentation, as well as numeric navigation data (e.g., range and bearing to the target sampling location) assists the vessel operator (when sampling on-water) in approaching and maintaining the station position while sampling.

Supplies and Equipment

- Cables (antenna to receiver, receiver to computer)
- Trimble Pro XRS GPS antenna
- Trimble Pro XRS GPS receiver with battery charger and batteries
- Trimble TSC1 handheld data logger unit with Asset Surveyor software
- Trimble GeoXT handheld GPS unit (antenna, receiver and computer all-in-one unit) with battery charger/docking station and cables
- Trimble® GeoBeacon™ receiver for precision of real-time differential GPS (use with GeoXT)
- Laptop computer and additional navigational monitor (if needed)
- Navigation software (e.g., Terrasync and Pathfinder Office)

- Laser range finder (use TruPulse™ 200 or 360 Laser Rangefinder - Blue Tooth™ enabled)
- Logbook or log sheets.

Procedures

Latitude and longitude coordinates will be obtained at the locations where surface water samples are collected. An average positioning objective is to accurately determine and record the positions of all sampling locations to within ± 2 m. Positioning accuracies on the order of $\pm 1-3$ m can be achieved by avoiding the few minutes per day when the satellites are not providing the same level of signal. The GPS provides the operator with a listing of the time intervals during the day when accuracies are decreased. Avoidance of these time intervals permits the operator to maintain better positioning accuracy.

On-Land Sampling Event

A Trimble Pro XRS backpack or a handheld Trimble GeoXT (equipped with a GeoBeacon™ receiver) DGPS unit may be used to direct the sampling team to the proposed sampling location. To expedite field activities, the target station coordinates may be entered in the navigation system database prior to beginning sampling. The DGPS antenna is located as close as possible to where the sampling will occur. Once the sample(s) have been collected at the appropriate location, the horizontal coordinates of the station are recorded in the field logbook. If necessary, the vertical elevation may be recorded as well.

On-Water Sampling Event

When collecting samples from a boat, the GPS Pathfinder Pro XRS system is used. The receiver is a real-time GPS mapping receiver combining a GPS receiver, a minimum shift keying (MSK) beacon differential receiver, and a satellite differential receiver in a single housing, the GPS Pathfinder Pro XRS receiver offers the flexibility for choosing a source for real-time differential corrections.

The GPS antenna is mounted right above the location where the sample will be collected. That is, the antenna is mounted vertically at the outboard end of the vessel's boom, at the top middle of an A-frame or at the outboard end of a davit. If this is not possible, the navigator must measure the distance between the sampler location and the antenna and enter an offset in the navigation program (e.g. TerraSync) to correct for that distance. The GPS antenna cable extends along the boom into the cabin where it is connected to the GPS receiver and a laptop. If available, an additional video screen is installed to allow the vessel operator to observe on-screen positioning data from the helm.

Alternatively, if sampling will be done from a different vessel, such as a drilling barge, a backpack or handheld DGPS unit may be used to position the sampling vessel over a proposed sampling location. The DGPS antenna is located as close as possible to where the drilling will occur (i.e., over the moon pool). The person operating the DGPS unit directs the sampling vessel operator to the sample station location.

Once the sampling vessel is at the appropriate location and is anchored, the horizontal coordinates of the station are recorded in the field logbook. To expedite field activities, the target station coordinates may be entered in the navigation system database prior to beginning sampling.

Positioning System Verification

GPS requires no calibration, as all signal propagation is controlled by the U.S. government (the Department of Defense for satellite signals and the U.S. Coast Guard and U.S. Forest Service for differential corrections). Verification of the accuracy of the GPS requires that coordinates be known for one (or more) horizontal control points within the study area. The GPS position reading at any given station can then be compared to the known control point. If possible, GPS accuracy should be verified at the beginning or at the end of each sampling day.

Station Positioning Activities

A consistent routine is used for each day's positioning activities. After successful reception of differential signals, the computer turned on, and the software booted. The accuracy of the system is verified at a horizontal control point, as described in the previous section.

At the beginning of a sampling day, the team leader defines the order in which each sampling station will be visited. The station locations are then selected one at a time from a number of pre-selected station locations that have been entered into the integrated navigation system database. Upon selection of a target station, the positioning data of the sampler is displayed on the computer screen or hand-held unit to assist the operator in proceeding to the station, and if on water work, in maintaining the station position during sampling. A confirmed position is recorded electronically each time a sample collection is attempted (this means that during sediment grab sampling and coring from a boat, the locations of both accepted and rejected grabs or cores are recorded). Upon recovery of the sampling device, the station position coordinates (i.e. northing (y) and easting (x) or latitude and longitude) are read from the archived computer file and recorded in the field logbook or on log sheets as a backup to the computer record. Time and water depth (if applicable) are also recorded. Ancillary information recorded in the field logbook may include personnel operating the GPS system, tidal phase or river stage for on-water work,

elevation for on-land work, type of sampling activity, and time when coordinates were collected.

References

Trimble Navigation Limited. 2001. TSC1 Asset Surveyor operation manual. Version 5.20. <http://trl.trimble.com/dscgi/ds.py/Get/File-8145/Oper.pdf>

Trimble Navigation Limited. 2007. GPS tutorial. Accessed on January 12, 2007. <http://www.trimble.com/gps/index.shtml>

ATTACHMENT 1

TRIMBLE PRO XRS AND TSC1 DESCRIPTION

The Trimble Pathfinder™ Pro XRS combines a high-performance GPS receiver and antenna, beacon differential receiver, and satellite differential receiver (Wide Area Augmentation System [WAAS]) capabilities in one compact unit. The Pro XRS also includes Trimble's advanced Everest™ technology, which allows users to collect accurate position data near walls, water, vehicles, or other surfaces that reflect satellite signals. Reflected signals, also called multipath signals, make it difficult for GPS receivers to accurately determine position. Everest uses a patented technique to remove multipath signals before measurements are used to calculate position.

Equipment Required

The GPS Pro XRS with a TSC1 data logger consists of the following:

- GPS receiver in backpack casing (with system batteries and cables)
- Hand-held data logger (TSC1) and cable, OR Laptop with Terrasync software installed and cable. (Note: Terrasync procedures are covered under Attachment 5.)
- Pro XRS antenna, range poles, and cable
- Compass and tape measure
- Spare 12-volt camcorder and 9-volt batteries (minimum of 2 each) (use only Kodak, Duracell, or Energizer 9-volt batteries)
- Battery charger and power cord.

Pro XRS and TSC1 Setup

Follow these procedures for the proper setup of the Pro XRS:

1. Ensure connections between batteries, receiver and data logger are correct and secure. The coaxial antenna cable connects from the GPS receiver port "ANT" to the base of the antenna. The TSC1 cable (a "pig-tail"-type cable) connects from the bottom or top of the TSC1 to the receiver port "B", where a 9-pin serial port dongle is attached. The dual Y-clip cables should be connected from the receiver to the batteries. Alternatively, if AC power is available (e.g., aboard a vessel), then the power cable for the battery charger can be attached directly to the receiver on some models.

2. Screw the three long antenna poles together (the shorter pole may be added if necessary for taller users). Screw on the antenna and connect its cable.
3. Put backpack and/or shoulder strap on. The pouch for the data logger should be in place around the waist strap/in backpack.
4. Screw antenna to the attachments on the top of the back-pack. Wind cord around pole, and use ensure the antenna is secure. Please be aware of overhead hazards, especially if working near low hanging power lines. Severe injury or death can result.

Basic Operation of the Pro XRS

Recording a Feature

Before beginning field use, ensure that all GPS configurations and settings are set correctly for the particular use of the Pro XRS and that an appropriate data dictionary is loaded onto the TSC1 (See Attachment 4 and 5 for typical settings). These steps outline the basic use of the GPS to document a sample position or any other defined "feature." Note that the TSC1 has both hard-keys and soft-keys that allow for its operation. The hard-keys are all the keys (e.g., letters and numbers) on its surface. The soft-keys are the F1 through F5 hardkeys. The function of these changes depending upon the context. These keys will be referred to with arrows around them (<soft-key>).

1. Turn data logger on outside in an open area. Wait for antenna to receive satellite signals. The display will read "Recording Almanac," "Too few SVs," and "PDOP too high." Continue to wait until enough satellites (a minimum of 4) are acquired, and the PDOP is below 5.0.
2. Ensure that the real-time settings are correct according to the parameters listed in Attachment 1.
3. Select DATA COLLECTION, and create a new rover file or open an existing file. This file should be named according to the format specified by the project GIS analyst. Note: If opening an existing file press <NEW> to access the "Antenna options" menu and "Start Feature" menu.
4. Enter the height of the antenna from the ground to the "Measurement Method" reference point shown in the "Antenna Options" menu and then press ENTER to bring up the "Start Feature" menu.

5. Pick the appropriate data dictionary to use with the rover file. Only one dictionary can be used with a rover file. Please consult with the project GIS analyst to formulate the most appropriate data dictionary for the type of sampling you wish to perform. The data dictionary entitled “Generic,” contains only a comment field, and is appropriate for simple navigation tasks. If using a data dictionary, make sure to become familiar with its attributes before recording information in the field.
6. Move to the location of the first feature for which you want to record the GPS position. Select the appropriate feature and press ENTER to begin logging. Log data points in accordance with the feature type. Point features should have at least 10 points collected at a stationary location. Line features should be collected while moving. If movement is stopped, press the <PAUSE> key. When movement starts again, press the <RESUME> key. Area features should be collected with enough points to define the outline of the area (e.g., a square building would have four single points, collected on each corner, and the <PAUSE> key would be used between each of the points).
7. Depending on the setup of the data dictionary, each feature may have one or more feature attributes. An attribute is used to record additional data associated with the feature. For example, the attributes assigned to a sediment sampling station could be sample number, station ID, sampling gear, sediment color, odor, etc. (The <PAUSE> key should be used while recording feature attributes to avoid too many data points being collected at one point feature. [Body movements while logging attributes for an extended time can decrease the accuracy of collection.] The <PAUSE> key must be used when recording attributes of a line or area feature because only one data point should be collected in a single location.) Once all attributes are entered and the feature data points are logged, press ENTER to complete and save the feature and move on to a new feature. Pressing ESC instead of ENTER will allow the user to abandon the logged feature without saving.
8. When all features in a given area have been recorded, from the “Data Collection” menu press ESC to exit data capture and then press <YES> to close the file. Features are appended and saved to the file after each collection, so there is no need to “save” the file. When the Pro XRS system is not in use, it should be turned off. If you need to come back to the same rover file later in the day, the rover file may be reopened at that time. Rover files may not be edited after 7 days from the first feature was created. Please consult the project GIS analyst for the best way to handle multi-week sampling projects. Ideally, files should be saved and sent to the GIS daily for differential corrections. Files older than a week will require access to archived base station files for differential corrections and will require additional GIS time for post-processing.

Post-processing may be done in the field if the appropriate software and internet connections are available.

9. At the end of each day, the rover file should be downloaded to a PC by using Pathfinder Office software and if possible, sent to the GIS team for post-processing and QA/QC checks.

Feature Collection Options

Offsets—The TSC1 can collect a point or line feature while standing at a set distance away from the feature. This option may be necessary because of obstructions such as tree cover, buildings, or car traffic. For a point feature, measure the distance between the object you want recorded and the Pro XRS antenna. Use the compass to determine the bearing (e.g., west is 270°). The bearing is the direction the point should be moved for it to be located in the correct place (e.g., if you are due north of the feature, the bearing is south or 180°; i.e., the position you want recorded is south of where you are standing). Estimate the inclination from the feature to the GPS antenna (if height determination is critical, a clinometer should be used). The inclination is the degree angle up from the feature to the antenna (e.g., if the feature is 5° below the antenna position, -5° would be entered). During data capture, from within the feature, press the <OFFSET> button, and enter the distance, bearing, and inclination. Press OK to complete the feature.

Note: This procedure describes an offset of a single feature. A constant offset may be applied to all features collected as well.

Nesting—While recording a line feature or an area feature, a point feature may be collected to avoid backtracking. While recording the line or area feature, press <PAUSE> and then <NEST>. The TSC1 will prompt for collection of a new feature. Move to the feature, and collect data as for any other point feature. When the feature is complete, press OK. The Pro XRS is ready to resume collecting data as part of the line/area feature: press <RESUME>. (Remember to continue moving before pressing resume to avoid having multiple positions recorded in the same place in the line or area feature.)

Segmenting—While moving along a line feature, changing the attributes of that line may be necessary (e.g., because of a change in surface type from paved to dirt road, dropping a benthic sledge at the bottom of a river and marking when the benthic tow starts). This change may be done without having to begin a new feature by pressing <PAUSE> and then <SEGMENT>. Change the appropriate attributes and then press <RESUME> to continue recording.

Repeat—The function allows the collection of a new feature with the same feature attributes as the previous feature. If features are not exactly the same, it also allows editing of the attributes.

Quickmark— Allows collection of point features while moving (e.g., from a car or a boat) by estimating the exact location. The use of this feature will not result in positionally accurate locations and is not recommended for most sampling operations.

Reviewing and Editing Features

It is possible to review or edit features collected in the field while still in the data capture mode. For example, it may be necessary to document the GPS location in the field logbook or to edit one of the feature's attributes. Without exiting data capture, press <REVIEW>. (If data capture is already complete, just press REVIEW and then select the appropriate rover file.) This step will display a list of data points including each feature collected. Scroll to the appropriate feature, and follow the steps below depending on the required action:

- To view the GPS location (e.g., lat/long), press <POS>
- To edit the attributes, press ENTER. Make any necessary edits to the attributes by scrolling through.
- To change or add an offset, press <POS>, then press <OFFSET>. Make any necessary changes.
- To delete a feature collected in error, press .

Navigating to an Existing Location

Waypoints

To use the Pro XRS to navigate to a previously established position, this position must be loaded into the TSC1 data logger as a waypoint, be present as a feature position in the data files, or must be generated in the field using the GPS unit. Waypoints may be entered into the TSC1 by:

- Manually entering coordinates
- Choosing previously recorded locations and importing them into the TSC1 by using Pathfinder Office
- Defining a location stored in a rover file saved to the TSC1 as a waypoint (see *Reviewing/Editing Features*, above)
- Creating a way point from the current position being shown by the operating GPS unit in the field.

Navigating

Usually the *Navigation* module (accessed by pressing MENU followed by Navigation) will be used to guide yourself to a target (waypoint or feature). You can also use the *Map* module (accessed by pressing MENU followed by Map) to:

- Orient yourself in the area you are working in
- Get a general indication of the location of a feature or waypoint that you want to find
- Find or select features or waypoints that you want to navigate to
- Plot a course from one place to another.

While in the Map screen, the GPS cursor x shows the current position reported by the receiver and is always shown on the Map screen (note: it may not always be within the visible part of the screen when panning or scrolling). The <OPTIONS> key can be used to hide or display the GPS trail (line of dots showing up to 60 previous positions), the heading showing the direction of travel, and other options on the map display.

A feature can be selected by pressing MENU, Data Collection to reach the “Start Feature” screen, and then REVIEW to access all features contained in the data file. The desired feature can then be highlighted and selected by pressing the <Target> key which adds a crossed flag to the feature. The Map screen can be re-accessed by selecting MENU, then Map, which will now show the highlighted feature with a crossed flag symbol on the Map screen. The user can then start moving toward the feature and the current position (shown by the x) will move closer to the target position as the user approaches.

There are two graphical modes of navigation with the Pro XRS in the TSC1 *Navigation* module. On both modes text information appears on the right of the screen in the *Info* panels, which can be configured by the user. The graphic modes available are the *Directional Dial* screen or the *Road* screen, which can be toggled between using the <Mode> key.

To navigate you need to select a target and then a start position. Each of these positions can be features from an open data file or a waypoint. A list of available features or waypoints can be accessed by pressing <TARGET> or <START>. Once the item has been chosen as a target it will show the crossed flags symbol in the list. Once a target has been selected, the Distance to Go appears at the bottom of the Navigation screen, which indicates the distance from the current GPS position to the target. Select a start position (not required but useful for calculating crosstrack error and other navigation information) by pressing <START>. A waypoint of the current GPS position can be created for use as the Start point by selecting <CREATE>. Once the Start position is selected, a flag symbol will appear next to the item in the list.

In the *Directional Dial* mode an arrow will appear that will always point at the target. This is the bearing to go (Note: you need to be moving for this to be accurate as it will lock if you are moving too slowly or are stopped). The triangle at the top of the circle represents the direction that you are going or heading. This triangle never moves, but by changing directions you can line up the arrow with the triangle. When the two are aligned you are heading in the direction of the target. When you are close to the target a bull's-eye (two concentric circles) will appear at the edge of the screen. This is warning you that the unit will be switching to the close up screen. A proximity alarm will sound and the directional arrow will be replaced by the bull's-eye on the close up screen. Your current position will be shown by an x and the target by the bull's-eye. Move so that the x is in the same location as the bull's-eye.

In the *Road* mode you navigate by walking down a road. Your position is shown by a stick figure and is always positioned in the center of the screen. The target (crossed flags) shows the point that you are navigating to. Your heading is shown by the top center of the screen and the bearing to go is shown by the direction of the road, which will rotate as you change your heading. Change your heading until the road is pointing at the top of the screen (Target is also at the top of the screen) and the edges are parallel to the sides of the screen. As you move toward the target the screen zooms in, so the road appears to get wider.

Downloading Rover Files

Upon returning to the office, all rover files should be downloaded from the TSC1 to a PC for post-processing. You will need the Trimble Pathfinder Office software installed on your computer. If not using a field laptop that already has the program installed, please contact your project GIS analyst for instructions on how to install the software.

Connect the TSC1 to your computer using the appropriate cables. In addition to the "pigtail" cable, you will also need a null modem, which is a 9-pin female to female cable, in order to plug into a PC serial port. Once connected, power up the TSC1 unit and navigate to MENU, File Manager, File Transfer. Then, open the Pathfinder software and navigate to the *Utilities>Data Transfer...* window from the menu bar. Select GIS Datalogger on COM1 (for most computer systems), and press the green connect button. Files can be downloaded from the TSC1 by selecting the Receive tab and choose the data file type from the Add pulldown menu. After downloading, all rover files and waypoints should be removed from the TSC1 to conserve memory. Rover files may be deleted from the File Manager menu.

1. Select MENU, File Manager, then delete file(s).
2. Select the rover file to be deleted, and press <ENTER>.
3. Confirm the deletion of this file by pressing <YES>.

Data dictionaries can be deleted in the same manner by selecting Data dictionaries from the File Manager menu. Waypoints may be deleted by selecting Utilities from the Main menu and then by selecting Waypoints followed by .

ATTACHMENT 2

TSC1 SETTINGS

The following are lists of menus that can be accessed through the TSC1 keypad. Please ensure that settings are correct before proceeding. Please do not make changes to the settings unless necessary. Each menu will list all available subheadings, the correct setting, and the available <soft-keys> to access additional menus. Comments are included only where necessary.

GPS Rover Options

Access this menu by selecting Configuration from the main menu and then select GPS Rover Options.

Logging Options	Setting	Comment
<u>Logging intervals</u>		
Point feature	1s	
Line/area feature	2s–5s	depending upon speed of movement
Not in feature	None	
Velocity	None	
Confirm end feature	No	
Minimum pos	10	
Carrier Mode	Off	
Carrier phase min time	10 min	
Dynamics code	Land	may be changed to sea or air, as appropriate
Audible click	Yes	
Log DOP data	Yes	
Log PPRT data	Yes	
Log QA/QC data	Yes	
Allow GPS update	Warn First	
Warning Distance	Any	
Position Mode Manual	3D	
Elevation Mask	15°	Should not go below 15° (accuracy decreases)
SNR Mask	6.0	Can raise to 7 if multi-path filtering is poor
PDOP Mask	5.0	Can be raised up to 8 – reduces accuracy
PDOP Switch	6.0	

Real-Time Input Options

This menu can be accessed from the GPS Rover options menu by selecting real-time input.

Option	Setting	Comment
Preferred Correction Source	Choice 1	Integrated Beacon
	Choice 2	Integrated WAAS
	Choice 3	Use uncorrected GPS
Correction age limit	20s	

Antenna Options

This menu can be accessed from the GPS Rover options menu by selecting Antenna Options.

Option	Setting	Comment
Height (from ground)	in m or ft	Enter correct user antenna height using measurement method indicated below
Measure Type	Uncorrected Integrated GPS/Beacon/Satellite	
Confirm	Per file	Can be changed to "Per feature" if antenna height varies and elevation is critical
Part Number	33580-50	Auto selected based on TYPE selected
Measurement Method	Bottom of Antenna Mount	

ATTACHMENT 3

ADDITIONAL SETTINGS FOR THE TSC1

Additional TSC1 settings can be found in the configuration menu. Items of particular importance are indicated in italics.

Configuration

This menu can be accessed by selecting Configuration from the main menu.

Configuration	Description
GPS base station options	For using a land base station or beacon for real time corrections
NMEA/TSIP output	Consult manual
Coordinate system	Changes coordinate system among latitude/longitude, UTM, and other coordinate systems. System can be converted, if necessary, after data capture by using Pathfinder Office software.
Map Display options	Change layers, scale, background files and items shown on the TSC1 screen during data collection
Navigation options	Changes Navigation parameters
Units and display	Changes various units, for example: length (e.g., feet, meters), elevation reference (e.g., MSL), <i>North reference</i> (i.e., true or magnetic). Units can be converted, if necessary, after data capture by using Pathfinder Office software.
Time and date	Changes to <i>local time</i> , 24 hour clock, date format, etc.
Quickmarks	Set-up parameters for use with quickmarks.
Constant offset	Set-up parameters for use with a constant offset.
External sensors	Connections with external sensors.
Hardware (TSC1)	TSC1 settings such as beep volume, contrast, <i>internal and external battery status</i> , software version, free space.

Contrast and Backlighting

The TSC1 display can be viewed in various light settings. Pressing FUNC, then L turns on the display backlight for viewing in dim lighting. In addition, the contrast can be adjusted by pressing FUNC, then E or F.

ATTACHMENT 4

PRE-SAMPLING ACTIVITIES BEFORE USE OF THE PRO XRS DGPS UNIT

Determination of Optimal Satellite-Use Time

Positioning accuracies on the order of $\pm 1-3$ m can be achieved by avoiding the few minutes per day when the satellites are not providing the same level of signal. The GPS provides the operator with a listing of the time intervals during the day when accuracies are decreased. Avoidance of these time intervals using Trimble's Mission Planning software permits the operator to maintain better positioning accuracy.

Mission Planning

Trimble's Planning software is a stand-alone software tool supporting any form of analysis to determine visibility for GPS and geostationary satellites. It can be downloaded for free at:

http://www.trimble.com/planningsoftware_ts.asp

The location can be picked from a list of cities from all over the world, select a location from the world map or type in the local WGS84 position to do more precise mission planning.

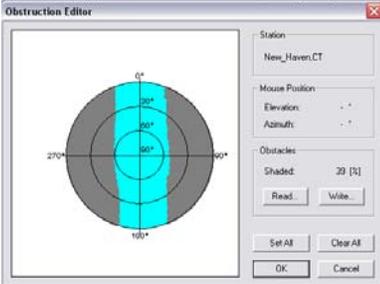
- Put in multiple station locations to determine the best time to observe these stations simultaneously.
- Get detailed sky plots (including obstructions) of the site for any time of the day to aid in determining the best available occupation times.
- Chart out the different DOP values by time
- Get a quick overview on the number of satellites available for the site, for any time of the day.

Using the Mission Planning Software

1. First, download the latest version of the Trimble Planning Software from the web site listed above. Be sure to download the latest Ephemeris file from the same page.

2. Install the software to a computer on which you have the appropriate permissions.
3. Start the Trimble Planning Software.
4. On the Main Menu, go to Almanac > Import > SSF...
5. Browse through the same folder where the Ephemeris file was saved. Select it and click Open.

Setting the GPS Survey Parameters

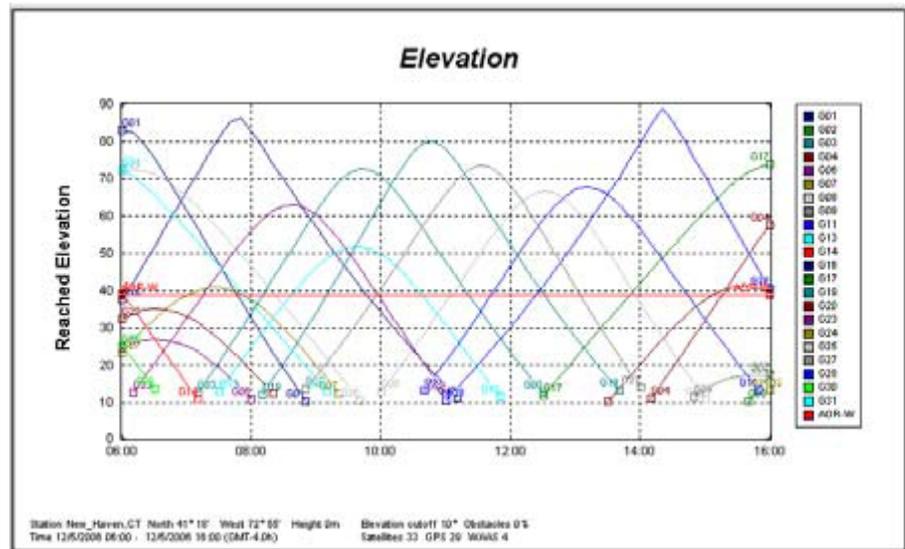
1. On the Main Menu, go to File>Station.
2. Click on the City name button to open the City Selector.
3. There are a number of options for selecting the area to survey. Depending upon the area to be surveyed, it may be more appropriate to manually enter Latitude/Longitude coordinates, or to use the Map Button to search for a station visually.
4. Select the city that is closest to the area to where the survey will be conducted.
5. If there are significant obstacles that will be confronted in the survey, click on the obstacles button and use the Obstruction Editor to define any obstructions that will be a factor in the survey (will the survey be in a canyon, the shadow of a mountain, etc?...).

6. Define the starting date/time and duration of the survey work.
7. Set the time zone for report format

Creating Planning Graphs

Once the survey parameters have been entered use the Toolbar to produce all the graphs created by the planning survey.

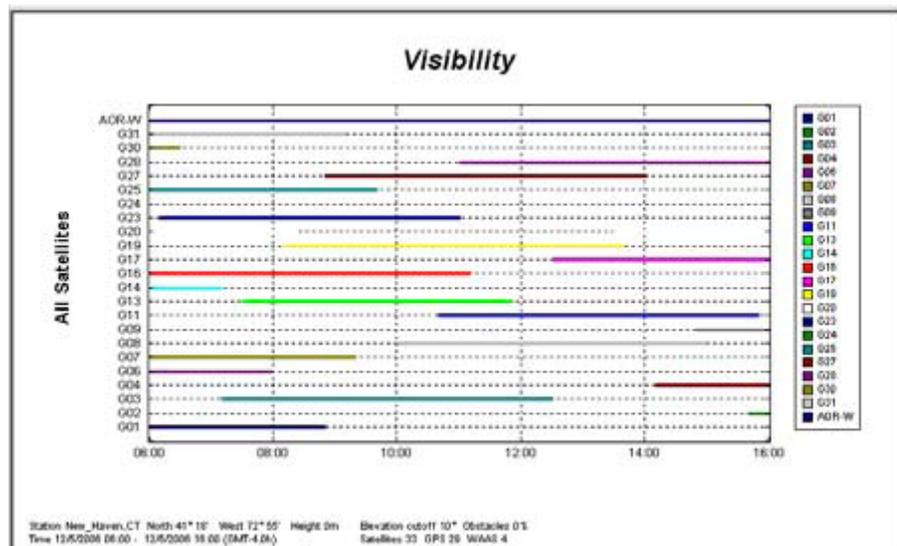
Elevation Graphs

The elevation graph will show satellites at very low elevations that do not significantly contribute to positioning calculations because of atmospheric interferences. It will also show the elevation in the sky for each satellite visible by the GPS receiver in the area across the time period defined. Note that this graph may be the most important for planning surveys in vertically developed urban environments.



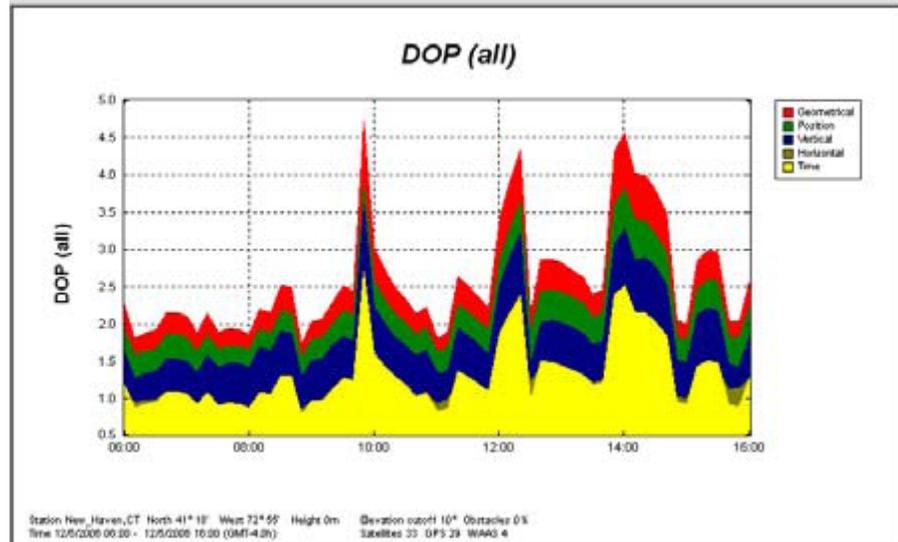
Visibility Graphs

This graph displays the visibility of satellites as a function of time.



DOP Graphs

Dilution of Precision (DOP) maps shows the satellite signal quality in relation to the number of satellites and their position in the sky and relative to each other. The lower the DOP value the better signal quality and the higher the positioning precision. This map is probably the best to use for a survey planning.



ATTACHMENT 5

MANAGING GPS DATA FROM TERRASYNC—A TUTORIAL

Introduction

Currently, positional data collected in the field is most often done with a Trimble GPS unit (see Integral's equipment list at the beginning of the SOP) interfaced with a laptop via Trimble's TerraSync software. This short tutorial is meant to serve as a guide to field personnel who need to understand how to retrieve and collect geographic data in the most efficient way possible with existing software.

Scope

This document is intended to be a reference for procedures involving:

1. Fixing files containing target stations that are more than 7 days old so that they can be updated
2. Adding features in GPS Pathfinder software (companion to TerraSync) and then importing them as base files in TerraSync.

This document is **not** intended to be a comprehensive manual for using Terrasync or Pathfinder software. It is assumed that the reader has received at least some training on how to use the basic features of Terrasync and is comfortable using MS Windows.

The Basics

GPS data collection at Integral currently utilized two pieces of complementary software: Terrasync – the interface for GPS navigation and data collection; and Pathfinder Office – a multi-use piece of software that acts as a conduit between GIS data files (shape files) and Terrasync GPS files. Pathfinder can also be used as a simple map editor in a pinch.

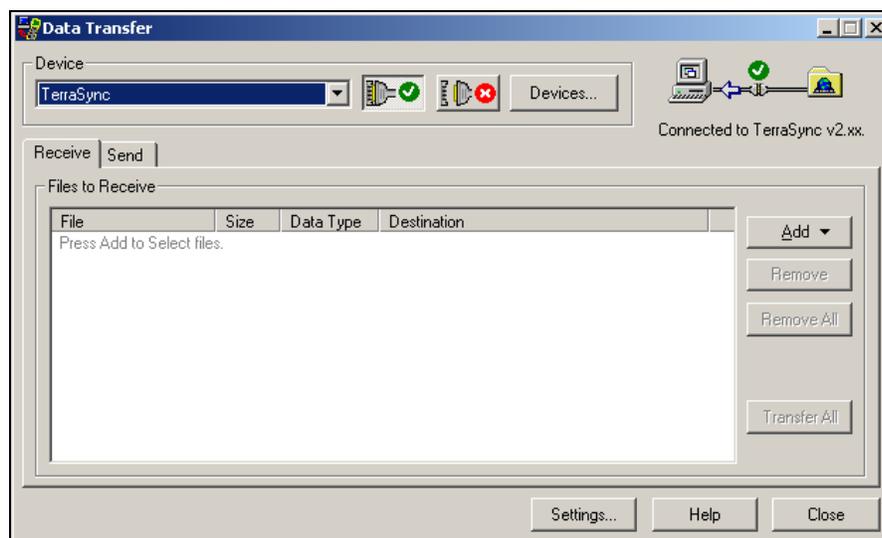
Installing the Correct Versions of Terrasync and Pathfinder

**** Important note *** : This tutorial uses Pathfinder Office version 4.00 and TerraSync version 3.05. It is very important to use the proper versions of this software due to compatibility issues. Licenses for TerraSync are reserved to one per computer or handheld GPS device. A floating license is available for Pathfinder Office and can be installed in several office computers .Please obtain installation instructions from GIS staff.*

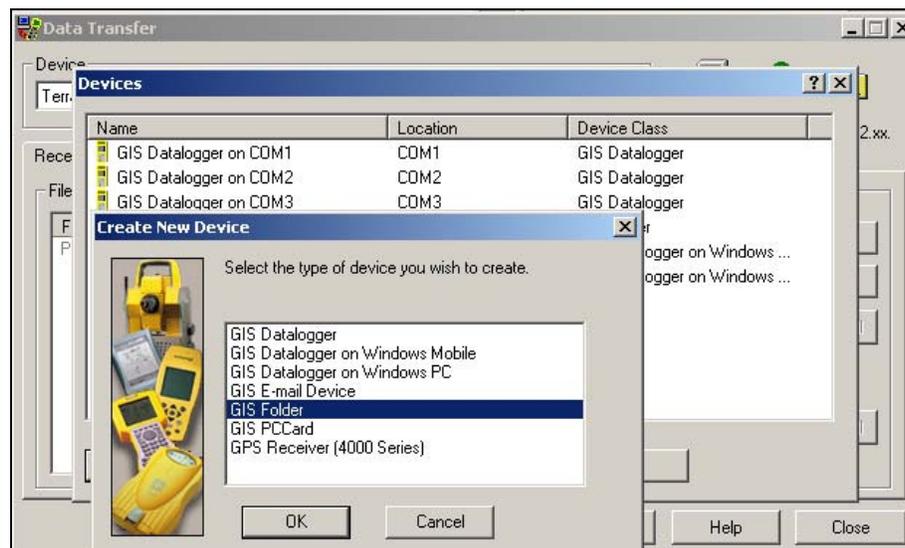
Initial Setup of TerraSync and Pathfinder Office

There are certain settings and configuration setups that are needed before Pathfinder Office can talk to TerraSync. Whether you are newly installing this software or have an existing installation, it is good to check to make sure these settings are in place.

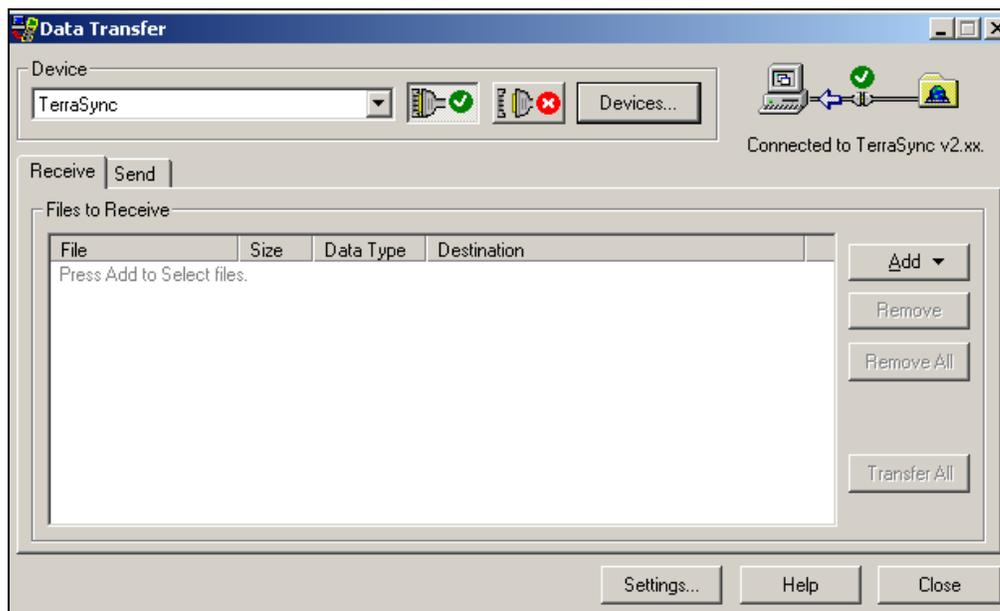
1. Open Pathfinder Office and go to the **>Utilities>Data Transfer...** menu. A dialog box similar to Figure 1 should greet you. This is the interface for communicating with TerraSync.



2. Click the **Devices** button, and then **New...**
3. You are then presented with a list of options, and you want 'GIS Folder'



4. Browse to the Terrasync data folder on your computer, which in most cases will be **C:\My Documents\TerraSync**
5. In the next box, 'Type' will be **TerraSync**, and 'Version' will be **v. 3.05**.
6. The next box prompts you for a name that will display in the device list. Shorten it to simply say **TerraSync**.
7. Now you should be able to go back to the Data Transfer dialog box, select TerraSync from the dropdown menu, press the 'connect' icon, and get a rewarding green check mark indicating success.



If this procedure does not work for you, it is likely that you have the wrong version of Pathfinder or TerraSync. For some reason, with each version upgrade of Pathfinder, connectivity to older versions of Terrasync is lost. You can check what version of Pathfinder you have installed by going to the **>Help>About GPS Pathfinder Office...** menu. To find out what version of Terrasync you have, you need to go to **C:\Program Files\TerraSync**, right-click on TerraSync.exe, and choose the version tab.

Common Issues

Handling Expired Files in Terrasync

One of the most common things that field personnel will have to deal with is the one week expiration date when trying to collect data with Terrasync (Figure 1). This is a safety feature of Terrasync to prevent too many days of logged in data being saved in a

single file, and unfortunately there is no solution that we know of. The following instructions will guide you through the process to make the files useable.

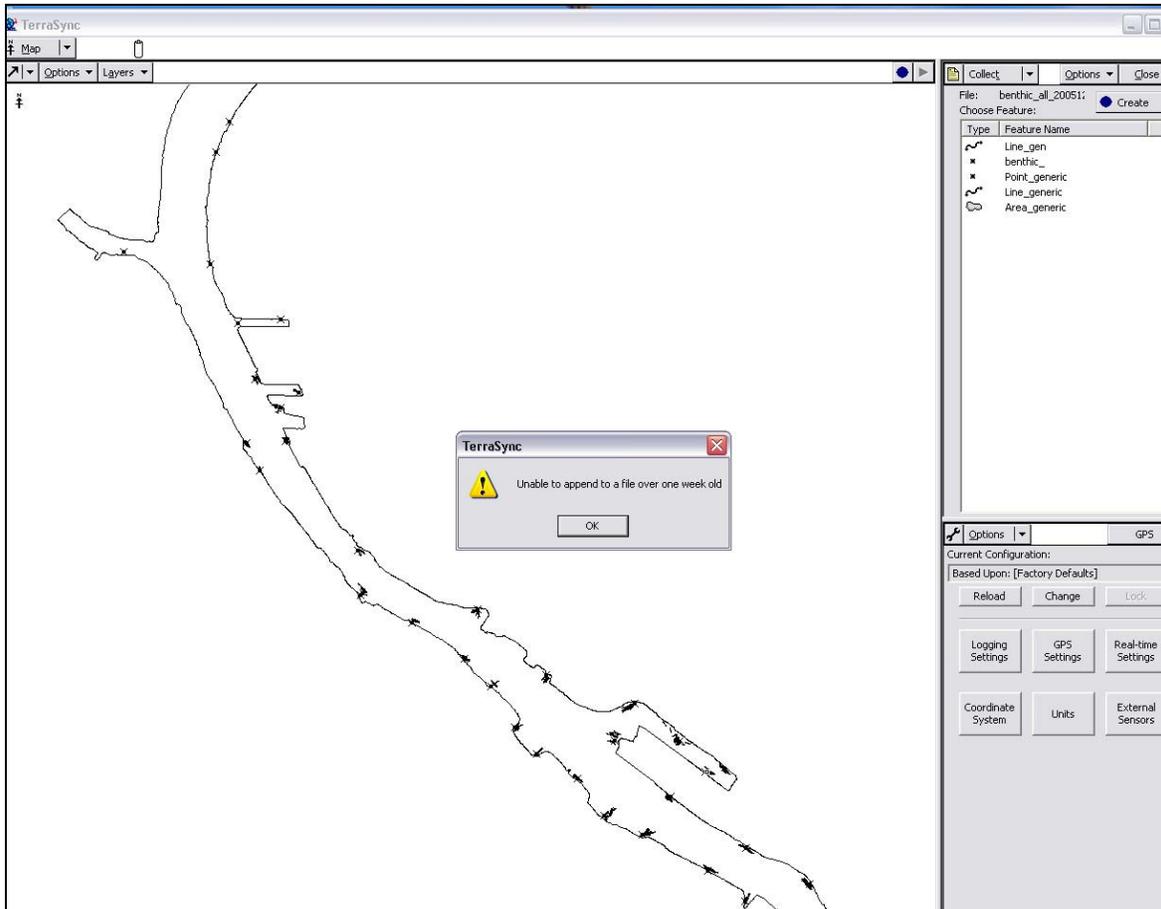


Figure 1: TerraSync file that is over one week old will not allow user to collect features. Note, the clock starts ticking when you collect your first feature in the field (not when the file was created)

Basically, there are two options depending on your needs. If you don't need to see your previously logged locations and just need to see the targets, you can use the original files provided by GIS staff (option 1). If you need to see previously occupied locations in order to make decisions about where to go next, then you will need to transfer the file to Pathfinder and back again (option 2).

Option 1: Move and replace logged files with original targets.

At the beginning of the field effort, you should receive a set of files with your target locations, most likely in a zip archive (.zip file extension). There will be six to eight files with the same name but with different extensions (see Figure 2). These files will have to

go into the C:\My Documents\TerraSync\ folder in order to be available to Terrasync.

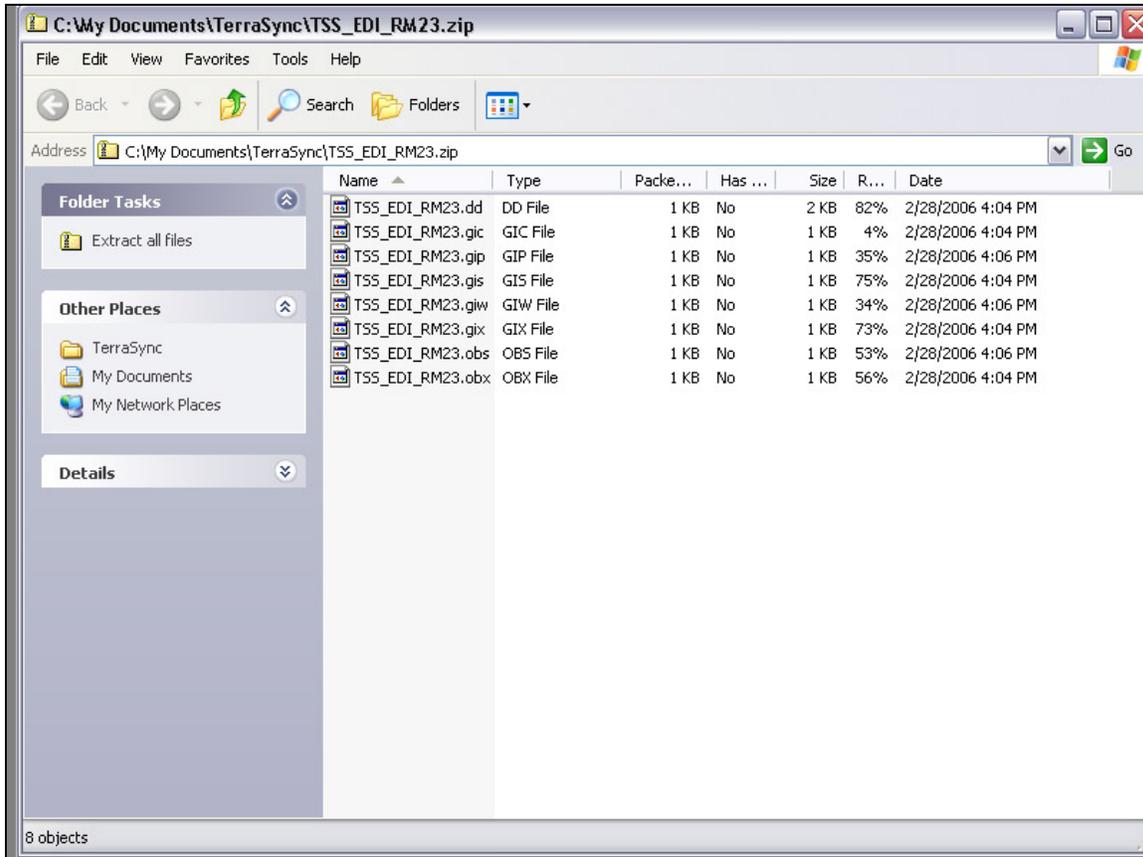


Figure 2: Example of file set to be unzipped into the TerraSync folder.

After you unzip these files to Terrasync, keep this zip archive around in an easy to find place (i.e. the Desktop or project GPS folder). The reason for this is that the one week clock does not start ticking until you begin collecting your first point in the field. Therefore, you can use this unadulterated file again, so long as you make a copy of the work you did the previous week. Here are the detailed steps to take:

1. Make sure you have the original files with the target locations available in a handy place. This will probably be the original zip archive. Also, **be sure to close TerraSync** while performing this process.
2. Navigate to C:\My Documents\TerraSync\ in Windows Explorer. Locate the files that you have been using the previous week. Make sure to get all the little files associated with the dataset. Note, that while it is useful to sort the files by date modified, you can miss some of the little files – it is highly recommended that you sort the files alphabetically.

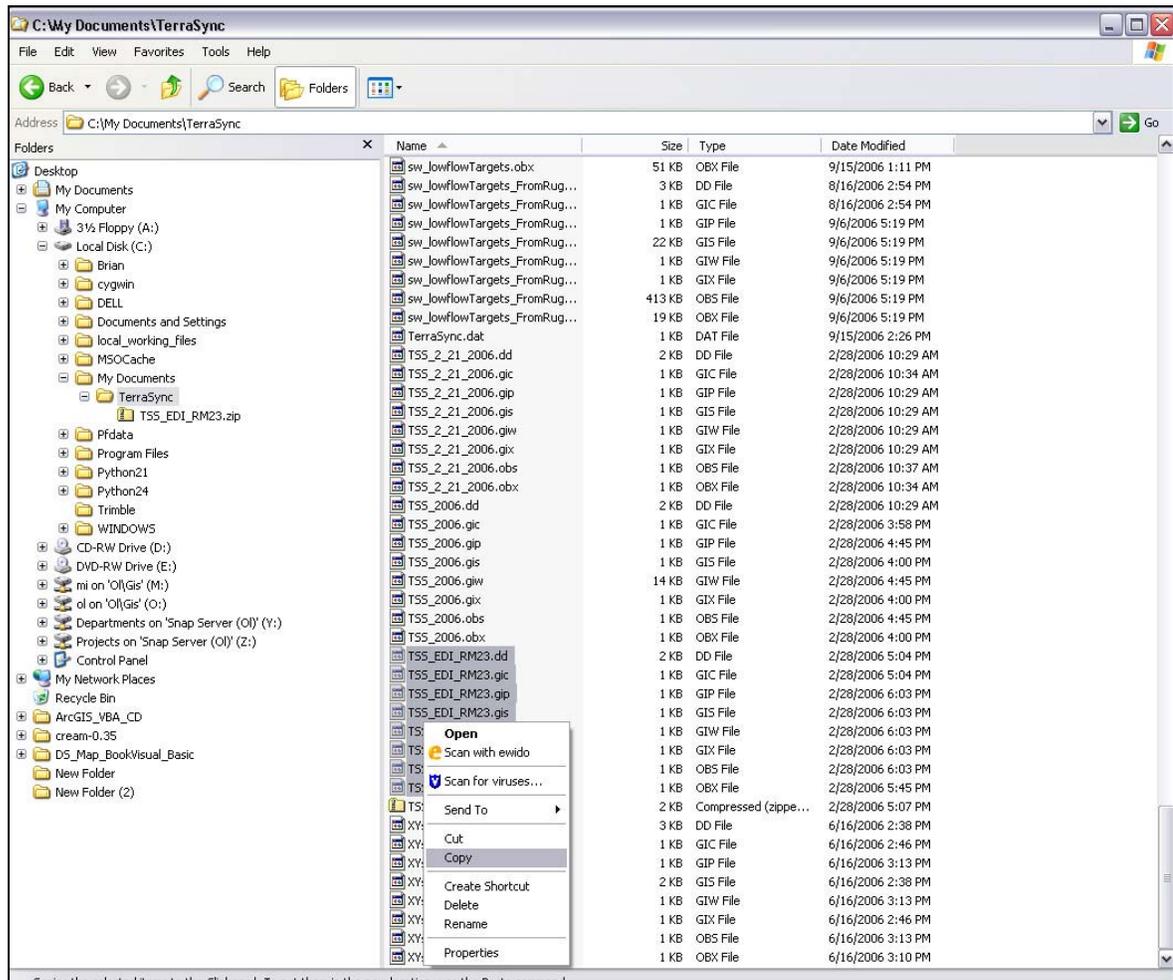


Figure 3: Selecting files to copy to a different directory

- Copy all of these files to a different directory, preferably one that is named appropriately to reflect the data and time period that you were collecting. For example C:\Documents and Settings\bpointer\Desktop\lampreyTargets_20060925. These files contain the data you have collected the previous week and should be backed up and/or emailed to the appropriate project manager or GIS staff.
- First, make sure you have made a copy of the original files. You can now safely replace the files you just copied with the ones from the original zip file. Simply right-click the zip archive, click "Extract All...", and when prompted to "Select a folder to extract files to", browse to C:\My Documents\TerraSync. If prompted about replacing existing files, select yes to all.

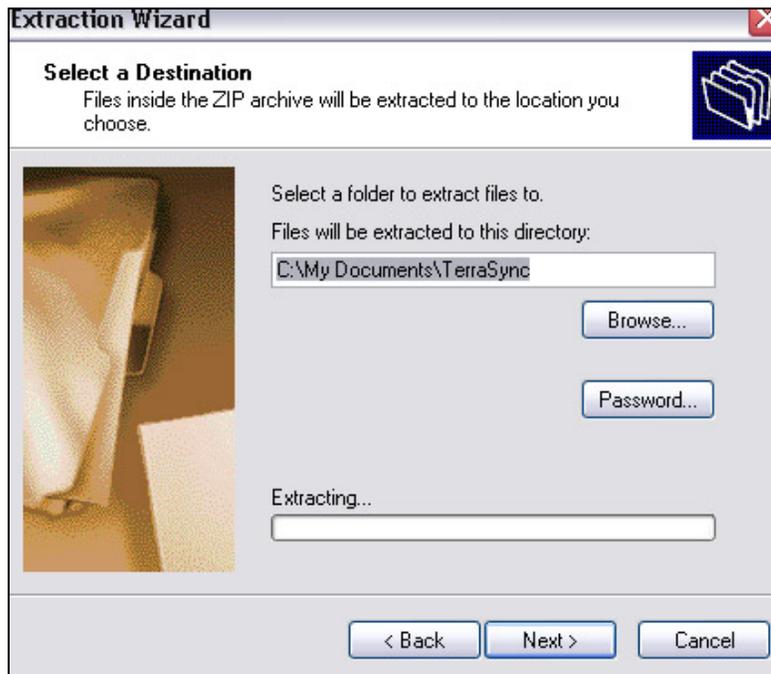


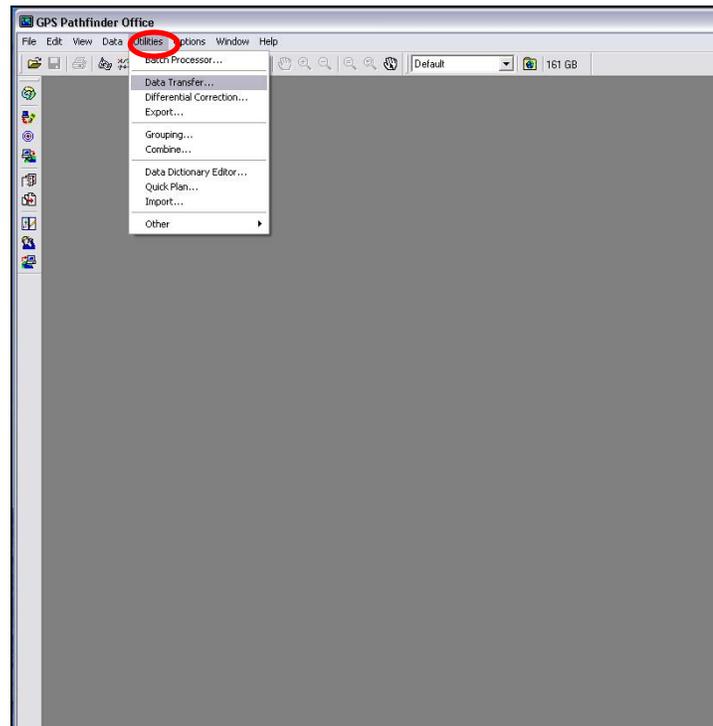
Figure 4: Extract (or copy) original target files into the TerraSync directory.

5. You should now be able to open the file in TerraSync and begin logging as normal.

Option 2: Transfer files back and forth from TerraSync.

If you need to be able to see the previously occupied positions from last week while positioning this week, you need to use Pathfinder to reset the file. This process will essentially combine the targets and actuals from last week into one file. This has its drawbacks though – once converted the actuals from last week will not be able to be corrected, so a backup procedure similar to the one in the previous option should be carried out to maintain data integrity. Here are the details.

1. For good data management, please backup the data files from the previous week using the procedure laid out in steps 1-3 in Option 1 above.
2. Close TerraSync and open up Pathfinder Office.
3. Go to the >Utilities>Data Transfer menu or just click the icon on the left.



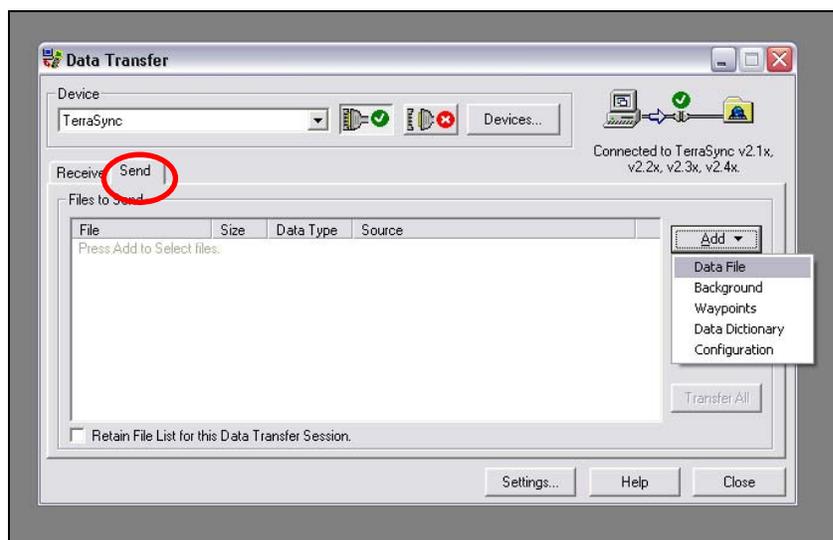
4. Ensure that the device listed is TerraSync. If not, follow the initial setup instructions at the beginning of this document. Most of the computers used for GPS logging are already setup for this.

There are two tabs, Receive and Send. Make sure that Receive is selected and then go to Add>Data File. Select the file(s) that you are using and select Open. The file should now be in the "Files to Receive" box. Click Transfer All and wait for the transfer to take place. If you have made the recommended backups, it is fine to replace any files.



Figure 5: Transferring file from TerraSync.

- Now select the Send tab, and go to Add>Data File. Select the file you just transferred (it will have the same name as the TerraSync file) and click Open. Now click Transfer All to move the file back to TerraSync.



By transferring the file back and forth from Terrasync to Pathfinder you have “reset the clock” and you may now update the file for an additional 7 days. This file will have your targets and actual positions from the last week, so it is important to be aware of the features you are selecting for navigation.

STANDARD OPERATING PROCEDURE SOP-2: SURFACE SEDIMENT SAMPLING

Scope and Application

The purpose of this SOP is to define and standardize the methods for collecting surface sediment samples from freshwater or marine environments. Surface sediments are defined as those from 0 to at most 1 ft (30 cm) below the sediment-water interface. The actual definition of surface sediments is typically program-specific and is dependent on the purpose of the study and the regulatory criteria (if any) to which the data will be compared.

This SOP utilizes and augments the procedures outlined in Puget Sound Estuary Program (PSEP; USEPA 1996) guidelines. A goal of this SOP is to ensure that the highest quality, most representative data be collected, and that these data are comparable to data collected by different programs that follow PSEP guidelines.

Summary of Method

Sediment samples for chemical and toxicity analysis are collected using a surface sediment sampling device (e.g., grab sampler). If a sample meets acceptability guidelines, overlying water is carefully siphoned off the surface, and the sediment is described in the field log. Sediment samples for chemical analysis may be collected directly from the sampler (e.g., volatile organic compounds and sulfides) or sediment from the sampler may be homogenized using decontaminated, stainless-steel containers and utensils prior to being placed in sample jars. Sediment from several sampler casts may also be composited and homogenized prior to being placed in sample jars.

Supplies and Equipment

A generalized supply and equipment list is provided below. Additional equipment may be required depending on project requirements.

- Grab sampler or box corer (see examples below in *Procedures for Sediment Sample Collection*)
- Field equipment:
 - Siphoning hose
 - Stainless-steel bowls or containers

- Stainless-steel spoons, spatulas, and/or mixer
- Decontamination supplies
- (Alconox™ detergent, 0.1 N nitric acid, methanol, hexane, deionized water)
- Personal protective equipment for field team (rain gear, safety goggles, hard hats, nitrile gloves)
- Photoionization detector (PID) and/or flame ionization detector (FID)
- First Aid kit
- Cell phone
- Camera
- Sample containers
- Bubble wrap
- Sample jar labels
- Clear tape
- Permanent markers
- Indelible black-ink pens
- Pencils
- Coolers
- Ice
- Documentation
 - Waterproof field logbook
 - Field Sampling Plan (FSP)
 - Health and Safety Plan (HASP)
 - Correction forms
 - Request for change forms
 - Waterproof sample description forms.

Procedures

Sediment Sample Collection

To collect sediment for chemical and biological analyses, a sampler that obtains a quantifiable volume of sediment with minimal disturbance of the sediments must be

employed. Additionally, the sampler should be composed of a material such as stainless-steel or aluminum, or have a non-contaminating coating such as Teflon™. Samplers capable of providing high-quality sediment samples include grab-type samplers (e.g., van Veen, Smith-McIntyres, Young grab, Power Grab and ponar grab) and box cores (Soutar, mini-Soutar, Gray-O'Hara, spade core). Some programs require a sampler that collects from a specific area (e.g., 0.1 m²). Most sampling devices are typically a standard size; however, some non-standard sizes are available to meet the requirements of specific programs. Grab samplers, especially the van Veen grab, are the most commonly used samplers to collect surface sediment. Power Grab samplers are often used for programs requiring collection of sediment deeper than 10 cm (4 in) or in areas with debris.

A hydraulic winch system should be used to deploy the sampler at a rate not exceeding 1 m/sec to minimize the bow wake associated with sampler descent. Once the sampler hits the bottom, the jaws are slowly closed and the sampler is brought to the deck of the vessel at a rate not exceeding 1 m/sec to minimize any washing and disturbance of the sediment within the sampler. At the moment the sampler hits the bottom, the time, depth, and location of sample acquisition are recorded in the field logbook.

Once onboard, the sampler is secured, any overlying water is carefully siphoned off, and the sample is inspected to determine acceptability. Criteria used to determine acceptability are those detailed in PSEP (1986), except when noted in the project-specific FSP. These criteria include but are not limited to:

- There is minimal or no excessive water leakage from the jaws of the sampler.
- There is no excessive turbidity in the water overlying the sample.
- The sampler is not over-penetrated.
- The sediment surface appears to be intact with minimal disturbance.
- The program-specified penetration depths are attained.

If the sample meets acceptability criteria, the sample is recorded and observations entered onto a sample description form or log. Once the sample has been characterized, the sediment is then subsampled for chemical and biological analyses.

Sample Processing

Sediment for chemical and/or toxicity analyses is removed from the sampler using a stainless-steel spoon. Depending on programmatic goals, the upper 30 cm (1 ft) of sediment is removed. To prevent possible cross contamination, sediments touching the margins of the sampler are not used.

Sample logs, labels, custody seals, and chain-of-custody forms are completed, and sample information is recorded in the field notebook.

Samples for volatile compounds (either organics or sulfides) are collected using a decontaminated stainless-steel spoon while sediment is still in the sampler. These sediments are not homogenized. The volatile organics sample jar should be tightly packed with sediment (to eliminate obvious air pockets) and filled so that there is no headspace remaining in the jar. Alternatively, if there is adequate water in the sediment, the container may be filled to overflowing so that a convex meniscus forms at the top, and the cap carefully placed on the jar. Once sealed, there should be no air bubbles. The sulfides sample is preserved with 0.2 N zinc acetate.

The remaining sediment is then placed into a pre-cleaned, stainless-steel bowl. Typically, sediment from a minimum of three separate casts of the sampler is composited at each station. Once a sufficient amount of sediment has been collected, the sediment is homogenized until it is of uniform color and has obtained a smooth consistency. It is then dispensed into pre-cleaned sample jars for the various chemical or biological analyses. Sample jars for biological analyses should be filled to the top with sediment to minimize available headspace. This procedure will minimize any oxidation reactions within the sediment. Sample jars for chemical analysis may be frozen for storage, leaving enough headspace left in the container to allow for expansion of the sediment upon freezing. Sample jars collected for VOC analysis will not be frozen.

After dispensing the sediment, the containers are then placed into coolers with ice and are either shipped directly to the analytical laboratories or transported to a storage facility. Excess sediment will be placed in Department of Transportation-approved 55 gallons drums and handled in accordance with SOP-11.

Sediment is described in accordance with ASTM D-2488 (SOP 4) on the sample log form.

Sampling equipment decontaminated in accordance with SOP-9, Equipment Decontamination.

Reference

USEPA. 1996. Puget Sound Estuary Program: Recommended protocols for measuring selected environmental variables in Puget Sound. Prepared for U.S. Environmental Protection Agency, Region 10, and Puget Sound Estuary Program, Seattle, WA. Tetra Tech and HRA, Inc., Bellevue, WA.

STANDARD OPERATING PROCEDURE SOP-3:

SUBSURFACE SEDIMENT SAMPLING USING A SPLIT- SPOON SAMPLER AND A GUS OR OSTERBERG SAMPLER EQUIPPED WITH A SHELBY TUBE

Scope and Application

This SOP describes Integral procedures for the collection of subsurface sediment samples using a split-spoon sampler and a Gregory Undisturbed Sampler (GUS) or Osterberg sampler equipped with a Shelby Tube. Sediment cores will be collected following ASTM Method D-1586-84, Standard Test Method for Penetration Test and Split-Barrel Sampling of Soils.

Supplies and Equipment

A generalized supply and equipment list is provided below. Additional equipment may be required depending on the project.

- Sampling device:
 - Hollow-stem auger drill rig (or equivalent Sonic rig)
 - Stainless-steel, 1.5-ft-long, 2-in-diameter split spoon; *or* 2.5-ft-long, 3-in-diameter split-spoon sampler or Shelby tubes
 - Stainless-steel or other liners, if required
 - Stainless-steel core catchers (as necessary)
 - Core extruder device, drill, ratchet, plugs
 - 55-gallon drums (if required)
- Field equipment:
 - Aluminum foil
 - Duct tape
 - Hack saw
 - Plastic sheeting
 - Pipe cutter

- Plunger (if necessary)
- Table or tray
- Ice (if storing cores)
- Stainless-steel bowls
- Stainless-steel spoons, spatulas, and/or mixer
- Assorted geology supplies (e.g., hand lens, grain-size card, scales, etc.)
- Decontamination equipment (SOP-9)
- Personal protective equipment for field team (rain gear, safety goggles, hard hats, nitrile gloves)
- Photoionization detector (PID)
- First Aid kit
- Cell phone
- Camera
- Sample containers
- Ziploc® bags
- Bubble wrap
- Clear tape
- Permanent markers
- Indelible ink pen
- Pencils
- Coolers
- Documentation:
 - Core description forms
 - Waterproof field logbook
 - Field Sampling Plan (FSP)
 - Health and Safety Plan (HASP)
 - Chain-of-custody seals
 - Sample labels
 - Correction forms

Procedures

Hollow-stem auger or equivalent (e.g., Sonic) drilling is used to obtain sediment cores using both split-spoon and GUS or Osterberg samplers equipped with a Shelby tube. Both split-spoons and Shelby tubes can collect similar-sized cores (2-ft-long, 3-in-diameter), although the methods of obtaining the cores differ. Split-spoons are hammered into the sediment, while Shelby tubes are hydraulically or pneumatically (with nitrogen gas) driven into the sediment. In addition, each half of a split-spoon sample is simply pulled apart to expose the core, while the sediment must be extruded from the Shelby tube. Once the core is exposed, the processing and handling of the core sample is identical.

The following sections describe the methods of collecting and "extruding" split-spoon and Shelby tube cores, respectively. Methods for processing and sampling the cores are also included.

Collection of Cores Using a Split-Spoon Sampler

1. Decontaminate the split-spoon sampler, liners (if used), and other equipment in accordance with SOP-9. If a stainless-steel split-spoon sampler without liners is used, the sampler should be fully decontaminated between all samples collected. If liners are used, liners should be fully decontaminated, while the split-spoon should be cleaned with Alconox[®], tap or seawater, and a distilled water rinse.
2. Insert stainless-steel liners into the split-spoon sampler, along with sand catchers, if required.
3. Attach the split-spoon sampler to the bottom end of a string of drill rod which extends from the top of the auger, through the hollow stem, and to the bottom of the borehole.
4. Attach a 140-pound (or other appropriate weight) hammer to the top of the drill rod string and drive the sampler into the soil at the bottom of the borehole.

NOTE: Record the hammer weight and blow counts in the field log. The blow counts are generally recorded for each 6-inch interval.

5. To drive the sampler into the sediment, alternately raise the hammer on a rope, which passes around a rotating cathead, and allow the hammer to free-fall 30 inches by suddenly releasing the tension on the cable.
6. Pull the sampler up from the bottom of the borehole on the drive rods and remove from the bottom of the drive rod string.

7. Remove the top assembly and the drive shoe from the sampler and open the tube by removing one-half of the split barrel. If liners are used, push the sediment from the liner, and arrange the liner sections in the appropriate order, taking care to maintain the integrity of the core.
8. If field organic vapor monitoring is required, immediately collect a representative sample from the sampler and place in a new, labeled Ziploc® bag for screening. The Ziploc® bag should be closed and allowed to sit in ambient air for 10 minutes prior to monitoring with an OVM or PID.
9. Process and subsample the core as described in sections below.
10. Advance the auger and repeat steps 1-9.

Collection of Cores Using GUS or Osterberg Samplers Equipped with Shelby Tubes

1. Decontaminate the Shelby tubes and other equipment in accordance with SOP-9. The Shelby tubes should be fully decontaminated between all samples collected. Core caps should be washed with Alconox® and water, and rinsed with distilled water, in accordance with SOP-9.
2. Attach the GUS or Osterberg sampler equipped with a Shelby tube to the bottom end of a string of drill rod that extends from the top of the auger, through the hollow stem, and to the bottom of the borehole.
3. Lower the coring assembly (rod with GUS or Osterberg sampler) until it is positioned at the sediment/water interface.
4. Hydraulically (or pneumatically) drive the core tube into the sediment until a 2-ft core is obtained.
5. Once the core is brought onboard, remove it from the rod, and immediately cap and tape both ends. It is preferable to put a layer of foil on each end prior to capping. Label the core with station, sampling depth interval, time of collection, and core orientation (top of core).
6. Place the core in an upright box or stand with ice until it is processed. Cover the cores in the holding box with a tarp to prevent sample contamination from airborne particles (e.g., vessel engine gases) and to keep them out of direct sunlight.
7. The Shelby tube cores may be processed on the barge or onshore near the site. During transit, the tubes must remain upright and cool.

8. When prepared to process a core, remove the cap from the upper end of the core (holes present where the core is attached to the sampler and rod). Place the core horizontally in the extruder core holder so that the open end is toward the extruder. Secure the core in the holder and remove the other cap at the bottom of the core. Place an appropriate-sized plug wrapped in foil into the top end of the core, insert the extruder rod and screw, and wind the plug until it touches the top end of the sediment. A tray wrapped in aluminum foil should be placed at the bottom end of the core, and a person wearing nitrile or polyethylene gloves should be present to catch and guide the core as it is extruded. Use a drill or ratchet (depending on how stiff the core is) to wind the screw, pushing the core from the Shelby tube. If the core is particularly stiff, it may be necessary to hit the side of the core tube with a rubber hammer or other device while winding the extruder. Alternatively, if the core is particularly soft, the core may be readily extruded by simply pushing the plug with a rod by hand.
9. If field organic vapor monitoring is required, immediately collect a representative sample from the sampler and place it in a new, labeled Ziploc® bag for screening. The Ziploc® bag should be closed and allowed to sit in ambient air for 10 minutes prior to monitoring with an OVM or PID.
10. Process and subsample the core as described in the following sections.
11. Advance the auger, and repeat steps 1-10.

Sampling and Processing the Subsurface Sediment Cores

1. Once the core is exposed, split the core lengthwise using a decontaminated knife or spoon.
2. If subsamples are to be collected for volatile organics, total sulfides, or acid volatile sulfides, collect them immediately after the core has been split. Use a decontaminated spoon to remove sediment along the entire length of the core for each subsample collected. Place the subsample into the appropriate jar according to the procedures described in SOP-6, label the jar, and place it in a cooler with ice (or blue ice). The volatile organics sample jar should be tightly packed with sediment (to eliminate obvious air pockets) and filled so that there is no headspace remaining in the jar. Alternatively, if there is adequate water in the sediment, the container may be filled to overflowing so that a convex meniscus forms at the top, and the cap carefully placed on the jar. Once sealed, there should be no air bubbles.
3. If required by the field sampling plan, place a sign above the sample, including station number, core depth, and date and time of core collection. In addition, place a measuring stick along the length of the core, and photograph the sediment core. Avoid touching the core with the scale or sign.

4. Describe the core, including such information as the vertical changes in sediment characteristics (e.g., texture, density, and moisture) and distribution of visible contamination, color and odor of the sediments, sediment texture, presence of debris (wood chips, wood fibers, human artifacts), presence of oily sheen, and visible fauna or biological structures in accordance with ASTM Method D2488 (SOP-4). This information should be recorded in the sediment coring log, along with other information listed in SOP-4, Sediment Borehole Logging.
5. Transfer sediment selected for chemical analyses to a decontaminated stainless-steel mixing bowl. Cover the bowl if more sediment from another core is composited with the sample.
6. Mix the sediment in the bowl until well homogenized (visibly uniform) and transfer it into the appropriately sized sample containers for the individual analyses (see SOP-2, Surface Sediment Sampling).
7. Verify that samples have been properly labeled and store them onsite in a cooler at 4°C until they are packaged for shipping (see SOPs 5 and 6).
8. Generally, at completion of sediment sampling activities at a station, collect all spilled and excess material and dispose of overboard at the original sampling location. However, dispose of material in accordance with applicable regulations and any directives issued by the client. It may be required to place excess material into DOT-approved 55-gallon drums (depending on level and type of contamination).
9. Decontaminate all sampling equipment, including internal components, prior to use, between sampling events, stations and depth intervals, and prior to demobilization in accordance with SOP-9, Equipment Decontamination.

STANDARD OPERATING PROCEDURE SOP-4: BOREHOLE LOGGING AND FIELD CLASSIFICATION OF SOILS AND SEDIMENT

Scope and Application

The following procedures establish the minimum information that must be recorded in the field to adequately document soil borehole advancement activities performed during field exploration. The borehole log form must be filled out completely.

This SOP presents the field classification of soils to be used by Integral field staff. In general, Integral has adopted the procedures provided in ASTM Method D-2488-00 attached, Standard Practice for Description and Identification of Soils. ASTM D-2488-00 uses the Unified Soil Classification System (USCS) for naming soils. Field personnel are encouraged to study these procedures prior to initiation of field work.

Soil descriptions should be precise and comprehensive without being verbose. The overall impression of the soil should not be distorted by excessive emphasis on minor constituents. In general, the similarities of consecutive soil samples should be emphasized and minor differences de-emphasized. These descriptions will be used to interpret aquifer properties and other potential contaminant transport properties, rather than interpret the exact mineralogy or tectonic environment. Integral is primarily interested in engineering and geochemical properties of the soil.

Soil descriptions should be provided in the Soil Description column of the soil boring log for each sample collected. If there is no difference between consecutive soil samples, subsequent descriptions can be noted as “same as above” or minor changes such as “increasing sand” or “becomes dark brown” can be added.

The format and order of soil descriptions should be as follows:

- Group symbol—Place in the Unified Symbol column
- USCS group name—Make identical to the ASTM D-2488-00 Group Name with the appropriate modifiers.
- Minor components
- Color
- Moisture
- Additional descriptions

Supplies and Equipment

- Soil log form
- Munsell® (or equivalent) soil color chart

Procedures

1. The USCS is an engineering properties system that uses grain size to classify soils. The first major distinction is between fine-grained soils (more than 50 percent passing the No. 200 sieve [75 µm/0.029 in.]) and coarse-grained soils (more than 50 percent retained by the No. 200 sieve). Small No. 200 sieves are necessary to classify soils that are near the cutoff size.
2. Fine-grained soils are classified as either silts or clays. Field determinations of silts and clays are based on observations of dry strength, dilatancy, toughness, and plasticity. Field procedures for these tests are included in ASTM D-2488-00. If these tests are used, the results should be included in the soil description. At least one complete round of field tests should be performed for a site if these materials are encountered, preferably at the beginning of the field investigation. The modifiers “fat” and “lean” are used by ASTM to describe soils of high and low plasticity. The soil group symbols (i.e., CL, MH) already indicate plasticity characteristics, and these modifiers are not necessary in the description. Soils with high plasticity can be emphasized by describing them as “silty CLAY with high plasticity.” Plasticity is an important descriptor because it is often used to interpret whether an ML soil is acting as either a leaky or a competent aquitard. For example, an ML soil can be dilatent/nonplastic and serve as a transport pathway, or it can be highly plastic and very impervious.
3. Coarse-grained soils are classified as either predominantly gravel or sand, with the No. 4 sieve (4.75 mm/0.19 in.) being the division. Modifiers are used to describe the relative amounts of fine-grained soil, as noted below:

Description	Percent Fines	Group Symbol
Gravel (sand)	<5 percent	GW, GP (SW, SP)
Gravel (sand) with silt (clay)	5–15 percent	Hyphenated names
Silty (clayey) gravel (sand)	>15 percent	GM, GC (SM, SC)

The gradation of a coarse-grained soil is included in the specific soil name (i.e., fine to medium SAND with silt). Estimating the percent of size ranges following the group name is encouraged for mixtures of silt, sand, and gravel. Use of the modifiers “poorly graded” or “well graded” is not necessary as they are indicated by the group symbol.

A borderline symbol is shown with a slash (GM/SM). This symbol should be used when the soil cannot be distinctly placed in either soil group. A borderline symbol should also be used when describing interbedded soils of two or more soil group names when the thickness of the beds are approximately equal, such as “interbedded lenses and layers of fine sand and silt.” The use of a borderline symbol should not be used indiscriminately. Every effort should be made to place the soil into a single group. (One very helpful addition to the soil log form description is the percentage of silt/sand/gravel. Even if the geologist did not have sufficient time to properly define the soil, this percentage breakdown allows classification at a later date.)

4. Minor components such as cobbles, roots, and construction debris should be preceded by the appropriate adjective reflecting relative percentages: trace (0–5 percent), few (5–10 percent), little (15–25 percent), and some (30–45 percent). The word “occasional” can be applied to random particles of a larger size than the general soil matrix (i.e., occasional cobbles, occasional brick fragments). The term “with” indicates definite characteristics regarding the percentage of secondary particle size in the soil name. It will not be used to describe minor components. If a nonsoil component exceeds 50 percent of an interval, it should be stated in place of the group name.
5. The basic color of a soil, such as brown, gray, or red, must be given. The color term can be modified by adjectives such as light, dark, or mottled. Especially note staining or mottling. This information may be useful to establish water table fluctuations or contamination. The Munsell® soil color chart designation is the Integral color standard. These charts are readily available and offer a high degree of consistency in descriptions between geologists.
6. The degree of moisture present in the soil should be defined as dry, moist, or wet. Moisture content can be estimated from the criteria listed in Table 3 of ASTM D-2488-00.

7. Features such as discontinuities, inclusions, joints, fissures, slickensides, bedding, laminations, root holes, and major mineralogical components should be noted if they are observed. Anything unusual should be noted. Additional soil descriptions may be made at the discretion of the project manager or as the field conditions warrant. The Soil Boring Log Form lists some optional descriptions, as does Table 13 of the ASTM standard. The reader is referred to the ASTM standard for procedures of these descriptions.
8. The contact between two soil types must be clearly marked on the soil boring log. The field geologist, who has the advantage of watching the drilling rate and cuttings removal and can talk with the driller in real time has a much better chance of interpreting the interval than someone in the office. If the contact is obvious and sharp, draw it in with a straight line. If it is gradational, a slanted line over the interval is appropriate. In the case where it is unclear, a dashed line over the most likely interval is used.



Standard Practice for Description and Identification of Soils (Visual-Manual Procedure)¹

This standard is issued under the fixed designation D 2488; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope *

1.1 This practice covers procedures for the description of soils for engineering purposes.

1.2 This practice also describes a procedure for identifying soils, at the option of the user, based on the classification system described in Test Method D 2487. The identification is based on visual examination and manual tests. It must be clearly stated in reporting an identification that it is based on visual-manual procedures.

1.2.1 When precise classification of soils for engineering purposes is required, the procedures prescribed in Test Method D 2487 shall be used.

1.2.2 In this practice, the identification portion assigning a group symbol and name is limited to soil particles smaller than 3 in. (75 mm).

1.2.3 The identification portion of this practice is limited to naturally occurring soils (disturbed and undisturbed).

NOTE 1—This practice may be used as a descriptive system applied to such materials as shale, claystone, shells, crushed rock, etc. (see Appendix X2).

1.3 The descriptive information in this practice may be used with other soil classification systems or for materials other than naturally occurring soils.

1.4 The values stated in inch-pound units are to be regarded as the standard.

1.5 *This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. For specific precautionary statements see Section 8.*

1.6 *This practice offers a set of instructions for performing one or more specific operations. This document cannot replace education or experience and should be used in conjunction with professional judgment. Not all aspects of this practice may be applicable in all circumstances. This ASTM standard is not*

intended to represent or replace the standard of care by which the adequacy of a given professional service must be judged, nor should this document be applied without consideration of a project's many unique aspects. The word "Standard" in the title of this document means only that the document has been approved through the ASTM consensus process.

2. Referenced Documents

2.1 ASTM Standards:

D 653 Terminology Relating to Soil, Rock, and Contained Fluids²

D 1452 Practice for Soil Investigation and Sampling by Auger Borings²

D 1586 Test Method for Penetration Test and Split-Barrel Sampling of Soils²

D 1587 Practice for Thin-Walled Tube Sampling of Soils²

D 2113 Practice for Diamond Core Drilling for Site Investigation²

D 2487 Classification of Soils for Engineering Purposes (Unified Soil Classification System)²

D 3740 Practice for Minimum Requirements for Agencies Engaged in the Testing and/or Inspection of Soil and rock as Used in Engineering Design and Construction³

D 4083 Practice for Description of Frozen Soils (Visual-Manual Procedure)²

3. Terminology

3.1 *Definitions*—Except as listed below, all definitions are in accordance with Terminology D 653.

NOTE 2—For particles retained on a 3-in. (75-mm) US standard sieve, the following definitions are suggested:

Cobbles—particles of rock that will pass a 12-in. (300-mm) square opening and be retained on a 3-in. (75-mm) sieve, and

Boulders—particles of rock that will not pass a 12-in. (300-mm) square opening.

3.1.1 *clay*—soil passing a No. 200 (75- μ m) sieve that can be made to exhibit plasticity (putty-like properties) within a range of water contents, and that exhibits considerable strength when air-dry. For classification, a clay is a fine-grained soil, or the

¹ This practice is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.07 on Identification and Classification of Soils.

Current edition approved Feb. 10, 2000. Published May 2000. Originally published as D 2488 – 66 T. Last previous edition D 2488 – 93¹.

² *Annual Book of ASTM Standards*, Vol 04.08.

³ *Annual Book of ASTM Standards*, Vol 04.09.

***A Summary of Changes section appears at the end of this standard.**

fine-grained portion of a soil, with a plasticity index equal to or greater than 4, and the plot of plasticity index versus liquid limit falls on or above the “A” line (see Fig. 3 of Test Method D 2487).

3.1.2 *gravel*—particles of rock that will pass a 3-in. (75-mm) sieve and be retained on a No. 4 (4.75-mm) sieve with the following subdivisions:

coarse—passes a 3-in. (75-mm) sieve and is retained on a ¾-in. (19-mm) sieve.

fine—passes a ¾-in. (19-mm) sieve and is retained on a No. 4 (4.75-mm) sieve.

3.1.3 *organic clay*—a clay with sufficient organic content to influence the soil properties. For classification, an organic clay is a soil that would be classified as a clay, except that its liquid limit value after oven drying is less than 75 % of its liquid limit value before oven drying.

3.1.4 *organic silt*—a silt with sufficient organic content to influence the soil properties. For classification, an organic silt is a soil that would be classified as a silt except that its liquid limit value after oven drying is less than 75 % of its liquid limit value before oven drying.

3.1.5 *peat*—a soil composed primarily of vegetable tissue in various stages of decomposition usually with an organic odor, a dark brown to black color, a spongy consistency, and a texture ranging from fibrous to amorphous.

3.1.6 *sand*—particles of rock that will pass a No. 4 (4.75-mm) sieve and be retained on a No. 200 (75-µm) sieve with the following subdivisions:

coarse—passes a No. 4 (4.75-mm) sieve and is retained on a No. 10 (2.00-mm) sieve.

medium—passes a No. 10 (2.00-mm) sieve and is retained on a No. 40 (425-µm) sieve.

fine—passes a No. 40 (425-µm) sieve and is retained on a No. 200 (75-µm) sieve.

3.1.7 *silt*—soil passing a No. 200 (75-µm) sieve that is nonplastic or very slightly plastic and that exhibits little or no strength when air dry. For classification, a silt is a fine-grained soil, or the fine-grained portion of a soil, with a plasticity index less than 4, or the plot of plasticity index versus liquid limit falls below the “A” line (see Fig. 3 of Test Method D 2487).

4. Summary of Practice

4.1 Using visual examination and simple manual tests, this practice gives standardized criteria and procedures for describing and identifying soils.

4.2 The soil can be given an identification by assigning a group symbol(s) and name. The flow charts, Fig. 1a and Fig. 1b for fine-grained soils, and Fig. 2, for coarse-grained soils, can be used to assign the appropriate group symbol(s) and name. If the soil has properties which do not distinctly place it into a specific group, borderline symbols may be used, see Appendix X3.

NOTE 3—It is suggested that a distinction be made between *dual symbols* and *borderline symbols*.

Dual Symbol—A dual symbol is two symbols separated by a hyphen, for example, GP-GM, SW-SC, CL-ML used to indicate that the soil has been identified as having the properties of a classification in accordance with Test Method D 2487 where two symbols are required. Two symbols are required when the soil has between 5 and 12 % fines or when the liquid

limit and plasticity index values plot in the CL-ML area of the plasticity chart.

Borderline Symbol—A borderline symbol is two symbols separated by a slash, for example, CL/CH, GM/SM, CL/ML. A borderline symbol should be used to indicate that the soil has been identified as having properties that do not distinctly place the soil into a specific group (see Appendix X3).

5. Significance and Use

5.1 The descriptive information required in this practice can be used to describe a soil to aid in the evaluation of its significant properties for engineering use.

5.2 The descriptive information required in this practice should be used to supplement the classification of a soil as determined by Test Method D 2487.

5.3 This practice may be used in identifying soils using the classification group symbols and names as prescribed in Test Method D 2487. Since the names and symbols used in this practice to identify the soils are the same as those used in Test Method D 2487, it shall be clearly stated in reports and all other appropriate documents, that the classification symbol and name are based on visual-manual procedures.

5.4 This practice is to be used not only for identification of soils in the field, but also in the office, laboratory, or wherever soil samples are inspected and described.

5.5 This practice has particular value in grouping similar soil samples so that only a minimum number of laboratory tests need be run for positive soil classification.

NOTE 4—The ability to describe and identify soils correctly is learned more readily under the guidance of experienced personnel, but it may also be acquired systematically by comparing numerical laboratory test results for typical soils of each type with their visual and manual characteristics.

5.6 When describing and identifying soil samples from a given boring, test pit, or group of borings or pits, it is not necessary to follow all of the procedures in this practice for every sample. Soils which appear to be similar can be grouped together; one sample completely described and identified with the others referred to as similar based on performing only a few of the descriptive and identification procedures described in this practice.

5.7 This practice may be used in combination with Practice D 4083 when working with frozen soils.

NOTE 5—Notwithstanding the statements on precision and bias contained in this standard: The precision of this test method is dependent on the competence of the personnel performing it and the suitability of the equipment and facilities used. Agencies that meet the criteria of Practice D 3740 are generally considered capable of competent and objective testing. Users of this test method are cautioned that compliance with Practice D 3740 does not in itself assure reliable testing. Reliable testing depends on several factors; Practice D 3740 provides a means for evaluating some of those factors.

6. Apparatus

6.1 *Required Apparatus:*

6.1.1 *Pocket Knife or Small Spatula.*

6.2 *Useful Auxiliary Apparatus:*

6.2.1 *Small Test Tube and Stopper (or jar with a lid).*

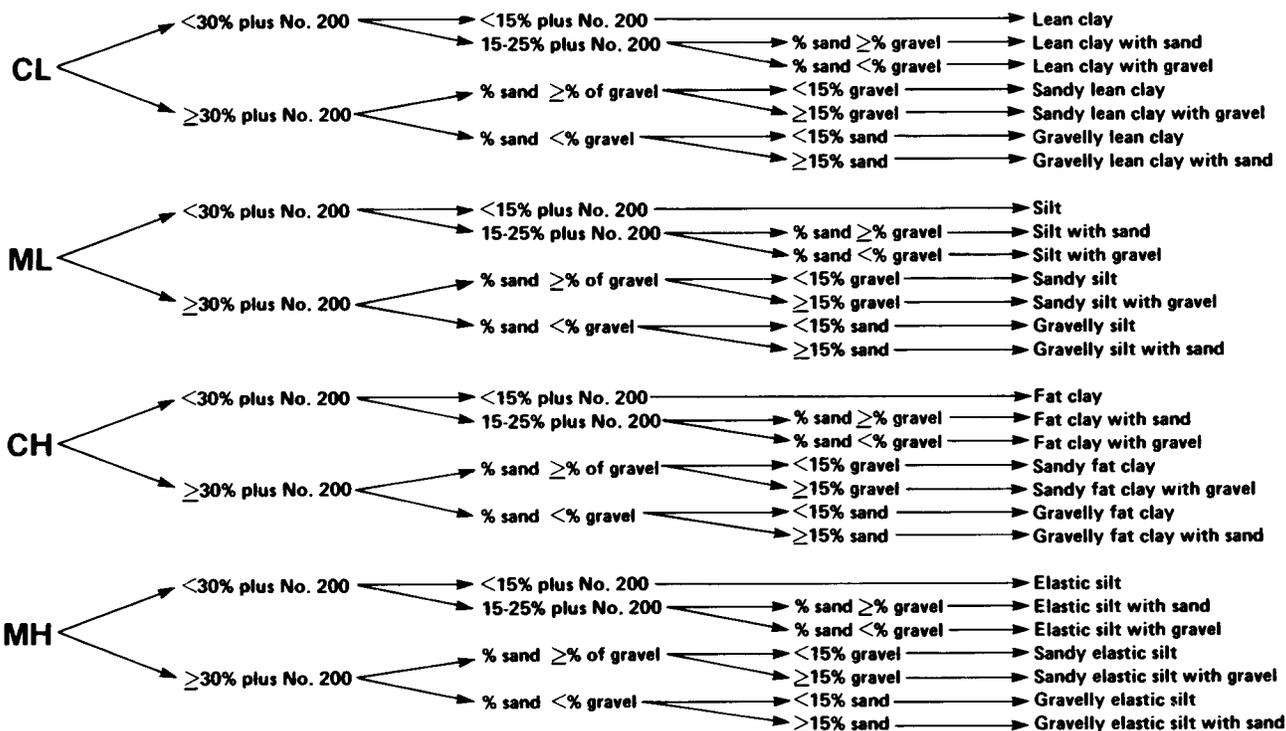
6.2.2 *Small Hand Lens.*

7. Reagents

7.1 *Purity of Water*—Unless otherwise indicated, references

GROUP SYMBOL

GROUP NAME

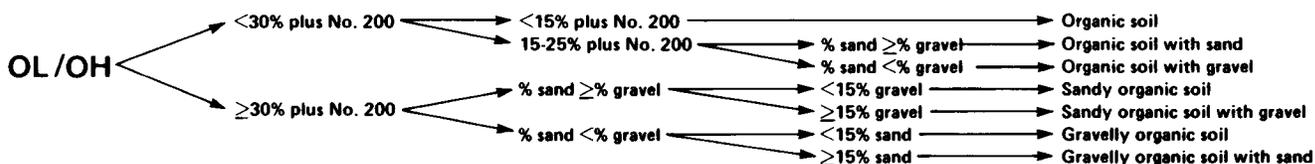


NOTE 1—Percentages are based on estimating amounts of fines, sand, and gravel to the nearest 5 %.

FIG. 1a Flow Chart for Identifying Inorganic Fine-Grained Soil (50 % or more fines)

GROUP SYMBOL

GROUP NAME



NOTE 1—Percentages are based on estimating amounts of fines, sand, and gravel to the nearest 5 %.

FIG. 1 b Flow Chart for Identifying Organic Fine-Grained Soil (50 % or more fines)

to water shall be understood to mean water from a city water supply or natural source, including non-potable water.

7.2 *Hydrochloric Acid*—A small bottle of dilute hydrochloric acid, HCl, one part HCl (10 N) to three parts water (This reagent is optional for use with this practice). See Section 8.

8. Safety Precautions

8.1 When preparing the dilute HCl solution of one part concentrated hydrochloric acid (10 N) to three parts of distilled water, slowly add acid into water following necessary safety precautions. Handle with caution and store safely. If solution comes into contact with the skin, rinse thoroughly with water.

8.2 **Caution**—Do not add water to acid.

9. Sampling

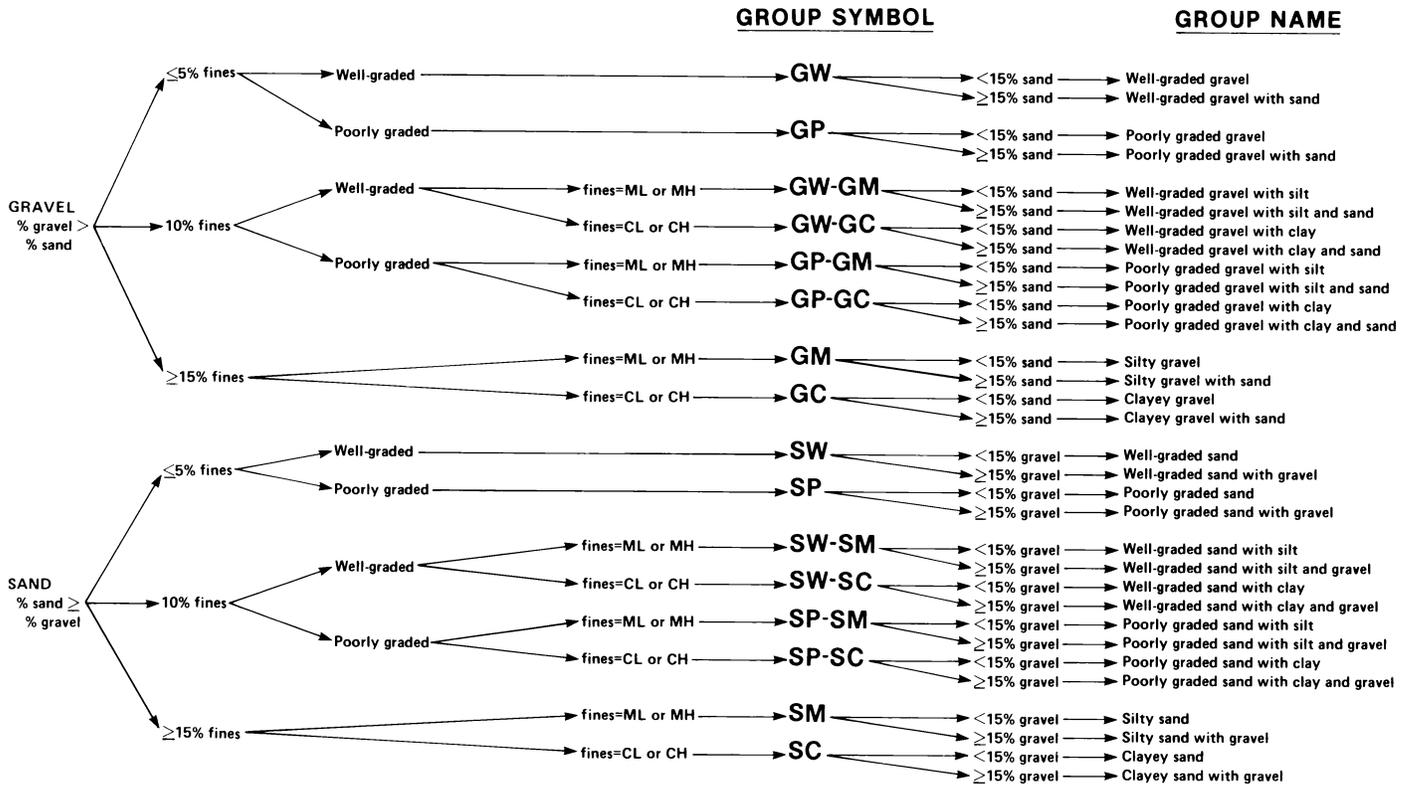
9.1 The sample shall be considered to be representative of the stratum from which it was obtained by an appropriate, accepted, or standard procedure.

NOTE 6—Preferably, the sampling procedure should be identified as having been conducted in accordance with Practices D 1452, D 1587, or D 2113, or Test Method D 1586.

9.2 The sample shall be carefully identified as to origin.

NOTE 7—Remarks as to the origin may take the form of a boring number and sample number in conjunction with a job number, a geologic stratum, a pedologic horizon or a location description with respect to a permanent monument, a grid system or a station number and offset with respect to a stated centerline and a depth or elevation.

9.3 For accurate description and identification, the minimum amount of the specimen to be examined shall be in accordance with the following schedule:



NOTE 1—Percentages are based on estimating amounts of fines, sand, and gravel to the nearest 5 %.

FIG. 2 Flow Chart for Identifying Coarse-Grained Soils (less than 50 % fines)

Maximum Particle Size, Sieve Opening	Minimum Specimen Size, Dry Weight
4.75 mm (No. 4)	100 g (0.25 lb)
9.5 mm (¾ in.)	200 g (0.5 lb)
19.0 mm (¾ in.)	1.0 kg (2.2 lb)
38.1 mm (1½ in.)	8.0 kg (18 lb)
75.0 mm (3 in.)	60.0 kg (132 lb)

NOTE 8—If random isolated particles are encountered that are significantly larger than the particles in the soil matrix, the soil matrix can be accurately described and identified in accordance with the preceding schedule.

9.4 If the field sample or specimen being examined is smaller than the minimum recommended amount, the report shall include an appropriate remark.

10. Descriptive Information for Soils

10.1 *Angularity*—Describe the angularity of the sand (coarse sizes only), gravel, cobbles, and boulders, as angular, subangular, subrounded, or rounded in accordance with the criteria in Table 1 and Fig. 3. A range of angularity may be stated, such as: subrounded to rounded.

10.2 *Shape*—Describe the shape of the gravel, cobbles, and boulders as flat, elongated, or flat and elongated if they meet the criteria in Table 2 and Fig. 4. Otherwise, do not mention the shape. Indicate the fraction of the particles that have the shape, such as: one-third of the gravel particles are flat.

10.3 *Color*—Describe the color. Color is an important property in identifying organic soils, and within a given locality it may also be useful in identifying materials of similar geologic origin. If the sample contains layers or patches of

TABLE 1 Criteria for Describing Angularity of Coarse-Grained Particles (see Fig. 3)

Description	Criteria
Angular	Particles have sharp edges and relatively plane sides with unpolished surfaces
Subangular	Particles are similar to angular description but have rounded edges
Subrounded	Particles have nearly plane sides but have well-rounded corners and edges
Rounded	Particles have smoothly curved sides and no edges

varying colors, this shall be noted and all representative colors shall be described. The color shall be described for moist samples. If the color represents a dry condition, this shall be stated in the report.

10.4 *Odor*—Describe the odor if organic or unusual. Soils containing a significant amount of organic material usually have a distinctive odor of decaying vegetation. This is especially apparent in fresh samples, but if the samples are dried, the odor may often be revived by heating a moistened sample. If the odor is unusual (petroleum product, chemical, and the like), it shall be described.

10.5 *Moisture Condition*—Describe the moisture condition as dry, moist, or wet, in accordance with the criteria in Table 3.

10.6 *HCl Reaction*—Describe the reaction with HCl as none, weak, or strong, in accordance with the criteria in Table 4. Since calcium carbonate is a common cementing agent, a report of its presence on the basis of the reaction with dilute hydrochloric acid is important.

10.7 *Consistency*—For intact fine-grained soil, describe the

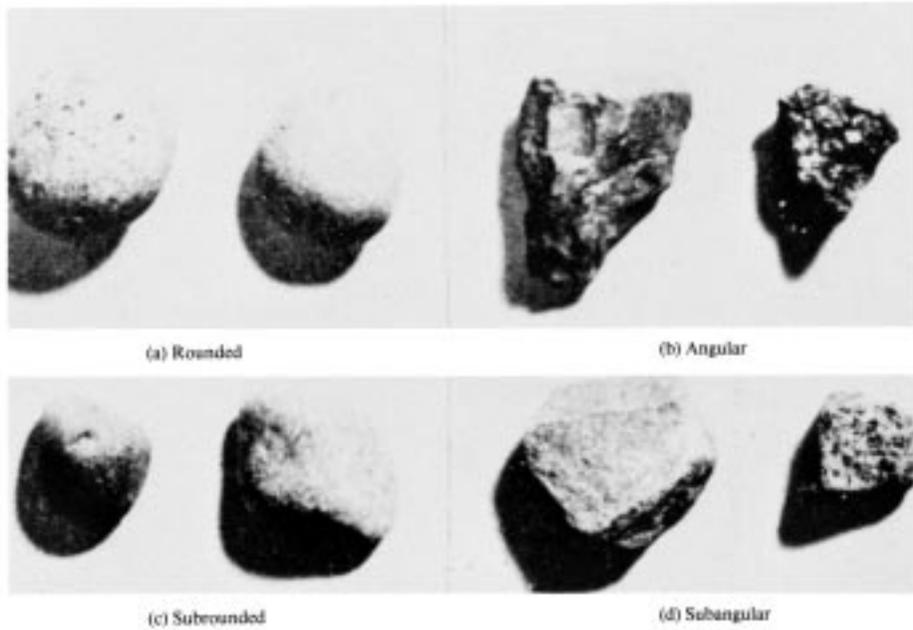


FIG. 3 Typical Angularity of Bulky Grains

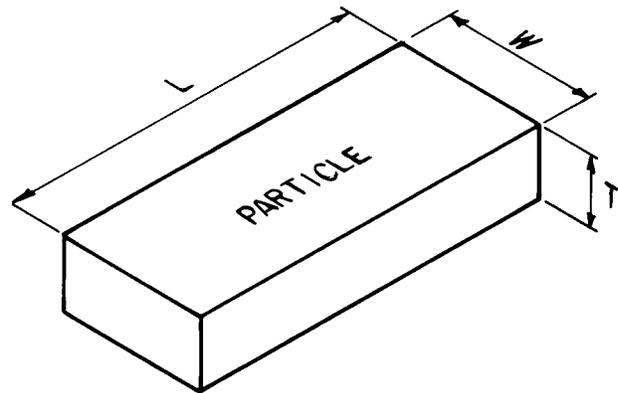
TABLE 2 Criteria for Describing Particle Shape (see Fig. 4)

The particle shape shall be described as follows where length, width, and thickness refer to the greatest, intermediate, and least dimensions of a particle, respectively.

Flat	Particles with width/thickness > 3
Elongated	Particles with length/width > 3
Flat and elongated	Particles meet criteria for both flat and elongated

PARTICLE SHAPE

W = WIDTH
T = THICKNESS
L = LENGTH



FLAT: $W/T > 3$
 ELONGATED: $L/W > 3$
 FLAT AND ELONGATED:
 - meets both criteria

FIG. 4 Criteria for Particle Shape

consistency as very soft, soft, firm, hard, or very hard, in accordance with the criteria in Table 5. This observation is inappropriate for soils with significant amounts of gravel.

10.8 *Cementation*—Describe the cementation of intact coarse-grained soils as weak, moderate, or strong, in accordance with the criteria in Table 6.

10.9 *Structure*—Describe the structure of intact soils in accordance with the criteria in Table 7.

10.10 *Range of Particle Sizes*—For gravel and sand components, describe the range of particle sizes within each component as defined in 3.1.2 and 3.1.6. For example, about 20 % fine to coarse gravel, about 40 % fine to coarse sand.

10.11 *Maximum Particle Size*—Describe the maximum particle size found in the sample in accordance with the following information:

10.11.1 *Sand Size*—If the maximum particle size is a sand size, describe as fine, medium, or coarse as defined in 3.1.6. For example: maximum particle size, medium sand.

10.11.2 *Gravel Size*—If the maximum particle size is a gravel size, describe the maximum particle size as the smallest sieve opening that the particle will pass. For example, maximum particle size, 1½ in. (will pass a 1½-in. square opening but not a ¾-in. square opening).

10.11.3 *Cobble or Boulder Size*—If the maximum particle size is a cobble or boulder size, describe the maximum dimension of the largest particle. For example: maximum dimension, 18 in. (450 mm).

10.12 *Hardness*—Describe the hardness of coarse sand and larger particles as hard, or state what happens when the

TABLE 3 Criteria for Describing Moisture Condition

Description	Criteria
Dry	Absence of moisture, dusty, dry to the touch
Moist	Damp but no visible water
Wet	Visible free water, usually soil is below water table

TABLE 4 Criteria for Describing the Reaction With HCl

Description	Criteria
None	No visible reaction
Weak	Some reaction, with bubbles forming slowly
Strong	Violent reaction, with bubbles forming immediately

TABLE 5 Criteria for Describing Consistency

Description	Criteria
Very soft	Thumb will penetrate soil more than 1 in. (25 mm)
Soft	Thumb will penetrate soil about 1 in. (25 mm)
Firm	Thumb will indent soil about ¼ in. (6 mm)
Hard	Thumb will not indent soil but readily indented with thumbnail
Very hard	Thumbnail will not indent soil

TABLE 6 Criteria for Describing Cementation

Description	Criteria
Weak	Crumbles or breaks with handling or little finger pressure
Moderate	Crumbles or breaks with considerable finger pressure
Strong	Will not crumble or break with finger pressure

TABLE 7 Criteria for Describing Structure

Description	Criteria
Stratified	Alternating layers of varying material or color with layers at least 6 mm thick; note thickness
Laminated	Alternating layers of varying material or color with the layers less than 6 mm thick; note thickness
Fissured	Breaks along definite planes of fracture with little resistance to fracturing
Slickensided	Fracture planes appear polished or glossy, sometimes striated
Blocky	Cohesive soil that can be broken down into small angular lumps which resist further breakdown
Lensed	Inclusion of small pockets of different soils, such as small lenses of sand scattered through a mass of clay; note thickness
Homogeneous	Same color and appearance throughout

particles are hit by a hammer, for example, gravel-size particles fracture with considerable hammer blow, some gravel-size particles crumble with hammer blow. “Hard” means particles do not crack, fracture, or crumble under a hammer blow.

10.13 Additional comments shall be noted, such as the presence of roots or root holes, difficulty in drilling or augering hole, caving of trench or hole, or the presence of mica.

10.14 A local or commercial name or a geologic interpretation of the soil, or both, may be added if identified as such.

10.15 A classification or identification of the soil in accordance with other classification systems may be added if identified as such.

11. Identification of Peat

11.1 A sample composed primarily of vegetable tissue in various stages of decomposition that has a fibrous to amor-

phous texture, usually a dark brown to black color, and an organic odor, shall be designated as a highly organic soil and shall be identified as peat, PT, and not subjected to the identification procedures described hereafter.

12. Preparation for Identification

12.1 The soil identification portion of this practice is based on the portion of the soil sample that will pass a 3-in. (75-mm) sieve. The larger than 3-in. (75-mm) particles must be removed, manually, for a loose sample, or mentally, for an intact sample before classifying the soil.

12.2 Estimate and note the percentage of cobbles and the percentage of boulders. Performed visually, these estimates will be on the basis of volume percentage.

NOTE 9—Since the percentages of the particle-size distribution in Test Method D 2487 are by dry weight, and the estimates of percentages for gravel, sand, and fines in this practice are by dry weight, it is recommended that the report state that the percentages of cobbles and boulders are by volume.

12.3 Of the fraction of the soil smaller than 3 in. (75 mm), estimate and note the percentage, by dry weight, of the gravel, sand, and fines (see Appendix X4 for suggested procedures).

NOTE 10—Since the particle-size components appear visually on the basis of volume, considerable experience is required to estimate the percentages on the basis of dry weight. Frequent comparisons with laboratory particle-size analyses should be made.

12.3.1 The percentages shall be estimated to the closest 5 %. The percentages of gravel, sand, and fines must add up to 100 %.

12.3.2 If one of the components is present but not in sufficient quantity to be considered 5 % of the smaller than 3-in. (75-mm) portion, indicate its presence by the term *trace*, for example, trace of fines. A trace is not to be considered in the total of 100 % for the components.

13. Preliminary Identification

13.1 The soil is *fine grained* if it contains 50 % or more fines. Follow the procedures for identifying fine-grained soils of Section 14.

13.2 The soil is *coarse grained* if it contains less than 50 % fines. Follow the procedures for identifying coarse-grained soils of Section 15.

14. Procedure for Identifying Fine-Grained Soils

14.1 Select a representative sample of the material for examination. Remove particles larger than the No. 40 sieve (medium sand and larger) until a specimen equivalent to about a handful of material is available. Use this specimen for performing the dry strength, dilatancy, and toughness tests.

14.2 Dry Strength:

14.2.1 From the specimen, select enough material to mold into a ball about 1 in. (25 mm) in diameter. Mold the material until it has the consistency of putty, adding water if necessary.

14.2.2 From the molded material, make at least three test specimens. A test specimen shall be a ball of material about ½ in. (12 mm) in diameter. Allow the test specimens to dry in air, or sun, or by artificial means, as long as the temperature does not exceed 60°C.

14.2.3 If the test specimen contains natural dry lumps, those that are about 1/2 in. (12 mm) in diameter may be used in place of the molded balls.

NOTE 11—The process of molding and drying usually produces higher strengths than are found in natural dry lumps of soil.

14.2.4 Test the strength of the dry balls or lumps by crushing between the fingers. Note the strength as none, low, medium, high, or very high in accordance with the criteria in Table 8. If natural dry lumps are used, do not use the results of any of the lumps that are found to contain particles of coarse sand.

14.2.5 The presence of high-strength water-soluble cementing materials, such as calcium carbonate, may cause exceptionally high dry strengths. The presence of calcium carbonate can usually be detected from the intensity of the reaction with dilute hydrochloric acid (see 10.6).

14.3 Dilatancy:

14.3.1 From the specimen, select enough material to mold into a ball about 1/2 in. (12 mm) in diameter. Mold the material, adding water if necessary, until it has a soft, but not sticky, consistency.

14.3.2 Smooth the soil ball in the palm of one hand with the blade of a knife or small spatula. Shake horizontally, striking the side of the hand vigorously against the other hand several times. Note the reaction of water appearing on the surface of the soil. Squeeze the sample by closing the hand or pinching the soil between the fingers, and note the reaction as none, slow, or rapid in accordance with the criteria in Table 9. The reaction is the speed with which water appears while shaking, and disappears while squeezing.

14.4 Toughness:

14.4.1 Following the completion of the dilatancy test, the test specimen is shaped into an elongated pat and rolled by hand on a smooth surface or between the palms into a thread about 1/8 in. (3 mm) in diameter. (If the sample is too wet to roll easily, it should be spread into a thin layer and allowed to lose some water by evaporation.) Fold the sample threads and reroll repeatedly until the thread crumbles at a diameter of about 1/8 in. The thread will crumble at a diameter of 1/8 in. when the soil is near the plastic limit. Note the pressure required to roll the thread near the plastic limit. Also, note the strength of the thread. After the thread crumbles, the pieces should be lumped together and kneaded until the lump crumbles. Note the toughness of the material during kneading.

14.4.2 Describe the toughness of the thread and lump as

TABLE 8 Criteria for Describing Dry Strength

Description	Criteria
None	The dry specimen crumbles into powder with mere pressure of handling
Low	The dry specimen crumbles into powder with some finger pressure
Medium	The dry specimen breaks into pieces or crumbles with considerable finger pressure
High	The dry specimen cannot be broken with finger pressure. Specimen will break into pieces between thumb and a hard surface
Very high	The dry specimen cannot be broken between the thumb and a hard surface

TABLE 9 Criteria for Describing Dilatancy

Description	Criteria
None	No visible change in the specimen
Slow	Water appears slowly on the surface of the specimen during shaking and does not disappear or disappears slowly upon squeezing
Rapid	Water appears quickly on the surface of the specimen during shaking and disappears quickly upon squeezing

low, medium, or high in accordance with the criteria in Table 10.

14.5 *Plasticity*—On the basis of observations made during the toughness test, describe the plasticity of the material in accordance with the criteria given in Table 11.

14.6 Decide whether the soil is an *inorganic* or an *organic* fine-grained soil (see 14.8). If inorganic, follow the steps given in 14.7.

14.7 Identification of Inorganic Fine-Grained Soils:

14.7.1 Identify the soil as a *lean clay*, CL, if the soil has medium to high dry strength, no or slow dilatancy, and medium toughness and plasticity (see Table 12).

14.7.2 Identify the soil as a *fat clay*, CH, if the soil has high to very high dry strength, no dilatancy, and high toughness and plasticity (see Table 12).

14.7.3 Identify the soil as a *silt*, ML, if the soil has no to low dry strength, slow to rapid dilatancy, and low toughness and plasticity, or is nonplastic (see Table 12).

14.7.4 Identify the soil as an *elastic silt*, MH, if the soil has low to medium dry strength, no to slow dilatancy, and low to medium toughness and plasticity (see Table 12).

NOTE 12—These properties are similar to those for a lean clay. However, the silt will dry quickly on the hand and have a smooth, silky feel when dry. Some soils that would classify as MH in accordance with the criteria in Test Method D 2487 are visually difficult to distinguish from lean clays, CL. It may be necessary to perform laboratory testing for proper identification.

14.8 Identification of Organic Fine-Grained Soils:

14.8.1 Identify the soil as an *organic soil*, OL/OH, if the soil contains enough organic particles to influence the soil properties. Organic soils usually have a dark brown to black color and may have an organic odor. Often, organic soils will change color, for example, black to brown, when exposed to the air. Some organic soils will lighten in color significantly when air dried. Organic soils normally will not have a high toughness or plasticity. The thread for the toughness test will be spongy.

NOTE 13—In some cases, through practice and experience, it may be possible to further identify the organic soils as organic silts or organic clays, OL or OH. Correlations between the dilatancy, dry strength, toughness tests, and laboratory tests can be made to identify organic soils in certain deposits of similar materials of known geologic origin.

TABLE 10 Criteria for Describing Toughness

Description	Criteria
Low	Only slight pressure is required to roll the thread near the plastic limit. The thread and the lump are weak and soft
Medium	Medium pressure is required to roll the thread to near the plastic limit. The thread and the lump have medium stiffness
High	Considerable pressure is required to roll the thread to near the plastic limit. The thread and the lump have very high stiffness

TABLE 11 Criteria for Describing Plasticity

Description	Criteria
Nonplastic Low	A 1/8-in. (3-mm) thread cannot be rolled at any water content. The thread can barely be rolled and the lump cannot be formed when drier than the plastic limit.
Medium	The thread is easy to roll and not much time is required to reach the plastic limit. The thread cannot be rerolled after reaching the plastic limit. The lump crumbles when drier than the plastic limit.
High	It takes considerable time rolling and kneading to reach the plastic limit. The thread can be rerolled several times after reaching the plastic limit. The lump can be formed without crumbling when drier than the plastic limit.

TABLE 12 Identification of Inorganic Fine-Grained Soils from Manual Tests

Soil Symbol	Dry Strength	Dilatancy	Toughness
ML	None to low	Slow to rapid	Low or thread cannot be formed
CL	Medium to high	None to slow	Medium
MH	Low to medium	None to slow	Low to medium
CH	High to very high	None	High

14.9 If the soil is estimated to have 15 to 25 % sand or gravel, or both, the words “with sand” or “with gravel” (whichever is more predominant) shall be added to the group name. For example: “lean clay with sand, CL” or “silt with gravel, ML” (see Fig. 1a and Fig. 1b). If the percentage of sand is equal to the percentage of gravel, use “with sand.”

14.10 If the soil is estimated to have 30 % or more sand or gravel, or both, the words “sandy” or “gravelly” shall be added to the group name. Add the word “sandy” if there appears to be more sand than gravel. Add the word “gravelly” if there appears to be more gravel than sand. For example: “sandy lean clay, CL”, “gravelly fat clay, CH”, or “sandy silt, ML” (see Fig. 1a and Fig. 1b). If the percentage of sand is equal to the percent of gravel, use “sandy.”

15. Procedure for Identifying Coarse-Grained Soils (Contains less than 50 % fines)

15.1 The soil is a *gravel* if the percentage of gravel is estimated to be more than the percentage of sand.

15.2 The soil is a *sand* if the percentage of gravel is estimated to be equal to or less than the percentage of sand.

15.3 The soil is a *clean gravel* or *clean sand* if the percentage of fines is estimated to be 5 % or less.

15.3.1 Identify the soil as a *well-graded gravel*, GW, or as a *well-graded sand*, SW, if it has a wide range of particle sizes and substantial amounts of the intermediate particle sizes.

15.3.2 Identify the soil as a *poorly graded gravel*, GP, or as a *poorly graded sand*, SP, if it consists predominantly of one size (uniformly graded), or it has a wide range of sizes with some intermediate sizes obviously missing (gap or skip graded).

15.4 The soil is either a *gravel with fines* or a *sand with fines* if the percentage of fines is estimated to be 15 % or more.

15.4.1 Identify the soil as a *clayey gravel*, GC, or a *clayey sand*, SC, if the fines are clayey as determined by the procedures in Section 14.

15.4.2 Identify the soil as a *silty gravel*, GM, or a *silty sand*,

SM, if the fines are silty as determined by the procedures in Section 14.

15.5 If the soil is estimated to contain 10 % fines, give the soil a dual identification using two group symbols.

15.5.1 The first group symbol shall correspond to a clean gravel or sand (GW, GP, SW, SP) and the second symbol shall correspond to a gravel or sand with fines (GC, GM, SC, SM).

15.5.2 The group name shall correspond to the first group symbol plus the words “with clay” or “with silt” to indicate the plasticity characteristics of the fines. For example: “well-graded gravel with clay, GW-GC” or “poorly graded sand with silt, SP-SM” (see Fig. 2).

15.6 If the specimen is predominantly sand or gravel but contains an estimated 15 % or more of the other coarse-grained constituent, the words “with gravel” or “with sand” shall be added to the group name. For example: “poorly graded gravel with sand, GP” or “clayey sand with gravel, SC” (see Fig. 2).

15.7 If the field sample contains any cobbles or boulders, or both, the words “with cobbles” or “with cobbles and boulders” shall be added to the group name. For example: “silty gravel with cobbles, GM.”

16. Report

16.1 The report shall include the information as to origin, and the items indicated in Table 13.

NOTE 14—*Example: Clayey Gravel with Sand and Cobbles, GC*—About 50 % fine to coarse, subrounded to subangular gravel; about 30 % fine to coarse, subrounded sand; about 20 % fines with medium plasticity, high dry strength, no dilatancy, medium toughness; weak reaction with HCl; original field sample had about 5 % (by volume) subrounded cobbles, maximum dimension, 150 mm.

In-Place Conditions—Firm, homogeneous, dry, brown

Geologic Interpretation—Alluvial fan

TABLE 13 Checklist for Description of Soils

1. Group name
2. Group symbol
3. Percent of cobbles or boulders, or both (by volume)
4. Percent of gravel, sand, or fines, or all three (by dry weight)
5. Particle-size range:
Gravel—fine, coarse
Sand—fine, medium, coarse
6. Particle angularity: angular, subangular, subrounded, rounded
7. Particle shape: (if appropriate) flat, elongated, flat and elongated
8. Maximum particle size or dimension
9. Hardness of coarse sand and larger particles
10. Plasticity of fines: nonplastic, low, medium, high
11. Dry strength: none, low, medium, high, very high
12. Dilatancy: none, slow, rapid
13. Toughness: low, medium, high
14. Color (in moist condition)
15. Odor (mention only if organic or unusual)
16. Moisture: dry, moist, wet
17. Reaction with HCl: none, weak, strong
<i>For intact samples:</i>
18. Consistency (fine-grained soils only): very soft, soft, firm, hard, very hard
19. Structure: stratified, laminated, fissured, slickensided, lensed, homogeneous
20. Cementation: weak, moderate, strong
21. Local name
22. Geologic interpretation
23. Additional comments: presence of roots or root holes, presence of mica, gypsum, etc., surface coatings on coarse-grained particles, caving or sloughing of auger hole or trench sides, difficulty in augering or excavating, etc.



NOTE 15—Other examples of soil descriptions and identification are given in Appendix X1 and Appendix X2.

NOTE 16—If desired, the percentages of gravel, sand, and fines may be stated in terms indicating a range of percentages, as follows:

Trace—Particles are present but estimated to be less than 5 %

Few—5 to 10 %

Little—15 to 25 %

Some—30 to 45 %

Mostly—50 to 100 %

16.2 If, in the soil description, the soil is identified using a classification group symbol and name as described in Test Method D 2487, it must be distinctly and clearly stated in log

forms, summary tables, reports, and the like, that the symbol and name are based on visual-manual procedures.

17. Precision and Bias

17.1 This practice provides qualitative information only, therefore, a precision and bias statement is not applicable.

18. Keywords

18.1 classification; clay; gravel; organic soils; sand; silt; soil classification; soil description; visual classification

APPENDIXES

(Nonmandatory Information)

X1. EXAMPLES OF VISUAL SOIL DESCRIPTIONS

X1.1 The following examples show how the information required in 16.1 can be reported. The information that is included in descriptions should be based on individual circumstances and need.

X1.1.1 *Well-Graded Gravel with Sand (GW)*—About 75 % fine to coarse, hard, subangular gravel; about 25 % fine to coarse, hard, subangular sand; trace of fines; maximum size, 75 mm, brown, dry; no reaction with HCl.

X1.1.2 *Silty Sand with Gravel (SM)*—About 60 % predominantly fine sand; about 25 % silty fines with low plasticity, low dry strength, rapid dilatancy, and low toughness; about 15 % fine, hard, subrounded gravel, a few gravel-size particles fractured with hammer blow; maximum size, 25 mm; no reaction with HCl (Note—Field sample size smaller than recommended).

In-Place Conditions—Firm, stratified and contains lenses of silt 1 to 2 in. (25 to 50 mm) thick, moist, brown to gray; in-place density 106 lb/ft³; in-place moisture 9 %.

X1.1.3 *Organic Soil (OL/OH)*—About 100 % fines with low plasticity, slow dilatancy, low dry strength, and low toughness; wet, dark brown, organic odor; weak reaction with HCl.

X1.1.4 *Silty Sand with Organic Fines (SM)*—About 75 % fine to coarse, hard, subangular reddish sand; about 25 % organic and silty dark brown nonplastic fines with no dry strength and slow dilatancy; wet; maximum size, coarse sand; weak reaction with HCl.

X1.1.5 *Poorly Graded Gravel with Silt, Sand, Cobbles and Boulders (GP-GM)*—About 75 % fine to coarse, hard, subrounded to subangular gravel; about 15 % fine, hard, subrounded to subangular sand; about 10 % silty nonplastic fines; moist, brown; no reaction with HCl; original field sample had about 5 % (by volume) hard, subrounded cobbles and a trace of hard, subrounded boulders, with a maximum dimension of 18 in. (450 mm).

X2. USING THE IDENTIFICATION PROCEDURE AS A DESCRIPTIVE SYSTEM FOR SHALE, CLAYSTONE, SHELLS, SLAG, CRUSHED ROCK, AND THE LIKE

X2.1 The identification procedure may be used as a descriptive system applied to materials that exist in-situ as shale, claystone, sandstone, siltstone, mudstone, etc., but convert to soils after field or laboratory processing (crushing, slaking, and the like).

X2.2 Materials such as shells, crushed rock, slag, and the like, should be identified as such. However, the procedures used in this practice for describing the particle size and plasticity characteristics may be used in the description of the material. If desired, an identification using a group name and symbol according to this practice may be assigned to aid in describing the material.

X2.3 The group symbol(s) and group names should be placed in quotation marks or noted with some type of distinguishing symbol. See examples.

X2.4 Examples of how group names and symbols can be incorporated into a descriptive system for materials that are not naturally occurring soils are as follows:

X2.4.1 *Shale Chunks*—Retrieved as 2 to 4-in. (50 to 100-mm) pieces of shale from power auger hole, dry, brown, no reaction with HCl. After slaking in water for 24 h, material identified as “Sandy Lean Clay (CL)”; about 60 % fines with medium plasticity, high dry strength, no dilatancy, and medium toughness; about 35 % fine to medium, hard sand; about 5 % gravel-size pieces of shale.

X2.4.2 *Crushed Sandstone*—Product of commercial crushing operation; “Poorly Graded Sand with Silt (SP-SM)”; about 90 % fine to medium sand; about 10 % nonplastic fines; dry, reddish-brown, strong reaction with HCl.

X2.4.3 *Broken Shells*—About 60 % gravel-size broken

shells; about 30 % sand and sand-size shell pieces; about 10 % fines; “Poorly Graded Gravel with Sand (GP).”

X2.4.4 *Crushed Rock*—Processed from gravel and cobbles in Pit No. 7; “Poorly Graded Gravel (GP)”; about 90 % fine,

hard, angular gravel-size particles; about 10 % coarse, hard, angular sand-size particles; dry, tan; no reaction with HCl.

X3. SUGGESTED PROCEDURE FOR USING A BORDERLINE SYMBOL FOR SOILS WITH TWO POSSIBLE IDENTIFICATIONS.

X3.1 Since this practice is based on estimates of particle size distribution and plasticity characteristics, it may be difficult to clearly identify the soil as belonging to one category. To indicate that the soil may fall into one of two possible basic groups, a borderline symbol may be used with the two symbols separated by a slash. For example: SC/CL or CL/CH.

X3.1.1 A borderline symbol may be used when the percentage of fines is estimated to be between 45 and 55 %. One symbol should be for a coarse-grained soil with fines and the other for a fine-grained soil. For example: GM/ML or CL/SC.

X3.1.2 A borderline symbol may be used when the percentage of sand and the percentage of gravel are estimated to be about the same. For example: GP/SP, SC/GC, GM/SM. It is practically impossible to have a soil that would have a borderline symbol of GW/SW.

X3.1.3 A borderline symbol may be used when the soil could be either well graded or poorly graded. For example: GW/GP, SW/SP.

X3.1.4 A borderline symbol may be used when the soil could either be a silt or a clay. For example: CL/ML, CH/MH, SC/SM.

X3.1.5 A borderline symbol may be used when a fine-grained soil has properties that indicate that it is at the boundary between a soil of low compressibility and a soil of high compressibility. For example: CL/CH, MH/ML.

X3.2 The order of the borderline symbols should reflect similarity to surrounding or adjacent soils. For example: soils in a borrow area have been identified as CH. One sample is considered to have a borderline symbol of CL and CH. To show similarity, the borderline symbol should be CH/CL.

X3.3 The group name for a soil with a borderline symbol should be the group name for the first symbol, except for:

CL/CH lean to fat clay
ML/CL clayey silt
CL/ML silty clay

X3.4 The use of a borderline symbol should not be used indiscriminately. Every effort shall be made to first place the soil into a single group.

X4. SUGGESTED PROCEDURES FOR ESTIMATING THE PERCENTAGES OF GRAVEL, SAND, AND FINES IN A SOIL SAMPLE

X4.1 *Jar Method*—The relative percentage of coarse- and fine-grained material may be estimated by thoroughly shaking a mixture of soil and water in a test tube or jar, and then allowing the mixture to settle. The coarse particles will fall to the bottom and successively finer particles will be deposited with increasing time; the sand sizes will fall out of suspension in 20 to 30 s. The relative proportions can be estimated from the relative volume of each size separate. This method should be correlated to particle-size laboratory determinations.

X4.2 *Visual Method*—Mentally visualize the gravel size particles placed in a sack (or other container) or sacks. Then, do the same with the sand size particles and the fines. Then, mentally compare the number of sacks to estimate the percentage of plus No. 4 sieve size and minus No. 4 sieve size present.

The percentages of sand and fines in the minus sieve size No. 4 material can then be estimated from the wash test (X4.3).

X4.3 *Wash Test (for relative percentages of sand and fines)*—Select and moisten enough minus No. 4 sieve size material to form a 1-in (25-mm) cube of soil. Cut the cube in half, set one-half to the side, and place the other half in a small dish. Wash and decant the fines out of the material in the dish until the wash water is clear and then compare the two samples and estimate the percentage of sand and fines. Remember that the percentage is based on weight, not volume. However, the volume comparison will provide a reasonable indication of grain size percentages.

X4.3.1 While washing, it may be necessary to break down lumps of fines with the finger to get the correct percentages.

X5. ABBREVIATED SOIL CLASSIFICATION SYMBOLS

X5.1 In some cases, because of lack of space, an abbreviated system may be useful to indicate the soil classification symbol and name. Examples of such cases would be graphical logs, databases, tables, etc.

X5.2 This abbreviated system is not a substitute for the full name and descriptive information but can be used in supplementary presentations when the complete description is referenced.

X5.3 The abbreviated system should consist of the soil classification symbol based on this standard with appropriate lower case letter prefixes and suffixes as:

Prefix:

Suffix:

s = sandy
g = gravelly

s = with sand
g = with gravel
c = with cobbles
b = with boulders

X5.4 The soil classification symbol is to be enclosed in parenthesis. Some examples would be:

<i>Group Symbol and Full Name</i>	<i>Abbreviated</i>
CL, Sandy lean clay	s(CL)
SP-SM, Poorly graded sand with silt and gravel	(SP-SM)g
GP, poorly graded gravel with sand, cobbles, and boulders	(GP)scb
ML, gravelly silt with sand and cobbles	g(ML)sc

SUMMARY OF CHANGES

In accordance with Committee D18 policy, this section identifies the location of changes to this standard since the last edition (1993^{e1}) that may impact the use of this standard.

(1) Added Practice D 3740 to Section 2.

(2) Added Note 5 under 5.7 and renumbered subsequent notes.

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STANDARD OPERATING PROCEDURES SOP-5: SAMPLE LABELING

Scope and Application

This SOP describes the general Integral procedures for sample labeling. The project-specific sampling and analysis plan (SAP) should be consulted to determine the exact sample identifiers and sample labels are required for a given project. If they are not specified in the SAP, the designations listed below should be followed.

Supplies and Equipment

- Site logbook
- Chain-of-custody form(s)
- Sample labels.

Procedures

Environmental samples will be labeled using a unique designation system consisting of:

- Sample identification number
- Tag number
- Sample location identification.

The following describes each of the numbers.

Sample ID Number

The sample ID number is a unique number that is generally assigned six digits, including a two-digit media code and a four-digit number. The media code may be site-specific, but the Integral default codes are as follows:

- SS—Surface soil
- BH—Subsurface soil or rock (typically from borehole)
- GW—Groundwater
- SW—Surface water

- PW—Pore water
- BT—Biota or biological tissue

The exact sample ID numbering scheme may vary from project to project. Variances in the sample numbering scheme will be described in the field sampling plan for the field effort. Each sample will be assigned a unique sample number. Note that in cases where samples consist of multiple bottles from the same location, each bottle will be assigned the same sample number and time. Replicates from the same location, however, will be assigned a different sample number and time, and the sample numbers of related field replicates will not necessarily have any shared content. Each field split of a single sample will also have a different sample number and time. The sample number is recorded on the sample label, the chain-of-custody form, and the field logbook.

Sample Tag Number

A different tag number is attached to each sample container. If the amount of material (i.e., everything associated with a single sample number) is too large for a single container, each container will have the same sample number and a different sample tag. A sample will also be split between containers if a different preservation technique is used for each container (i.e., because different analyses will be conducted).

The sample tag number is a unique five- or six-digit number assigned to each sample label (or “tag”) for multiple bottles per sample. Integral sample labels come with a pre-printed sample tag number. The purpose of the tag number is to provide a unique tracking number to a specific sample bottle. This allows for greater flexibility in tracking sample bottles and assists in field quality control when filling out documentation and shipping. Sample tags are not used by many other consultants, and there may be resistance from such firms during teaming situations. However, experience has shown that tags can be very valuable, both in the field and while processing data from field efforts.

Sample tag numbers will be recorded on the sample label (typically pre-printed), the chain-of-custody form, and the field logbook. Tag numbers are used by laboratories only to confirm that they have received all of the containers that were filled and shipped. Data are reported by sample number.

Sample Location ID

The sample location ID is a unique designation that identifies where the sample was collected. For sediment samples, this number is frequently the station ID (e.g., WB-10). The sample ID will also indicate if the sample is a field quality control sample (e.g., WB-10-DUP). The sample ID is recorded in the field logbook *only* and is not provided on the sample label or chain-of-custody form.

Sample Documentation

The SAP, or an appendix to the SAP, presents examples of how sample labeling information should be documented in the field logbook or borehole log. More or less information may be required on a site-specific basis.

STANDARD OPERATING PROCEDURE SOP-6: SAMPLE PACKAGING AND SHIPPING

Scope and Application

Specific requirements for sample packaging and shipping must be followed to ensure the proper transfer and documentation of environmental samples collected during field operations. Procedures for the careful and consistent transfer of samples from the field to the laboratory are outlined herein. This SOP presents the method to be used when packing samples that will either be hand delivered or shipped by commercial carrier to the laboratory.

Equipment and Supplies Required

Specific equipment or supplies necessary to properly pack and ship environmental samples include the following:

- Project-specific sampling and analysis plan (SAP)
- Project-specific field logbook
- Sealable airtight bags (assorted sizes) (e.g., Ziplocs[®])
- Wet ice in doubled, sealable bags; frozen Blue Ice[®]; or dry ice
- Coolers
- Bubble wrap
- Fiber reinforced packing tape and duct tape
- Clear plastic packing tape
- Scissors or knife
- Chain-of-custody (COC) forms
- Chain-of-custody seals
- Large plastic garbage bags (preferably 3 mil [0.003 inch] thick)
- Paper towels
- “Fragile,” “This End Up,” or “Handle With Care” labels
- Mailing labels
- Airbills for overnight shipment

Procedure

The logistics for sample packaging and shipping should be specifically tailored to each study. In some cases, samples may be transferred from the field to a local storage facility where they can be either frozen or refrigerated. Depending on the logistics of the operation, field personnel may transport samples to the laboratory themselves or utilize a commercial courier or shipping service. If a courier service is used, then Integral field personnel need to be aware of any potentially limiting factors to timely shipping (e.g., availability of overnight service and weekend deliveries to specific areas of the country, shipping regulations “restricted articles” [e.g., dry ice, formalin]) prior to shipping the samples.

Sample Preparation

The following steps should be followed to ensure the proper transfer of samples from the field to the laboratories:

At the sample collection site:

1. Appropriately document all samples using the proper logbooks or field forms (see SOP-8), required sample container identification (i.e., sample labels with tag numbers), and chain-of-custody (COC) form. Fill out the COC form as described in SOP-7, and use the sample labeling techniques provided in SOP-5.
2. Make sure all applicable laboratory quality control sample designations have been made on the COC forms. Samples that will be archived for future possible analysis should be clearly identified on the COC form and should be also be labeled as “Do Not Analyze: Hold and archive for possible future analysis” as some laboratories interpret “archive” to mean continue holding the residual sample after analysis.
3. Notify the laboratory contact and the Integral project quality assurance/quality control (QA/QC) coordinator that samples will be shipped and the estimated arrival time. Send copies of all COC forms to Integral’s project QA/QC coordinator or project manager, as appropriate.
4. Ensure that samples remain in the possession of the sampling personnel at all times. Any temporary onsite sample storage areas will be locked and secured to maintain sample integrity and chain-of-custody requirements.
5. Clean the outside of all dirty sample containers to remove any residual material that may lead to cross-contamination.

6. Fill out the chain-of-custody form as described in SOP-7, and retain the back (pink) copy of the form for the project records prior to sealing the cooler. Check sample containers against the chain-of-custody form to ensure all of the samples that were collected are in the cooler.
7. Store each sample container in an individual sealable plastic bag that allows the sample label to be read. Volatile organic analyte (VOA) vials must be encased in a foam sleeve or in bubble wrap before being sealed in bags.
8. If the samples have a required storage temperature, place a sufficient amount of ice in the sample cooler to maintain the temperature inside the cooler (e.g., 4°C) throughout the sampling day.

At the sample processing area (immediately after sample collection):

1. If the samples have a required storage temperature, then the samples should be cooled to and maintained at that temperature prior to shipping. For example, a sufficient amount of ice must be present in each sample cooler to maintain the temperature inside the cooler at 4°C until processing begins to ship the samples to the testing laboratory.
2. Be aware of holding time requirements for project-specific analytes and arrange the sample shipping schedule accordingly.
3. Place samples in secure storage (i.e., locked room or vehicle) or ensure they remain in the possession of Integral sampling personnel before shipment. Lock and secure any sample storage areas to maintain sample integrity and chain-of-custody requirements.
4. Store samples in the dark (e.g., keep coolers shut).

At the sample processing area (just prior to shipping):

1. Check sample containers against the COC form to ensure all samples intended for shipment are accounted for.
2. Choose the appropriate size cooler (or coolers) and make sure that the outside and inside of the cooler is clean of gross contamination. If the cooler has a drain on the outside at the bottom of the cooler, the drain should be capped and thoroughly taped shut with duct tape.
3. Ensure the cooler is lined with bubble wrap and a large plastic bag (preferably a bag with a thickness of 3 mil) is opened and placed inside the cooler.

4. Individually wrap each glass container (which at the sample collection site had already been placed in an individual sealable plastic bag) in bubble wrap using either tape or a rubber band to hold the bubble wrap in place. Place the wrapped samples into the large plastic bag in the cooler, leaving sufficient room for ice to keep the samples cold (i.e., 4°C).
5. If temperature blanks have been provided by the testing laboratory, include one temperature blank in each sample cooler.
6. If the samples have a required storage temperature, add enough wet ice or Blue Ice® to keep the samples refrigerated during overnight shipping (i.e., 4°C). Always over-estimate the amount of ice that you think will be required. Ice should be enclosed in a sealable plastic bag and then placed in a second sealable plastic bag to prevent leakage. Avoid separating the samples from the ice with excess bubble wrap because it will insulate the containers from the ice. After all samples and ice have been added to the cooler, use bubble wrap (or other available clean packing material) to fill any empty space to keep the samples from shifting during transport.
7. If possible, consolidate all VOA samples in a single cooler and ship them with (a) trip blank(s) if the project-specific quality assurance project plan calls for one.
8. Sign, date, and include any tracking numbers provided by the shipper on the COC form. Remove the back (pink) copy of the original COC form and retain this copy for the project records.
9. Place the rest of the signed COC form in a sealable bag and tape the bag containing the form to the inside of the cooler lid. Each cooler should contain an individual COC form for the samples contained in each respective cooler. If time constraints impact sample shipping and it becomes necessary to combine all of the samples onto a single set of COC forms and the shipment contains multiple coolers, indicate on the outside of the respective cooler "Chain-of-Custody Inside."
10. After the cooler is sufficiently packed to prevent shifting of the containers, close the lid and seal it shut with fiber-reinforced packing tape. The cooler should be taped shut around the opening between the lid and the bottom of the cooler and around the circumference of the cooler at both hinges.
11. As security against unauthorized handling of the samples, apply two chain-of-custody seals across the opening of the cooler lid (example provided in Attachment 2-1). One seal should be placed on the front right portion of the cooler and one seal should be placed on the back left portion of the cooler. Be sure the seals are properly affixed to the cooler so they are not removed during shipment. Additional tape across the seal may be necessary if the outside of the cooler is wet.

Sample Shipping

Hand-Delivery to the Testing Laboratory

1. Notify the laboratory contact and the Integral project QA/QC coordinator that samples will be delivered to the laboratory and the estimated arrival time.
2. All environmental samples that are hand-delivered to the testing laboratory will be received by the laboratory on the same day that they were packed in the coolers.
3. Fax or scan and email copies of all COC forms to the Integral project QA/QC coordinator. Note: Prior to faxing, it may be necessary to photocopy the COC form on a slightly darker setting so that the form is readable after it has been faxed. Never leave the original COC form in the custody of non-Integral staff.

Shipped by Commercial Carrier to the Laboratory

1. Use a mailing label and label the cooler with destination and return addresses, and add other appropriate stickers, such as "This End Up," "Fragile," and "Handle With Care." If the shipment contains multiple coolers, indicate on the mailing label the number of coolers that the testing laboratory should expect to receive (e.g., 1 of 2; 2 of 2). Place clear tape over the mailing label to firmly affix it to the outside of the cooler and to protect it from the weather. This is a secondary label in case the airbill is lost during shipment.
2. Fill out the airbill as required and fasten it to handle tags provided by the shipper (or the top of the cooler if handle tags are not available).
3. If samples need to be frozen (-20°C) during shipping, then dry ice will need to be placed in the sample cooler. Be aware of any additional shipping, handling, and special labeling requirements that may be required by the shipper for these samples.
4. Benthic infauna samples will need to be preserved with formalin in the field prior to shipping. Be aware of any additional shipping, handling, and special labeling requirements that may be required by the shipper for these samples.
5. Notify the laboratory contact and the Integral project QA/QC coordinator that samples will be shipped and the estimated arrival date and time. All environmental samples that are shipped at 4°C or -20°C will be shipped overnight for next morning delivery. Fax or scan and email copies of all COC forms to the Integral project QA/QC coordinator. Note: Prior to faxing, it may be necessary to photocopy the COC form on a slightly darker setting so that the form is readable after it has been faxed. Never leave the original COC form in the custody of non-Integral staff.

STANDARD OPERATING PROCEDURE SOP-7: SAMPLE CUSTODY

Scope and Application

This SOP describes Integral procedures for custody management of environmental samples.

A stringent, established program of sample chain-of-custody will be followed during sample storage and shipping activities to account for each sample. The procedure outlined herein will be used with SOP-6, which covers sample packaging and shipping; SOP-8, which covers the use of field logbooks and other types of field documentation; and SOP-5, which covers sample labeling. Chain-of-custody (COC) forms ensure that samples are traceable from the time of collection through processing and analysis until final disposition. A sample is considered to be in a person's custody if any of the following criteria are met:

1. The sample is in the person's possession
2. The sample is in the person's view after being in possession
3. The sample is in the person's possession and is being transferred to a designated secure area
4. The sample has been locked up to prevent tampering after it was in the person's possession.

At no time is it acceptable for samples to be outside of Integral personnel's custody unless the samples have been transferred to a secure area (i.e., locked up). If the samples cannot be placed in a secure area, then an Integral field team member must physically remain with the samples (e.g., at lunch time one team member must remain with the samples).

Chain-of-Custody Forms

The COC form is the critical because it documents sample possession from the time of collection through the final disposition of the sample. The form also provides information to the laboratory regarding what analyses are to be performed on the samples that are shipped.

The COC form will be completed after each field collection activity and before the samples are shipped to the laboratory. Sampling personnel are responsible for the care and custody of the samples until they are shipped. When transferring possession of the

samples, the individuals relinquishing and receiving the samples must sign the COC form(s), indicating the time and date that the transfer occurs.

The COC forms each consist of 3-part carbon-less paper with white, yellow, and pink copies. The pink copy is kept by the sampling team leader. The white sheet and the yellow sheet will be placed into a plastic sealable bag and secured to the inside top of each transfer container (e.g., cooler). The pink sheet will be retained by the field staff for filing at the Integral Project Manager's location. Each COC form has a unique 4-digit number. This number and the samples on the form shall be recorded in the field logbook. Integral also uses computer-generated COC forms. If computer-generated forms are used, then the forms must be printed in triplicate and all three sheets signed so that two sheets can accompany the shipment to the laboratory and one sheet can be retained on file at the Integral Project Manager's location. Alternatively, if sufficient lead time is available, the computer-generated forms will be printed on 3-part carbon-less paper.

The project-assigned sample number and the unique tag number at the bottom of each sample label will be recorded on the COC form. The COC form will also identify the sample collection date and time, the type of sample, the project, and the sampling personnel. In addition, the COC form provides information on the preservative or other sample pretreatment applied in the field and the analyses to be conducted by referencing a list of specific analyses or the statement of work for the laboratory. The COC form will be sent to the laboratory along with the sample(s).

Procedures

The following guidelines will be followed to ensure the integrity of the samples:

1. Each COC form must be appropriately signed and dated by the sampling personnel. The person who relinquishes custody of the samples must also sign this form.
2. At the end of each sampling day and prior to shipping or storage, chain-of-custody entries will be made for all samples. Information on the labels and tags will be checked against field logbook entries.
3. The COC form should not be signed until the information has been checked for inaccuracies by the sampling team leader. All changes should be made by drawing a single line through the incorrect entry and initialing and dating it. Revised entries should be made in the space below the entries. Any blank lines remaining on the COC form after corrections are made should be marked out with single lines that are initialed and dated. This procedure will preclude any unauthorized additions.

4. At the bottom of each COC form is a space for the signatures of the persons relinquishing and receiving the samples and the time and date that the transfer occurred. The time that the samples were relinquished should match exactly the time they were received by another party. Under no circumstances should there be any time when custody of the samples is undocumented.
5. If samples are sent by a commercial carrier not affiliated with the laboratory, such as Federal Express (FedEx) or United Parcel Service (UPS), the name of the carrier should be recorded on the COC form. Any tracking numbers supplied by the carrier should be also entered on the COC form. The time of transfer should be as close to the actual drop-off time as possible. After the COC forms are signed and the “pink” copy has been removed, they should be sealed inside the transfer container.
6. If errors are found after the shipment has left the custody of sampling personnel, a corrected version of the forms must be made and sent to all relevant parties. Minor errors can be rectified by making the change on a copy of the original with a brief explanation and signature. Errors in the signature block may require a letter of explanation.
7. Samples that are archived internally at Integral must be accompanied by a COC form and an Archive Record form.
8. Upon completion of the field sampling event, the sampling team leader will be responsible for submitting all COC forms to be copied. A discussion of copy distribution is provided in SOP-AP2.

Custody Seal

As security against unauthorized handling of the samples during shipping, two custody seals will be affixed to each sample cooler. The custody seals will be placed across the opening of the cooler (front right and back left) prior to shipping. Be sure the seals are properly affixed to the cooler so they cannot be removed during shipping. Additional tape across the seal and around the cooler may be prudent.

Shipping Air Bills

When samples are shipped from the field to the testing laboratory via a commercial carrier (e.g., Federal Express, UPS), an air bill or receipt is provided by the shipper. The air bill number (or tracking number) should be noted on the applicable COC forms or alternatively the applicable COC form number should be noted on the air bill to enable the tracking of samples if a cooler becomes lost.

Acknowledgement of Sample Receipt Forms

In most cases, when samples are sent to a testing laboratory, an Acknowledgment of Sample Receipt form is faxed to the project QA/QC coordinator the day the samples are received by the laboratory. It is the responsibility of the person receiving this form to review the form and make sure that all the samples that were sent to the laboratory were received by the laboratory and that the correct analyses were requested. If an error is found, the laboratory must be called immediately. Decisions made during the telephone conversation should be documented in writing on the Acknowledgment of Sample Receipt Form. In addition, corrections should be made to the COC form and the corrected version of the COC form should be faxed to the laboratory.

Archive Record Forms

On rare occasions, samples are archived at an Integral office. If samples are to be archived at Integral, it is the responsibility of the project manager to complete an Archive Record form. This form is to be accompanied by a copy of the COC form for the samples, and will be placed in a locked file cabinet. The original COC form will remain with the samples in a sealed Ziploc bag.

STANDARD OPERATING PROCEDURE SOP-8: FIELD DOCUMENTATION

Scope and Application

The integrity of each sample from the time of collection to the point of data reporting must be maintained throughout the study. Proper record keeping will be implemented in the field to allow samples to be traced from collection to final disposition.

All information relevant to field operations must be properly documented to ensure that activities are accounted for and can be reconstructed from written records to the extent that someone not present at the site can reconstruct the activity without relying on the memory of the field crew. Several types of field documents will be used for this purpose and should be consistently used by field personnel. Field documentation should include only a factual description of site-related activities and observations made. Field personnel should not include superfluous comments or speculation regarding the field activities or observations made.

Field Logbooks

During field sampling events, field logbooks are used to record all daily field activities. The purpose of the field logbook is to document events that occur and record data measured in the field to the extent that someone not present at the site can reconstruct the activity without relying on the memory of the field crew.

The field logbook is issued by the Project Manager (or designee) to the appropriate site personnel for the direction of onsite activities (e.g., Reconnaissance Survey Team Leader, Sampling Team Leader). It is the responsibility of this person (or designee) to keep the site logbook current while in his or her possession, and return it to the Project Manager or turn it over to another field team.

A separate bound, waterproof field logbook with consecutively numbered pages will be completed using indelible ink for each sampling event. All daily field activities will be documented in indelible ink in this logbook and no erasures will be made. All corrections should consist of a single line-out deletion, followed by the author's initials and the date. The author will initial and date each page of the field logbook. The author will sign and date the last page at the end of each day, and a line will be drawn through the remainder of the page.

The project name, dates of the field work, site name and location (city and state), and Integral contract number should be written on the cover of the field logbook. If more than one logbook is used during a single sampling event, then the upper right hand corner of the logbook will be annotated (e.g., Volume 1 of 2, 2 of 2) to indicate the number of logbooks used during the field event. Field logbooks will be stored in a secure manner when not in use in the field. At a minimum, the sampler will record the following information in the field logbook:

- Project name, project location, and contract number
- Purpose and description of the field task
- Project start date and end date
- Date and time of entry (24-hour clock)
- Time and duration of daily sampling activities
- Weather conditions at the beginning of the field work and any changes that occur throughout the day, including the approximate time of the change (e.g., wind speed and direction, rain, thunder, wave action, current, tide, vessel traffic, temperature of both the air and water, thickness of ice if present)
- Name and affiliation of person making entries and other field personnel and their duties, including the times that they are present
- The location and description of the work area, including sketches, map references, and photograph log, if appropriate
- Level of personal protection being used
- Onsite visitors (names and affiliations), if any, including the times that they are present
- The name, agency, and telephone number of any field contacts
- Notation of the coordinate system used to determine the station location information
- The sample identifier and analysis code for each sample to be submitted for laboratory analysis, if not included on separate field data sheets
- All field measurements made (or reference to specific field data sheets used for this purpose), including the time that the measurement was collected and the date of calibration, if appropriate
- The sampling location name, date, gear, water depth (if applicable), and sampling location coordinates, if not included on separate field data sheets
- The type of vessel used (e.g., size, power, type of engine) (for aquatic sampling only)

- Specific information on each type of sampling activity
- The sample type (e.g., groundwater, soil, surface sediment), sample number, sample tag number, and preservatives used (if any), if not included on separate field data sheets
- Sample storage methods
- Cross-references of numbers for duplicate samples
- A description of the sample [source and appearance, such as soil or sediment type, color, texture, consistency, presence of biota or debris, presence of oily sheen, changes in sample characteristics with depth, presence/location/thickness of the redox potential discontinuity (RPD) layer, and odor] and penetration depth, if not included on separate field data sheets
- Estimate of length and appearance of recovered cores, if not included on separate field data sheets
- Photographs (uniquely identified) taken at the sampling location, if any
- Details of the work performed
- Variations, if any, from the project-specific sampling and analysis plan (SAP) or standard operating protocols and reasons for deviation
- Details pertaining to unusual events which might have occurred during sample collection (e.g., possible sources of sample contamination, equipment failure, unusual appearance of sample integrity, control of vertical descent of the sampling equipment)
- References to other logbooks or field forms used to record information (e.g., field data sheets, health and safety log)
- Any field results not appearing the field data sheets (if used), including station identification and location, date, and time of measurement
- Sample shipment information (e.g., shipping manifests, COC form numbers, carrier, air bill numbers, time addresses)
- A record of quantity of investigation derived wastes (if any) and storage and handling procedures.

During the field day, as listed above, a summary of all site activities should be recorded in the logbook. The information need not duplicate anything recorded in other field logbooks or field forms (e.g., Site Health and Safety Officer's logbook, calibration logbook, field data sheets), but should summarize the contents of the other logbooks and refer to the page locations in these logbooks for detailed information.

If measurements are made at any location, the measurements and equipment used must either be recorded in the field logbook or reference must be made to the logbook and page number(s) on which they are recorded. All maintenance and calibration records for equipment should be traceable through field records to the person using the instrument and to the specific piece of instrumentation itself.

Upon completion of the field sampling event, the sampling team leader will be responsible for submitting all field logbooks to be copied. A discussion of copy distribution is provided below.

Field Data Forms

Occasionally, additional field data forms are generated during a field sampling event (e.g., groundwater monitoring form, sediment core profile form, water quality measurement form) to record the relevant sample information collected during a sampling event. For instructions regarding the proper identification of field data forms, sampling personnel should consult the project-specific SAP.

Upon completion of the field sampling event, the sampling team leader will be responsible for submitting all field data forms to be copied. A discussion of copy distribution is provided below.

Photographs

In certain instances, photographs (print or digital) of sampling stations may be taken using a camera-lens system with a perspective similar to the naked eye. Photographs should include a measured scale in the picture, when practical. Photographs may also be taken of sample characteristics and routine sampling activities. Telephoto or wide-angle shots will not be used because they cannot be used in enforcement proceedings. The following items should be recorded in the field logbook for each photograph taken:

1. The photographer's name or initials, the date, the time of the photograph, and the general direction faced (orientation)
2. A brief description of the subject and the field work portrayed in the picture
3. For print photographs, the sequential number of the photograph and the roll number on which it is contained
4. For digital photographs, the sequential number of the photograph, the file name, the file location, and back-up disk number (if applicable).

Upon completion of the field sampling event, the sampling team leader will be responsible for submitting all photographic materials to be developed (prints) or to be copied (disks), as appropriate. The prints or disks (as appropriate) and associated negatives will be placed in the project files (at the Integral Project Manager's office). Photo

logs and any supporting documentation from the field logbooks will be photocopied and placed in the project files with the prints or disks.

Equipment Calibration Records

Equipment calibration records, including instrument type and serial number, calibration supplies used, calibration methods and calibration results, date, time, and personnel performing the calibration, should be recorded in the field logbook. At a minimum, equipment used during the investigation should be calibrated daily in accordance with the manufacturers' recommendations.

Distribution of Copies

Two copies of all field logbooks and additional field data forms will be made at Integral. The first copy will be stamped with a "COPY" stamp. This copy will be placed in the project file and will be available for general staff use. The second copy will be stamped with a "FILE" stamp. This copy will be placed in the data management file with the laboratory data packages and will be used by the data management and quality assurance staff only. The original field logbooks and forms will be placed in a locked file cabinet.

Set-up of Locking File Cabinet

Each project will have its own file folder in a locking file cabinet. The folder label will include the project name and contract number. As many as six kinds of files will be included in this folder for each project:

- Field logbook(s)
- Additional field data forms
- Photographs
- COC forms
- Acknowledgment of Sample Receipt forms
- Archive Record form (to be completed only if samples are archived at an Integral field storage facility or Integral laboratory).

STANDARD OPERATING PROCEDURE SOP-9: EQUIPMENT DECONTAMINATION

Scope and Application

To prevent potential cross contamination of samples, all reusable sediment sampling and processing equipment will be decontaminated before each use. At the sample collection site, a decontamination area will be established in a clean location, upwind of actual sampling locations, if possible. This is where all sediment sampling and processing equipment will be cleaned. Decontaminated equipment will be stored away from areas that may cause recontamination. When handling decontamination chemicals, field personnel will follow all relevant procedures and will wear protective clothing as stipulated in the site-specific health and safety plan.

This SOP describes procedures for decontamination of sampling equipment, drilling equipment, and other tools that could come in contact with contaminated media (Ecology 2003, PSEP 1997).

Supplies and Equipment

- Plastic sheeting
- Steam cleaner and collection basin (if required)
- 55-gallon, DOT-approved drums (if required)
- Non-phosphate detergent (e.g., Alconox® or Liquinox®)
- Acid rinses (inorganic constituents), either reagent-grade diluted nitric or hydrochloric acid (if required)
- Solvent rinses (organic constituents), either pesticide-grade methanol, hexane, isopropanol or acetone (if required)
- Polyethylene or polypropylene tub (to collect solvent rinsate)
- Deionized or distilled water rinse available from retail stores. Note that distilled water generally contains low levels of organic contaminants and can not be used for field blanks (must receive reagent-grade from laboratory).
- Tap water rinse from local tap water.
- 5-gallon buckets, or other appropriate containers
- Scrub brushes

- Teflon™ squirt bottles
- Gloves (e.g., nitrile or polyethylene)
- Personal protective clothing (as specified in the site-specific health and safety plan)

Procedures

Drill Rig or Test Pit Sampling Equipment Decontamination Procedures

1. Decontaminate sampling equipment before use, between samples and stations, and upon completion of sampling operations.
2. Equipment used during drilling/test pit operations should be decontaminated in the Exclusion Zone prior to transport to the Support Zone (refer to site-specific HASP).
3. If the steam-cleaning location is in an area outside of the Exclusion Zone, remove loose sediment on the drill rig, augers, drill pipe, and rods, and other large equipment at the drill site, then move the equipment directly to the steam-cleaning decontamination area for more thorough cleaning.
4. To decontaminate a drill rig or backhoe, pressure wash with a steam cleaner using potable water rinse upon mobilization, between drilling locations, and upon demobilization. Cleaning water can generally be allowed to drain directly on the ground near the station (refer to the field sampling plan [FSP]).
5. To decontaminate auger, drill rods, and other downhole tools, pressure wash with a steam cleaner and potable water rinse upon mobilization, between drilling locations, and upon demobilization. All decontamination fluids are to be containerized for proper disposal.
6. To decontaminate split-spoon and hand-auger samplers, wash with laboratory-grade detergent/water solution, rinse with tap water and a final distilled water rinse. If the samplers were exposed to visibly contaminated sediments (e.g., creosote, diesel, etc), dry the sampler off with clean paper towels and carefully rinse the equipment with hexane from a squirt bottle, letting the excess solvent drain into a waste container (which may need to be equipped with a funnel). A hexane rinse should be followed by another distilled water rinse. To the extent possible, allow to air dry prior to sampling. If the split-spoon is not used immediately, wrap it in aluminum foil. All decontamination fluids are to be containerized for proper disposal.

Decontamination of Sampling Implements and Processing Materials

1. Decontaminate sampling implements (e.g., spoons and knives) and other processing materials such as mixing bowls and pans before use, between samples, and upon completion of sampling operations.
2. To decontaminate sampling spoons, mixing bowls, and other hand-held tools, wash with a scrub brush using a laboratory-grade detergent/water solution (Liquinox® or Alconox® solution), rinse with tap water, followed by distilled water or ASTM Type II reagent-grade water. As described above, if the sediment is visibly contaminated, a hexane rinse may be necessary. This is followed by another distilled water rinse. To the extent possible, allow to air dry. Once decontaminated, this equipment will be wrapped in aluminum foil to prevent contamination by airborne contaminants during transportation to the sampling site. Containerize all decontamination fluids for proper disposal.
3. To decontaminate sampling spoons used to collect volatile organics, wash the spoon with a scrub brush using a laboratory-grade detergent/water solution, and rinse with distilled water. Wrap the spoon in aluminum foil. The solvent rinse is eliminated in order to avoid interference with the analysis. Containerize all decontamination fluids for proper disposal.
4. If necessary, to decontaminate wash buckets, pressure wash with a steam cleaner using a laboratory-grade detergent/water solution and potable water rinse upon mobilization, between station locations, upon demobilization, or as needed during sampling operations.

After decontaminating all of the sampling equipment, the disposable gloves and used foil will be placed in garbage bags and disposed of in an appropriate solid waste landfill.

References

Ecology. 2003. Sediment sampling and analysis plan appendix. Guidance on the development of sediment sampling and analysis plans meeting the requirements of the sediment management standards (Chapter 173-204 WAC). Washington State Department of Ecology, Olympia, WA.

PSEP. 1997. Puget Sound Estuary Program: recommended guidelines for sampling marine sediment, water columns, and tissue in Puget Sound. Final report. Prepared for the Puget Sound Estuary Program, U.S. Environmental Protection Agency, Region 10, Office of Puget Sound, Seattle, WA, and Puget Sound Water Quality Authority, Olympia, WA.

STANDARD OPERATING PROCEDURE SOP-10: PREPARATION OF FIELD QUALITY CONTROL SAMPLES FOR SEDIMENTS

Scope and Application

This SOP describes the purpose, preparation, and collection frequency of field duplicate samples, field replicate samples, matrix spike/matrix spike duplicates, equipment rinsate blanks, bottle blanks, trip blanks, temperature blanks, environmental blanks, and reference materials (i.e., a standard reference material, a certified reference material, or other reference material; for the purposes of this document the acronym SRM will be used for all types of reference materials) for sediment samples. Not all of the field quality control (QC) samples discussed in this SOP may be required for a given project. The specific field quality control samples will be identified in the project-specific field sampling and analysis plan (FSP) and quality assurance project plan (QAPP). For most projects, Integral's recommended field QC samples are: an equipment rinsate blank, a field duplicate, and trip blanks if volatile organic compounds (VOCs) are to be analyzed. Definitions of all potential QC samples are described below.

As part of the quality assurance/quality control (QA/QC) program, all field QC samples will be sent to the laboratories blind. To accomplish this, field QC samples will be prepared and labeled in the same manner as regular samples, with each QC sample being assigned a unique sample number that is consistent with the numbering for regular samples. All of the containers with preservatives that are required to complete the field QC sample for the applicable analyte list shall be labeled with the same sample number. The sample ID for field quality control samples should allow data management and data validation staff to identify them as such and should only be recorded in the field logbook. Under no circumstances should the laboratory be allowed to use reference materials, rinsate blanks, or trip blanks for laboratory QC analysis (i.e., duplicates, matrix spike, and matrix spike duplicates). To prevent this from happening, regular samples should be selected and marked on the chain-of-custody/sampling analysis request (COC/SAR) form or the laboratory should be instructed to contact the project QA/QC coordinator to select appropriate samples for each sample group.

Field quality control samples will be prepared at least once per sampling event, and certain types will be prepared more often at predetermined frequencies. If the number of samples taken does not equal an integer multiple of the intervals specified in this SOP, the number of field quality control samples is specified by the next higher multiple. For example, if a frequency of 1 quality control sample per 20 is indicated and 28 samples are

collected, 2 quality control samples will be prepared. The text below describes the preparation and frequency of field quality control samples required for sediment sampling activities, and shall be followed, unless different frequency requirements are listed in the FSP and QAPP.

The following table lists the quality control sample types and suggested frequencies for sediment sampling programs. Because sediment quality control sampling may require assessment of site cross-contamination, additional blanks may be required. A detailed explanation of each quality control sample type with the required preparation follows.

Table 1. Field Quality Control Sample Requirements

Quality Control Sample Name	Abbreviation	Location	Preparation Method	Frequency ^a
Duplicate	DUP	Sampling site	Additional natural sample	One per 20 samples. May not be applicable if REP is being collected.
Replicate	REP	Sampling site	Additional natural sample	One replicate per 20 samples. May not be applicable if DUP is being collected.
Matrix spike/matrix spike duplicate	MS/MSD	Sampling site	Additional sample bottles filled for laboratory quality control requirements	One per 20 samples.
Equipment rinsate blank	ER	Sampling site	Deionized water collected after pouring through and over decontaminated equipment	Minimum of one per sampling event per type of sampling equipment used and then 1:20 thereafter.
Bottle blank	BB	Field	Unopened bottle	One per sample episode or one per bottle type.
Trip blank	TB	Laboratory	Deionized water with preservative	One pair per each VPC sample cooler shipment
Temperature blank	TMB	Laboratory	Deionized water	One per sample cooler.
Environmental blank	EB	Field	Bottle filled at sample site with DI water	One per 20 samples.
Standard reference material	SRM	Field laboratory or Sampling site	SRM ampules or other containers for each analyte group	One set per 50 samples or one per episode.

^a Frequencies provided here are general recommendations; specific frequencies should be provided in the project-specific FSP or QAPP.

Field Duplicate Samples

Field duplicate (or split) samples are collected to assess the homogeneity of the samples collected in the field and the precision of the sampling process. Field duplicates will be prepared by collecting two aliquots for the sample and submitting them for analysis as separate samples. Field duplicates will be collected at a minimum frequency of 1 per 20 samples or once per sampling event, whichever is more frequent. The actual number of field duplicate samples collected during a sampling event will be determined on a case-by-case basis by the project QA/QC coordinator (consult the project-specific FSP and QAPP, as the requirements on frequency of field duplicate collection may vary by EPA region or state).

Field Replicate Samples

Field replicate samples are co-located samples collected in an identical manner over a minimum period of time to provide a measure of the field and laboratory variance, including variance resulting from sample heterogeneity. Field replicates will be prepared by collecting two completely separate samples from the same station and submitting them for analysis as separate samples. Field replicates will be collected at a minimum frequency of 1 per 20 samples or once per sampling event, whichever is more frequent. If field duplicate samples are collected, then it is unlikely that field replicate samples will also be collected during a sampling event. The actual number of field replicate samples collected during a sampling event will be determined on a case-by-case basis by the project QA/QC coordinator (consult the project-specific FSP and QAPP, as the requirements on frequency of field duplicate collection may vary by EPA region or state).

Matrix Spike/Matrix Spike Duplicates

The matrix spike/matrix spike duplicate (MS/MSD) analyses provide information about the effect of the sample matrix on the design and measurement methodology used by the laboratory. To account for the additional volume needed by the laboratory to perform the analyses, extra sample volumes may be required to be collected from designated sediment stations. MS/MSDs may be collected at a minimum frequency of 1 per 20 samples or once per sampling event, whichever is more frequent. The actual number of extra bottles collected during a sampling event will be determined on a case-by-case basis by the project QA/QC coordinator (consult the project-specific FSP and QAPP, as the requirements may vary by analyte group).

Equipment Rinsate Blanks

Equipment rinsate blanks will be used to help identify possible contamination from the sampling environment and/or from decontaminated sampling equipment. Equipment

rinsate blanks will be prepared by pouring laboratory distilled/deionized water through, over, and into the decontaminated sample collection equipment, then transferring the water to the appropriate sample containers and adding any necessary preservatives. Equipment rinsate blanks will be prepared for all inorganic, organic, and conventional analytes at least once per sampling event per the type of sampling equipment used. The actual number of equipment rinsate blanks prepared during an event will be determined on a case-by-case basis by the project QA/QC coordinator (consult the project-specific FSP and QAPP, as the requirements on frequency of equipment rinsate blank collection may vary by EPA region or state).

Bottle Blanks

The bottle blank is an unopened sample bottle. Bottle blanks are submitted along with sediment samples to ensure that contaminants are not originating from the bottles themselves because of improper preparation, handling, or cleaning techniques. If required, one bottle blank per lot of prepared bottles will be submitted for analysis. If more than one type of bottle will be used in the sampling (e.g., HDPE or glass), then a bottle blank should be submitted for each type of bottle and preservative. The actual number of bottle blanks analyzed during a project will be determined on a case-by-case basis by the project QA/QC coordinator (consult the project-specific FSP and QAPP as the requirements on frequency of bottle blank analysis may vary by EPA region or state).

To prepare a bottle blank in the field, set aside one unopened sample bottle from each bottle lot sent from the testing laboratory. Label the bottle as "Bottle Blank" on the sample label (and in the "Remarks" column on the COC/SAR form), and send the empty bottle to the laboratory with the field samples.

Trip Blanks

Trip blanks will be used to help identify whether contaminants may have been introduced during the shipment of the sediment samples from the field to the laboratory for VOC analyses only. Trip blanks are prepared at the testing laboratory by pouring distilled/deionized water into two 40-mL VOC vials and tightly closing the lids. Each vial will be inverted and tapped lightly to ensure no air bubbles exist.

The trip blanks will be transported unopened to and from the field in the cooler with the VOC samples. A trip blank shall be labeled and placed inside the cooler that contains newly collected VOC samples and it shall remain in the cooler at all times. A trip blank must accompany samples at all times in the field. One trip blank (consisting of a pair of VOC vials) will be sent with each cooler of samples shipped to the testing laboratory for VOC analysis.

Temperature Blanks

Temperature blanks will be used by the laboratory to verify the temperature of the samples upon receipt at the testing laboratory. Temperature blanks will be prepared at the testing laboratory by pouring distilled/deionized water into a vial and tightly closing the lid. The blanks will be transported unopened to and from the field in the cooler with the sample containers. A temperature blank shall be included with each sample cooler shipped to the testing laboratory.

Field Blanks

The field blank is prepared in the field to evaluate potential background concentrations present in the air and in the distilled/deionized water used for the final decontamination rinse. If unpreserved bottles are to be used, then the appropriate preservative (i.e., for metals samples use a 10-percent nitric acid solution to bring sample pH to 2 or less) must be added, as may be required. Field blanks should be collected at a minimum frequency of 1 in 20 samples. The actual number of field blanks analyzed during a project will be determined on a case-by-case basis by the project QA/QC coordinator (consult the project-specific FSP and QAPP, as the requirements on frequency of field blank analysis may vary by EPA region or state).

To prepare a field blank in the field, open the laboratory-prepared sample bottle while at a sample collection site, fill the sample bottle with distilled/deionized water and then seal. Assign the field blank a unique sample number, label the bottle, and then send the bottle to the laboratory with the field samples.

Reference Materials

Reference materials (i.e., a standard reference material, a certified reference material, or other reference material; for the purposes of this document the acronym SRM will be used for all types of reference materials) are samples containing known analytes at known concentrations that have been prepared by and obtained from EPA-approved sources. The SRMs have undergone multilaboratory analyses using a standard method which provides certified concentrations. When available for a specific analyte, SRM samples provide a measure of analytical performance and/or analytical method bias (i.e., accuracy) of the laboratory. Several SRMs may be required to cover all analytical parameters. For all analytes where available, one SRM will be analyzed at a frequency of one per 50 samples. The actual number of SRMs analyzed during a project will be determined on a case-by-case basis by the project QA/QC coordinator (consult the project-specific FSP and QAPP, as the requirements on frequency of SRM analysis may vary by EPA region or state).

STANDARD OPERATING PROCEDURE SOP-11: INVESTIGATION-DERIVED WASTE HANDLING

Scope and Application

This SOP presents the method to be used when handling investigation-derived wastes during field sampling activities.

Supplies and Equipment

- 55-gallon drums
- Paint markers
- Tools (to open and close drum)
- Drum labels.

Procedures

1. Containerize solid wastes by placing them in properly labeled, Department of Transportation (DOT)-approved, 55-gallon drums or other approved containers. Do not combine solid residues known to be from a contaminated area with other residues.
2. Label drums as "NON-CLASSIFIED WASTE MATERIAL: LABORATORY ANALYSIS IN PROGRESS". Include on the labels a drum number, the type of material, site address, accumulation date, and generator name and phone number.
3. Properly close, seal, and stage all filled or partially filled drums before demobilization.
4. Profile the drums based on the analytical results from corresponding borehole samples, or waste characterization samples collected from the drums. Once the drums are profiled, dispose of them in accordance with applicable regulations.
5. Maintain a drum inventory in the field logbook.

6. Sampling activities will generate personal protective equipment and miscellaneous debris that need to be disposed of. Remove gross contamination from these items, and place the items in plastic bags. Interim storage of these materials in plastic bags is acceptable. Dispose of the bags at an appropriate solid waste facility dumpster at the end of each day.

STANDARD OPERATING PROCEDURE SOP-12: HYDROCARBON FIELD SCREENING FOR SOIL AND SEDIMENT

Scope and Application

This SOP presents the qualitative field screening methods for hydrocarbons in soil.

Equipment/Reagents Required

- Clean, stainless-steel or plastic pan
- Camera (if necessary)
- Ziploc® bags
- Photo-ionization detector (PID)

Procedures

Headspace Field Screening

1. Calibrate PID in accordance with the manufacturer's specifications.
2. Label Ziploc® bag with the sample number.
3. Place representative soil sample in Ziploc® bag until bag is approximately one-quarter full (if sample recovery is sufficient). Seal Ziploc® bag and homogenize sample.
4. Allow bag to sit at ambient temperature for approximately 10 minutes. Place PID wand into bag, being careful not to contact soil with PID probe. Also be careful not to let any ambient air in the bag as this may cause dilution.
5. Gently shake Ziploc® bag and record highest sustained reading in the field logbook or borehole log.

Visual Screening

Visual screening consists of inspecting the soil or sediment for the presence of stains indicative of residual petroleum hydrocarbons. Visual screening is generally more

effective in detecting the presence of heavier petroleum hydrocarbons, such as motor oil, or when hydrocarbon concentrations are high.

1. Visually inspect soil or sediment sample.
2. Look for indications of the presence of hydrocarbons, which typically include a mottled appearance or dark discoloration of the soil.
3. Record observations in logbook. Note: Visual observations do not definitively indicate the presence of hydrocarbons.

Sheen Testing

Sheen testing involves immersion of the soil or sediment sample in water and observing the water surface for signs of a sheen.

1. Place a representative soil or sediment sample into a clean, stainless-steel or plastic pan filled with deionized water with as little disturbance as possible.
2. Record observations in the logbook. Visual evidence of a sheen forming on the surface of the water is classified as follows:
 - **No sheen (NS)**—No visible sheen on the water surface.
 - **Colorless Sheen (CS)**—Light, nearly colorless sheen; spread is irregular, not rapid; film dissipates rapidly (**Note:** light colorless sheens can be confused with sheens produced by organic content). Note that this sheen may or may not indicate the presence hydrocarbons.
 - **Heavy Sheen (HS)**—Light to heavy colorful film with iridescence; stringy, spread is rapid; sheen flows off the sample; most or all of water surface is covered with sheen.

ATTACHMENT B

FIELD FORMS

Sample Label

Site: _____	integral <small>consulting inc.</small>
Sample No.: _____	
Matrix: _____	Date: _____
Filtered (Y/N): _____ <small>(if applicable)</small>	Time: _____
Analysis: _____ <small>(optional)</small>	Pres: _____
Sampler: _____	
Tag Number: <u>1813</u>	

Custody Seal

CUSTODY SEAL		integral <small>consulting inc.</small>
Date: _____	Time: _____	
Sampler Signature: _____		

FIELD CHANGE REQUEST (FCR) FORM

Project Name: _____

Project No.: _____

Client: _____

Request No.: FCR-_____

To: _____

Date: _____

Field Change Request Title: _____

Description:

Recommended Change:

Field Operations Lead (or designee)

Signature

Date

Approval:

Project Manager

Signature

Date

Distribution:

- LSS Project Manager
- Integral Project Manager
- Field Operations Lead
- QA Officer
- Project File
- Other:



"Rite in the Rain"[®]
ALL-WEATHER
ENVIRONMENTAL
No. 550F

ATTACHMENT 3

SOP FOR DIVER-PLACEMENT AND RETRIEVAL OF PASSIVE SAMPLERS

Attachment 3

SOP for Diver-Placement and Retrieval of Passive Samplers and Co-located Sediment Samples

Standard Operating Procedures for Diver-Placement and Retrieval of Passive Samplers and Co-located Sediment Samples

1. SCOPE AND APPLICATION

This standard operating procedures (SOP) document presents detailed descriptions of methodologies for divers to follow during the placement and retrieval of passive samplers and collection of co-located sediment samples for the River Mile 11E (RM11E) supplemental remedial investigation/feasibility study (RI/FS). The purpose of this document is to provide a clear set of protocols for the field and dive team to review and follow in order to ensure data of sufficient quality and consistency are collected to meet project objectives described in the Porewater Sampling and Analysis Plan (SAP). This SOP includes procedures for a reconnaissance survey to test and confirm the sampling methodology will be successful in the field conditions at the site.

2. METHOD SUMMARY

Porewater samplers consist of pre-fitted 10 x 50 cm polyethylene (PE) strips mounted into aluminum sampling frames. A photo showing the passive sampling device (PSD) assembly is shown in Figure 1. Divers will install the samplers at the selected sampling locations, to a target depth of 30 cm below mud line (bml), leaving 20 cm of the PE extending above the mudline in the overlying surface water. The sampler will be left to interrogate the sediment and overlying water for approximately 60 days. At the time of retrieval, the divers will first insert a 40 x 10 cm diameter core approximately 2 inches away from the PSD location, and then remove the PSDs from the sediment bed. The core will then be withdrawn with a cap placed over the bottom of the tube. The PSD, complete with the polyethylene strip still inside, will be brought to the surface, initially cleaned of mud, labeled, wrapped in aluminum foil, and stored on ice for transport to the laboratory. The collected cores will be capped and labeled in the field. The PE and collected sediment will be transported in separate ice filled coolers to ALS's laboratory in Kelso, Washington for further processing.



3. PRE-DIVE BRIEFING

- 3-1 Review the Ballard Marine Construction (BMC) Dive, and Health and Safety Plans (HSP) with the dive team.
- 3-2 Review the current day activities and associated portions of the RM11E passive sampling SOP with the dive team at the start of each day's dive operations.
- 3-3 Inspect the sampling equipment to ensure it will function properly.
- 3-4 Verify that the diver has the required gear.
- 3-5 Verify that the underwater video equipment and communication equipment is operating.
- 3-6 Verify that the dGPS is operating correctly, and reporting at least three satellite signals.
- 3-7 Review the method to establish the sample location (below) and water depth on the river bed below the dock (such as measurement from pilings).

4. NAVIGATION

- 4-1 All sample locations will be established using a differential global positioning system (dGPS). Navigation and recording of site coordinates will be in Oregon State Plan North coordinates. A check of the dGPS will occur by taking a reading at either the inside corner upstream (approximately SE) of the Glacier Dock, or the inside downstream corner (approximately NE) of the Cargill Dock. The dGPS reading will be taken at the same location at the beginning and end of each sampling day, and recorded in the field log book. Navigation accuracy will be ± 3 ft. If multiple dGPS are onboard, the units will be checked against one another and have an accuracy of ± 3 ft. If the dGPS readings are not consistent, the Field Director will make a determination as to which unit will be used to locate stations. Justification for that decision will be recorded in the Field Logbook.
- 4-2 Target sampling stations are identified in Table 2-3 of the SAP. The boat will navigate to the fixed coordinates of each location, and lower an anchor attached to line onto the position immediately below the dGPS antenna. To the extent practical in the moving river current, the line will be drawn vertical and the position again confirmed with the dGPS. The position will be recorded in the field log book and on the PSD Log.
- 4-3 It is preferable that the boat remain on station using an anchor or a shoreline tie off. Live-boat operations are permitted, but only within the safety parameters defined in the BMC HSP.
- 4-4 The diver will enter the water and slowly proceed down the anchor line to the river bed, taking care to minimize disturbance of the sediment.
- 4-5 The Field Director (FD) onboard the boat will view the general sample location on video, look for areas of soft sediment and minimal debris, and coordinate the selection of the actual sampling location with the diver. Observations on the target sampling location will be recorded in the field sampling log.
- 4-6 If the diver is required to move the location, the line anchor will be moved to the actual sampling location, and a new coordinate fix will be taken. The sample location may be moved within 10 meters (approximately 30 feet) of the location identified in Table 1. The rationale for moving the location, along with the new coordinates is recorded in the field notebook and onto the PSD Log.
- 4-7 If sample locations must be moved more than 10 meters from the initial target, the FD will contact the EPA Remedial Program Manager (RPM) to discuss proposed field changes. If the RPM cannot be reached, the FD will call and/or e-mail the Project Manager for EPA's oversight contractor CDM, to discuss proposed field changes. A Field Change Request form will be submitted via e-mail as a follow up to any sampling location changes (see Attachment 1).

5. RECONNAISSANCE SURVEY PROCEDURES

- 5-1 The scope and objective for the reconnaissance survey is presented in Section 4.4 of the Porewater SAP. The reconnaissance survey was completed on May 2, 2014. The methods used during that survey are documented in this SOP because subsequent sections reference these procedures.
- 5-2 Navigation and underwater confirmation of the target location are as described in Section 4 of this SOP.
- 5-3 A PSD fitted with blank polyethylene (PE) sheeting will be lowered to the diver on a clipped line after confirmation of the sampling location.
- 5-4 The diver's helmet cam will be operational throughout dive-portion of the reconnaissance survey. The video from the procedure will become part of the record for the reconnaissance survey.
- 5-5 At the confirmed target location, the diver will report the general bottom conditions (e.g., sediment type, presence of debris) to the surface team. The diver will install the PSD parallel to the flow of the river, by pushing or hammering the device into the sediments up to the fixed stop legs on the sampler, which are preset to allow 30 cm of PE exposure to surface sediment and 20 cm exposure to the overlying water. The PSD will be driven at a slow, steady rate; the process of insertion should take 0.5 - 1 minute. The diver may gently rock the sample device if resistance is encountered. During the PSD placement, the diver will communicate with the boat to describe the degree of ease/difficulty associated with the push, and whether refusal is encountered prior to completion. This information is recorded into the field log notebook.
- 5-6 Should refusal be encountered prior to full sampler insertion, the diver will gently withdraw the sampler and inspect the PE for any rips or tears. If a rip or tear is present, a new sampler will be lowered to the diver for a second attempt. Results of the initial insertion attempt are recorded in the field log and onto the PSD Log.
- 5-7 In the event of refusal, the diver, in communication with the FD, will visually examine the area again in an approximately 1 m arc, targeting a location that at the surface appears to be free of debris and rubble. The diver will then repeat Steps 5-3 and 5-4 for a total of three attempts at a target location. If all three attempts are unsuccessful, this will be noted in the field log, and the reconnaissance team will proceed to the next location.
- 5-8 Upon successful placement, the diver will carefully remove the stainless steel covers from both sides of the PSD, and clip them to the carabineer connected to the boat line. After removal of the covers, one minute is allowed to elapse to allow for the sediment to consolidate around the device. If possible, a photograph or video will be taken. The sampling device will then be withdrawn by slowly pulling the frame vertically from the

sediment. If necessary, a gentle rocking motion may be used to assist in the release of the frame. Upon withdrawal, the diver will note any tears or rips in the PE to the surface team, and then signal the surface team to bring the PSD assembly to the surface. The diver will remain at the sampling location until confirmation by the surface team that there are no rips or tears to the PE.

- 5-9 Once the diver and sampling device are safely on-board, the FD will again inspect the PE for rips or tears, note those in the log book, and take a photograph of the sampler.
- 5-10 The reconnaissance team can then weigh anchor, and proceed to the next location and repeat Steps 5-1 through 5-8. A sampler with intact PE can be used at the next test station.

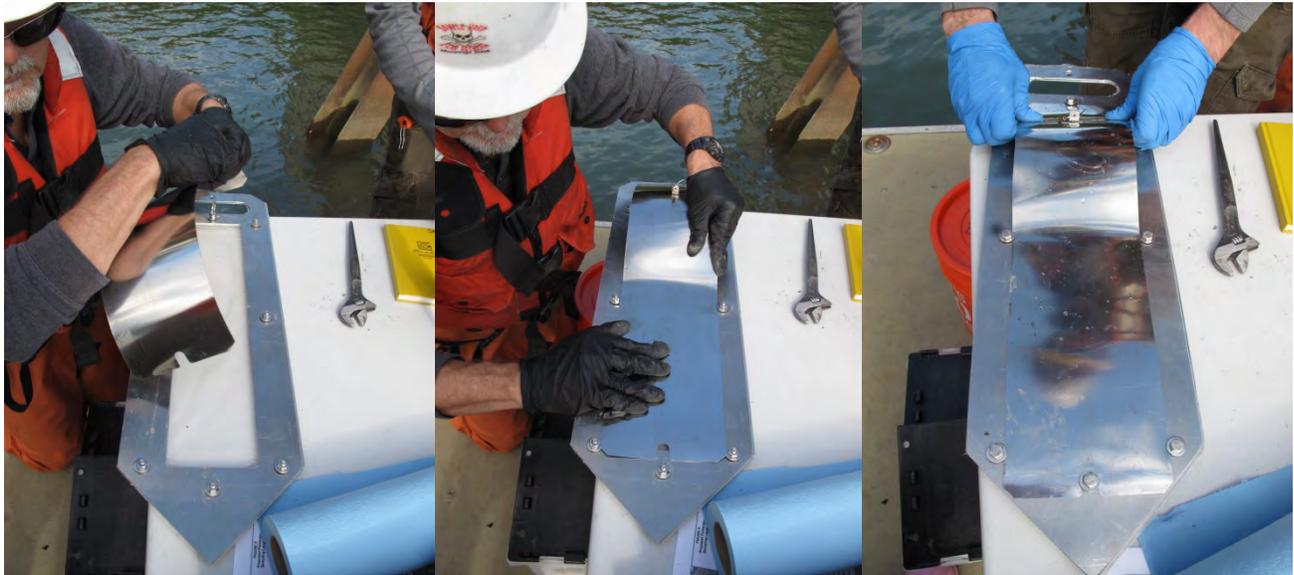
6. FIELD PLACEMENT OF PASSIVE SAMPLING DEVICES

- 6-1 The scope and objective for the field deployment of the passive sampling devices is presented in Section 4.5 of the Porewater SAP.
- 6-2 The diver's helmet cam will be operational throughout the dive-portion of the field placement. The video from the procedure will become part of the Porewater Characterization Report.
- 6-3 Porewater samplers fitted with PE that have been impregnated with PCB performance reference compounds (PRC) will arrive from the laboratory wrapped in aluminum foil and ready for deployment. All personnel handling the PE samplers must be attired in Level D personal protective gear and wear new nitrile gloves for each sampler at all times. Care should be taken to avoid any contact with the polyethylene film in the frame.
- 6-4 Navigation and underwater confirmation of the target location are as described in Section 4 of this SOP.
- 6-5 The FD will take the sampler and fit it into the hammer assembly shown in Figure 1. Each sampler should arrive at the station fitted with the PE, and with the stainless steel PE-protective plates in place. Should for any reason those plates come off, or need to be put onto another sampler, Figure 2 shows generally how those are placed onto the sampler. The FD is responsible for ensuring that the plate covers, and the entire passive samplers are correctly assembled and ready for deployment.
- 6-6 The diver will enter the water and occupy the location on the river bed indicated by the anchor line as the sampling site. Once on the anchor, the passive sampling assembly will be carefully lowered down to the diver. Until the sampler is secure in the sediment, the PE sampler will be attached via a carabineer to a weighted tag line secured to the sample boat.

- 6-7 At the confirmed target location, the diver will report the general bottom conditions (e.g., sediment type, presence of debris) to the surface team. The diver will insert the PSD assembly into the sediment, parallel to the flow of the river, and push or hammer the sampler into the sediments up to the fixed stop legs on the hammer assembly, which are preset to allow 30 cm of PE exposure to surface sediment and 20 cm exposure to the overlying water. The sampler should be driven at a slow, steady rate; the process of insertion should take 0.5 - 1 minute. The diver may gently rock the sample device if/when resistance is encountered. During the insertion, the diver will communicate with the boat to describe the degree of ease/difficulty associated with the push, and whether refusal is encountered prior to completion. This information is recorded into the field log notebook. After successful insertion, the diver will pull the two (2) protective plates, and pull the pin to release the hammer assembly from the sampler. It may be necessary for the diver to hold the sampler in place while removing the hammer assembly.
- 6-8 Should refusal be encountered prior to full sampler insertion, the PSD will be gently withdrawn and inspected to determine if the protective plates are still in place. If the plates are in place, the diver may proceed with a second attempt at sample deployment. If the plates are not in place, the diver will inspect the PE for any rips or tears. If the diver observes any rips or tears in the PE membrane, sample deployment with that device will be aborted and a new PSD lowered to the diver in order to proceed. Results of the initial insertion attempt are recorded in the field log and onto the PSD Log.
- 6-9 If it is necessary to locate an alternate location to place the samplers, the diver, in communication with the FD, will visually inspect the area again in an approximately 1 m arc, targeting a location that at the surface appears to be free of debris and rubble. The diver will then repeat Steps 6-6 through 6-8 for a total of three attempts at a target location. The maximum radius from the target location that can be used without confirmation with EPA is 10 m.
- 6-10 If all three attempts fail, and the sample locations must be moved more than 10 meters from the initial target, the FD will contact the EPA Remedial Program Manager following the procedures listed in Step 4-7.
- 6-11 Upon successful insertion of the sampler, the FD will record the date, the time, and the coordinates of the sample location in the field log and on the PSD Log. Individual pictures from the diver helmet cam of each location will become part of the Porewater Characterization Report.
- 6-12 After successful deployment of the PSD, a second sampling assembly will be lowered to the diver. The second sampler will be inserted approximately 8 inches (two fist-widths) from the first sampler following the procedures in Step 6-7.
- 6-13 Once a successful sampler-insertion has been achieved, the weighted tag line secured to the boat will be released to the diver. Two tag lines will be attached to each sampler and

each tag line will be attached to an anchor point. At the inshore stations (PW002, PW003, and PW006), the tag lines will be secured to the nearest piling or other suitable tie-point. For the offshore stations (PW001, PW004, and PW005) the diver will secure the tag lines parallel to the flow of the river into the sediment using a shore anchor, or similar-constructed anchor. The tag lines serve two purposes: to provide anchorage to secure the sampler frame to the river bed during deployment, and to help locate the sampler again at the end of the deployment period. For all the offshore stations, a Benthos ALP365 Pinger will be attached to one of the samplers to assist in the location and retrieval of samplers. For the up-river station (PW007), the preferred method will be to secure the sampler via lines to a fixed upland or in-river structure. If a secure structure is not available, that station will also be secured with anchored tag lines.

- 6-14 Upon successful insertion of the sampler, the FD will record the date, time, measured water depth, any issues related to sampler placement, and sample coordinates in the field log and on the PSD Log.
- 6-15 Upon completion, the dive/field team may then proceed to the next sampling location.



RM11 East Project
Portland, OR

Figure-2:
Installation of PE Plate Cover

7. RETRIEVAL OF PASSIVE SAMPLING DEVICE

- 7-1 The scope and objectives for the field retrieval of the passive sampling devices is presented in Section 4.5 of the Porewater SAP.
- 7-2 The diver's helmet cam will be operational throughout the dive-portion of the passive sampler retrieval. The video will be become part of the Porewater Characterization Report.
- 7-3 Porewater samplers are fitted with PE that has been impregnated with PCB PRCs. All personnel handling the PE samplers must be attired in Level D personal protective gear and wear new nitrile gloves for each sampler. Care must be taken to (1) use only one pair of gloves per passive sampling unit, (2) to minimize contact with the polyethylene strip in the sampler, and (3) to prevent any contact between the sampled sediment and the polyethylene sheets.
- 7-4 The procedures for navigation and target station location are as described in Section 4 of this SOP.

- 7-5 The dive boat will return to the station coordinates recorded at the time of sampler placement. Navigating with the dGPS, an anchored line will be dropped onto the station coordinates as close as practicable to the station location.
- 7-6 For the inshore stations (PW002, PW003, and PW006), and the upriver station (PW007), the tag line previously secured to a piling or other tie-point will be located, and the diver will follow the line to the samplers, and proceed with Steps 7-10 through 7-13, and then the sediment sampling described in Section 8 of this SOP.
- 7-7 For the offshore stations (PW001, PW004 and PW005), the passive samplers will be located using a hand-held pinger locator (Benthos DPL-275). Prior to entering the water the FD will check to confirm the locator is (1) working, and (2) that a signal from the sampler is being received
- 7-8 For the offshore stations the diver will enter the water with the hand-held pinger locator (Benthos DPL-275), and descend down the anchor line to the approximate sediment location. It is expected that the diver will be able to locate the sampler by sound. In the event the diver is able to quickly locate the sampler, they can proceed with sampler retrieval, as described below.
- 7-9 In the event the diver cannot locate the tied tag line for the inshore stations, or the sampler by sound for the offshore stations, the diver will proceed to conduct a search arc from the estimated location to locate the sampler tag line. The diver will swim in 180^o search arcs in approximately 3 ft intervals out from the station location anchor line. Visibility is expected to be low during this search; the diver has the option of using a common garden hand rake to pull through the sediment to snag the tag line.
- 7-10 Upon location of the tag line and sampler, the diver will first proceed to pull out the tag line anchors from the sediment (or release the tag line from the tie-point), and float the line to the surface. It may be necessary to use a small lift bag to bring the tag line to the surface. The diver must confirm that the tag line is still attached to the sampler, and the boat crew must confirm that the tag line is securely fixed on the deck before the sampler may be pulled from the sediment. This is to ensure the sampler will not accidentally float away during retrieval.
- 7-11 The diver will measure the distance from the mudline to the top of the exposed PE frame, and report that distance to the FD, who will record that measure in the field notebook.
- 7-12 Prior to extracting the PSD, the sediment core sampler will be driven in between the two PSDs following the procedures defined in Steps 8-5 through 8-7. Care must be taken by the diver to ensure that (1) the core is driven between the two PSD samplers approximately two inches (2 diver-gloved fingers) from each sampler, and (2) that the core drive is strictly vertical in order to not contact and potentially damage the PE sheet,

and (3) that the integrity of the sediment stratigraphy for core logging at the laboratory is preserved.

- 7-13 Once the core sampler is in place, the passive sampling frames may then be withdrawn (one at a time) by slowly pulling the frame vertically from the sediment. If necessary, a gentle rocking motion may be used to assist in the release of the frame. Upon withdrawal, the diver will note any tears or rips in the PE to the surface team, and then notify the support team that the sampler may be lifted to the surface via the tag line. The diver will remain at the sampler location to complete collection of the sediment core, as described in Section 8 of this SOP.
- 7-14 Once the passive porewater sampler is onboard, it will be processed according to the procedures described in Section 9 of this SOP.
- 7-15 All samples from a site (PE and sediment) must be labeled, secured, properly packed, and placed into an ice cooler according to the procedures in Section 9 of this SOP, before the field crew may move to the next location.

8. SEDIMENT CORE COLLECTION

- 8-1 Retrieved sediment cores may have contaminated mud on the exterior of the sample tube when they reach the surface. All boat personnel handling sediment core samplers must wear new nitrile gloves at all times.
- 8-2 The procedures for navigation and target station location are as described in Section 4 of this SOP.
- 8-3 The diver's helmet cam will be operational throughout the dive-portion of the field placement. The video from the procedure will become part of the Porewater Characterization Report.
- 8-4 The sediment core sample will be collected by the diver from between the passive porewater sampler location as described previously in Step 7-12.
- 8-5 A tag line will be clipped to the sediment core sampler, and carefully lowered to the diver. The hand-core samplers will be constructed of pre-cleaned 10 cm (4-inch) diameter aluminum barrels approximately 45 cm in length, and fitted with a bottom core-catcher. The tag line will remain clipped to the sampler throughout coring and retrieval.
- 8-6 The diver will push the sample tube into the sediment between the two PE samplers as described previously in Step 7-12. The desired sample depth is 30 cm (12 inches) below the mudline; the diver should attempt to push the core barrel 40 cm into the sediment. As required, the diver may gently rock the sampler back and forth, and if necessary, hammer the tube into the sediment if significant resistance is encountered.

- 8-7 Once the core has been advanced to the minimum acceptable depth of 30 cm below mudline, the diver will so indicate and the FD will record the time of sample collection in the field notebook and on the sample collection log.
- 8-8 Prior to proceeding with the core withdrawal, the passive samplers will be removed and secured as described previously in Step 7-13.
- 8-9 The diver will then withdraw the core sampler, placing caps over the open core barrel on the top and bottom of the tube, and signal the support boat that the core may be pulled to the surface. The diver will make careful note of where the core collection hole in the sediment is, and wait at the location until the FD indicates that a successful sample has been collected.
- 8-10 Once the core is on board, any excess water in the core barrel is decanted, and the amount of material retained in the core tube is measured and recorded in the field log. Recovery is defined as the amount of sediment retained (acquisition) in the core tube divided by the amount the core tube penetrated into the sediment column (penetration). The minimum acceptable recovery is 30 cm.
- 8-11 In the event that insufficient material is retained, the contents of the core barrel will be discarded, the core barrel cleaned, and lowered back to diver for a second attempt. The second drive will be two inches (two diver fingers) upstream of the original location. If a third attempt is needed, the third drive will be made two inches downstream of the original location. Up to three attempts will be made, at which time the EPA RPM will be contacted to discuss further options for sediment collection.
- 8-12 For each core attempt, the station name, latitude/longitude, time of collection, depth to mudline, the river elevation at the time of collection and depth of penetration are noted in the field log.
- 8-13 Once the core barrel is onboard, it will be handled according to the procedures described in Section 9 of this SOP.
- 8-14 All samples from a site (PE and sediment) must be labeled, secured, properly packed, and placed into an ice filled cooler according to the procedures in Section 9 of this SOP before the field crew may move to the next location.

9. FIELD PROCESSING OF PE SAMPLERS AND SEDIMENT CORES

- 9-1 Once onboard the boat, the PE in the samplers will be immediately rinsed with laboratory reagent-grade water and rubbed with a clean Kimwipe™, and at least one additional rinse

to remove as much adhering sediment as possible¹. All personnel handling the PE samplers must be attired in Level D personal protective gear and wear new nitrile gloves for each sampler.

- 9-2 The PE sampler will be photographed, and the general condition of the PE will be noted in the field log (e.g., intact, tears in the PE, biofouling, presence of oil, etc.).
- 9-3 The sample's identification number will be recorded onto the sampler sleeve, and then the entire sampler will be wrapped in aluminum foil. The station identification number will be recorded with an indelible marker on the aluminum foil, along with the date and time.
- 9-4 The PE sampler will then be placed into the ice filled cooler for transport to ALS in Kelso, WA for processing and analysis.
- 9-5 Sediment core samples collected will also have the station ID recorded onto the sample tube; this can be scratched directly onto the tube. The core lids will be secured with duct tape, and the sample ID, date and time will be written using an indelible marker onto the taped lids with an arrow indicating the direction to the surface of the sediment. "TOP" will be written onto the taped lid indicating the sediment surface.
- 9-6 These secured cores will then be placed upright into an ice filled cooler for transport to ALS.
- 9-7 The samples must remain in the custody of the FD or SAC at all times during the transport to, and during processing at ALS.

¹ Additional cleaning of the PE will occur at the laboratory to remove all remaining sediment, prior to analysis.

ATTACHMENT 4

BALLARD MARINE CONSTRUCTION DIVE OPERATIONS PLAN



Ballard Marine Construction 727 S. 27th St. Washougal, WA 98671 866.782.6750

Dive Operations Plan (DOP)

Dalton, Olmsted & Fuglevand, Inc. (DOF)
Diver-Assisted Porewater and Sediment Sampling
Portland, OR

This Dive Operations Plan (DOP) has been prepared by Ballard Marine Construction (Ballard MC) for the River Mile 11 East Diver-Assisted Porewater and Sediment Sampling Project in Portland, OR, as set forth in the SOP for Diver-Placement and Retrieval of Passive Samplers and Co-located Sediment Samples (SOP) (SEE, 5/21/2014). This DOP is in general accordance with the Association of Diving Contractors International. (ADCI) Consensus Standards for Commercial Diving and Underwater Operations, OSHA 29 CFR Part 1910, Subpart T – Commercial Diving Operations, WISHA Standards for Commercial Diving Operations, Ch. 296-37 WAC, U.S. Environmental Protection Agency Diving Safety Manual (Rev. 1.2); U.S. Coast Guard (USCG) Diving Policies and Procedures Manual, Vol.1; USCG 46 CFR Subpart B Ch.197 and the U.S. Navy Dive Manual. Once accepted by Dalton, Olmsted & Fuglevand (DOF) and the Environmental Protection Agency (EPA), a hard copy of the DOP will be available at the dive site. This DOP will be reviewed at a pre-dive meeting.

This DOP will not be altered, revised or changed without the consent of DOF.

- A. Client Point-of-Contact (POC):** Paul Fuglevand; Mobile (206) 660-3079; pfuglevand@dofnw.com
- B. Client Onsite Point of Contact (POC)** Tim Thompson; Mobile (206) 619-4109
- C. Date of Submission:** June 20, 2014; Rev 5
- D. DOP Prepared By:** Rebekah Feasel; Safety Manager; Mobile (360) 989-0920; Rebekah.Feasel@BallardMC.com.
- E. On-Site Dive Team Members:** The dive crew will consist of a total of four (4) personnel. Dive crew manning levels are in accordance with the ADCI, WISHA and the EPA. All dive team members meet the training and certification requirements for 29 CFR 1910.120 (OSHA) Hazardous Waste Operations and Emergency Response (HAZWOPER).

Table 1: Names, Positions and Duties of On-Site Dive Team Members

Name	Position	Duties
Justin Siewert	Dive Supervisor	<ul style="list-style-type: none"> - Overall-in-Charge of all diving operations, safety and logistics at the dive site. Has the authority and responsibility to discontinue diving operations in unsafe conditions. - Familiar with all dive tasks and team members; evaluates qualification and physical fitness of divers; inspects all equipment and conducts pre-dive briefings and post-dive interviews. - May serve as the primary diver and chamber operator (emergencies), also; may serve as Stand-by Diver Tender in depths < 100 feet.

Name	Position	Duties
Steven Crouchley Shane Veentjer Michael Wright Mathew Shumaker (Alternate) Joshua Leibing (Alternate) Tyler Hills (Alternate) Dana Gordon (Alternate)	Diver/Tender Decon Tech	<ul style="list-style-type: none"> - Perform all required underwater tasks as directed by the Diving Supervisor. - Stand by for emergency deployment and/or to assist primary diver(s) as directed by the Diving Supervisor. - <u>As tender:</u> Checks the diver's equipment and topside air supply for proper operation. - Constantly tends diver umbilical and lines to eliminate excess slack or tension. - Provides emergency assistance as directed by the Diving Supervisor. - May act as the Chamber Operator. - Will decontaminate the diver and all gear/equipment that enters the exclusion zone.

F. List of Diving Equipment: The following equipment will be provided by Ballard MC and mobilized to the jobsite.

Primary Air System:

- One (1) 25.6 cu.ft/min (cfm) Surface-Supplied LP Air Compressor with volume tank incorporating an inlet check valve, pressure gauge, and drain valve; breathing air filter system, , LP hose whips, CO monitor, and associated filter rack assemblies

Secondary Air System:

- Two (2) DOT 3AA2400 K-cylinders charged to minimum 2,200 psi, on-line and immediately accessible by the dive supervisor

Diver Equipment:

- Diving Helmets - Kirby Morgan Superlite (Models 27-77) with non-return and exhaust valve; worn, utilized and maintained according to manufacturer standards; series exhaust valves consisting of a minimum tri-exhaust (SL-27 model helmet)
- Diver-worn Emergency Gas Supply - minimum 30 ft³ bailout air cylinder for depths ≤30ft, minimum 50 ft³ bailout air cylinder required in depths ≥ 50ft
- Minimum of two (2) diving umbilical hoses (3/8" Gates Model 33HB), marked in depth increments IAW Association of Diving Contractors International (ADCI)

- Variable-volume diving dry suits with appropriate thermal protection and quick-disconnect inflator hose; vulcanized rubber, fully encapsulating with integrated boots, dry gloves (neoprene gloves may be worn on top of dry gloves to provide chaffing protection) and over boots
- ADCI approved 5-point diver safety harnesses with positive buckling device and D-ring strain relief
- Dive knife or cutting device
- Dive weights (as required to maintain buoyancy)

Diver-Support Equipment

- Emergency portable oxygen system with non-rebreather mask, pocket mask with O₂ inlet, demand regulator and AMBU bag capable of ventilating a non-breathing diver; immediately available on dive site; minimum Jumbo D cylinder (:60 O₂ supply)
- One (1) floating spine board, Miller Board or Stokes litter (with floatation), with color-coded straps, quick release buckles and a head/neck immobilizer; immediately available on dive site
- First aid kit and/or medical trauma kit
- Automated external defibrillator
- Pneumo-fathometer gauges
- Two-way diver-surface voice communications equipment
- Color underwater video equipment; recordable to DVD format
- VHF Radios; as required to establish communications with onsite personnel
- 1-meter square code alpha flag and recreational dive flag
- Sufficient fuel for the job (diesel and/or gasoline)
- ABC fire extinguisher; one (1) per on-site combustion engine/compressor

Decontamination Equipment:

- Rain Gear/water resistant coveralls
- Face shields/eye protection
- Nitrile chemical resistant/Neoprene gloves
- Dry gloves
- Nitrile exam gloves
- Rubber boots/boot covers
- Containment pools/tubs
- Potable water with hose and nozzle
- Simple Green
- Pump sprayer (labeled with contents)
- Scrub brushes
- Antibacterial gel hand sanitizer
- Disinfectant wipes
- Paper towels/plastic sheeting
- Heavy duty drum liners
- Trash can labeled "Contaminated Waste"
- Marking tape/sharpie markers/duct tape
- PFDs/hard Hats (for decon area)

Supplemental DOP Publications/Certifications Available On-Site:

- U.S. Navy Dive Manual (Rev. 6) Air decompression tables
- Ballard MC Safe Practices Manual (includes OSHA Subpart –T)
- U.S. Environmental Protection Agency Diving Safety Manual (Rev. 1.2)
- ADCI Consensus Standards for Commercial Diving & Underwater Operations (6th Ed.)
- Activity Hazard Analysis (AHA)
- Emergency Management Plan (EMP)
- Equipment, air purity and personnel certifications
- Line Pull Signal Chart (will be reviewed and available to dive support personnel)

G. Updated and/or amended diver or dive-team credentials: If requested, updated and/or amended dive team credentials will be submitted to DOF with the required supporting documentation.

H. Diving Platform: The dive station will be staged on a 28ft landing craft style dive vessel. Divers will dive from a 30ft support barge, where sample processing will also take place. A securely-mounted, corrosion resistant ladder extending at least three (3) feet below the water and above the deck (capable of supporting the weight of two fully-equipped divers) will be provided for entering and exiting the water. The ladder may be used along with the floating spine board/stokes litter to safely extract an injured diver.

I. Dive Objectives: Ballard MC will be conducting surface-supplied diving operations assist DOF with collection of sediment samples and installation and retrieval of of porewater sampling equipment.

J. Schedule & Location:

- *Start Date & Time:* TBD, see Dive Windows
- *Dive Windows:* Two dive events are planned: One to install the porewater samplers (1-2 days), and one to retrieve the porewater samplers and collect sediment samples (1-2 days). The first dive event is currently scheduled to occur between July 26 and August 4, 2014 for porewater sample installation and the second dive event is scheduled to occur between October 17 and 27, 2014 for retrieval of porewater samples and sediment sampling. The actual dates of the dive events are dependent on when the Cargill and Glacier docks are open. If both docks are not clear at the time of a dive event then the dive event may be split into two different days with two mobilizations.
- *Dive Location:* Willamette River, (RM11.2 to 11.5) near and adjacent to the Cargill and Glacier Docks and into the adjacent navigation channel in Portland, OR
Cargill Dock (O-Dock): 45.535284,-122.67547
Glacier Dock: 45.537023,-122.678195
- *Work Schedule:* Eight hour to twelve hour days depending on work progress.
- *Project Duration:* Both dive events each expected to take one to two days each.

K. Diving Method: Surface-Supplied Air Diving will be utilized for this project. Back-up air will consist of two (2) DOT 3AA2400 K-cylinder(s) and diver-worn EGS as described in Section E. All back-up air supplies will be consistent with the diver's primary breathing medium.

L. Type of Dive: No-Decompression, Air

M. Work Description: An inspection of all certified dive equipment and the dive station will be facilitated by the Diving Supervisor prior to beginning dive operations. A dive safety briefing and work meeting, including all dive-team members and on-site personnel specific to this project, will take place immediately prior to commencement of the dive. This meeting will include review of this DOP, decon procedures, line pull signals and emergency procedures, including a review of the Emergency Management Plan (EMP). Underwater video will be recorded in DVD format throughout the project to document conditions.

It would be safest for in-water personnel to perform planned tasks without a vessel at the dock(s) due to the fact that LOTO cannot be established. Without LOTO, planned or unplanned operation of vessel systems are uncontrolled and unknown, posing a considerable hazard to a diver working near (or with umbilical routed near) these systems. Because the absence or presence of a vessel (and what type of vessel) remains unknown at this time, BMC presents the following consideration for the Dive Supervisor, who has ultimate authority over the safety and health of all dive team personnel and operations:

- If feasible, attempt to establish an exclusion area off the stern of the vessel of a distance appropriate to the vessel's size
- If feasible, establish an exclusion area surrounding the vessel
 - This would also depend on depth at time of dive and current
 - We would need positive sight of divers exhaust bubbles, and tender variation of the umbilical length marks
- The diver will not dive under any vessel will in port
 - This would cut off access above to the dive in an emergency
- Vessel traffic in the area is also a factor
 - We cannot have traffic crossing our diver's umbilical
- If possible, attempt to establish communications with the vessel master or dock to communicate that a diver will be working outside of determined exclusion zones and request notification prior to energization of vessel systems

The dive supervisor will be responsible for determining when or if the operation or environment poses an unnecessary risk to in-water or topside dive crew members and has the duty and authority to abort operations to protect health, safety and company assets.

Divers will install and retrieve passive porewater sampling devices and collect sediment samples as set forth in the SOP for Diver-Placement and Retrieval of Pasive Samplers and Co-located Sediment Samples (SEE, 5/21/2014) and as directed by Client Onsite Point of Contact. Specific sampling locations and sampling equipment will be provided by Client Onsite Point of Contact. There will be one diver in the water at a time for these operations.

N. PPE for Divers and Topside Personnel: Ballard MC has classified this diving environment as CAT 2 as defined by the US Navy in their technical manual *Guidance for Diving in Contaminated Waters*.

Dive Site Contaminants:

- Water: Bacteria
- Sediment: PCB's, metals, phthalates (plasticizers), pesticides & dioxins (toxic compounds/pollutants)

Divers:

Divers will don Level One (1) Protection consisting of fully encapsulating diving dress before entering the Exclusion (Hot) Zone. Level One Protection includes vulcanized rubber dry suits fitted with mating (integrated) neck dams appropriate to the diver’s helmet model, integrated dry boots with over boot protection and bell-cuff dry gloves. Diving helmets will be SL 27 model (consisting of a tri-exhaust system) or greater to provide appropriate series exhaust valves for contaminated water diving operations.

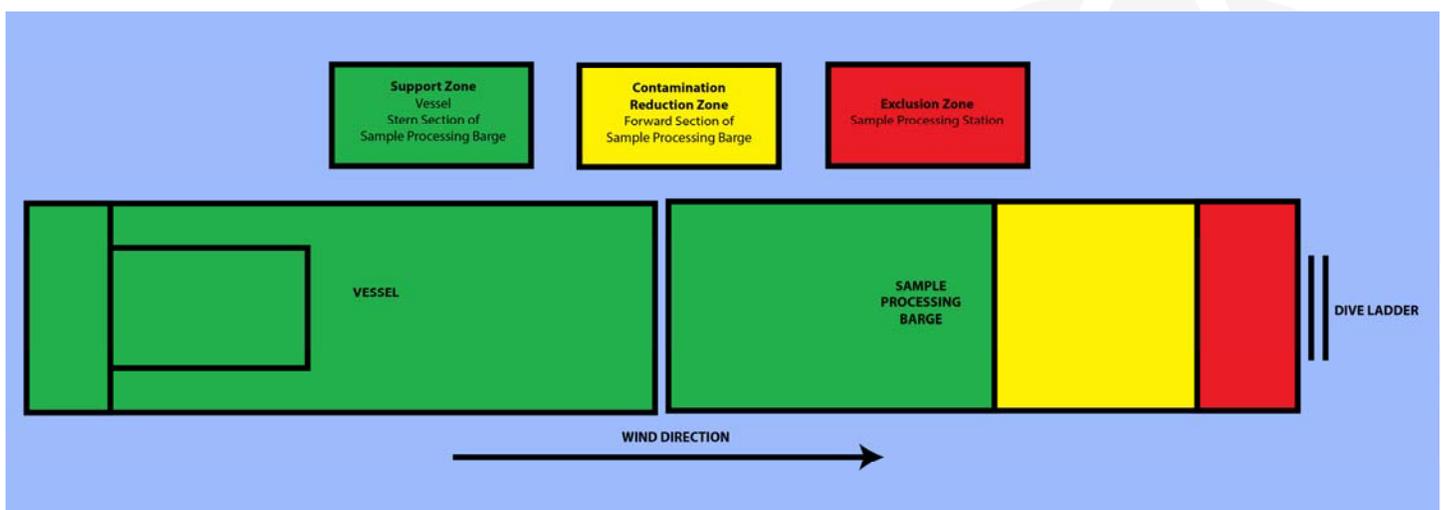
All diver-worn equipment will be tested for integrity and function prior to diving operations. Nitrile exam gloves will be worn underneath dry gloves with chemical gloves donned over the dry gloves. Neoprene gloves may be worn over dry gloves to provide chaffing and additional thermal protection. This system also allows redundant protection in the likely event of glove puncture. Procedures for handling glove puncture or dive gear integrity issues are explained in Section P of this DOP.

Any actual or suspected breach of a Level One diving system requires immediate termination of diving operations.

Topside Personnel:

All personnel working in the Contamination Reduction (Warm) Zone will don Level D protection at minimum as there is a high likelihood that support personnel will be splashed by surface water, sediment and/or by the decontamination solution. Level D protection will consist of disposable rain gear or water-proof coveralls, rubber boots or boot covers, nitrile gloves and safety glasses with a face shield. PPE will be worn when handling any equipment that has not been fully decontaminated. In addition to proper PPE, Tenders must wear a personnel floatation device (PFD) as the outermost layer.

- O. Zone Management System:** The worksite will be broken up into three (3) zones to effectively contain and minimize the spread of contaminants during the work shift and planned operations. The following diagram shows how the zone management system will be implemented on the dive site. These zones will be identified to all dive team members during the pre-shift meeting.



These zones may be identified using physical/visible means if the supervisor desires, however, physical means used to identify zones CANNOT interfere with a rescue or diver recovery methods.

P. Decontamination Procedure: Decon personnel will utilize potable water and Simple Green to decontaminate the diver, dive gear and all tools and/or hoses that entered the exclusion zone. Simple Green may be mixed in a solution or used in concentration depending on the degree of contamination. For purposes of dive planning, Simple Green will be mixed into solution at 50% cleaner and 50% potable water. Pump sprayers will be clearly labeled identifying its contents and the solution or mix percentages. The following procedure is subject to modification at the supervisor’s discretion.

Step/Action	Decon on Dive Vessel
<p>1. Initial potable water rinse</p>	<p>Diver will hold at the top of the ladder or on the landing ramp and rinsed head-to-toe with potable water. Diver remains on the ladder or landing ramp for the next 5 steps.</p> <p><i>Divers have the option of removing their weight belts now or in the next step. Weight belts will be temporarily stored in containment and will be decontaminated after the diver.</i></p>
<p>2. Removal of accessory gear/equipment</p>	<p>Divers will remove weight belts and bail out with harness.</p> <p><i>Gear will be placed in containment and sprayed with Simple Green solution. Solution will sit on gear for at least 5 min before potable water rinse.</i></p>
<p>3. Remove disposable nitrile outer gloves</p>	<p>Tenders will remove and dispose of outer gloves in a lined container labeled “Contaminated Waste”.</p> <p><i>Dry gloves will be inspected for any obvious tears or punctures. Dry gloves ARE NOT removed at this time.</i></p>
<p>4. Apply Simple Green solution</p>	<p>Simple Green solution is applied to the diver head-to-toe.</p> <p><i>Solution will sit on the diver for at least 5 min before potable water rinse.</i></p>
<p>5. Diver scrub down</p>	<p>The diver is scrubbed completely with brushes.</p> <p><i>Particular attention must be paid to the helmet, neck, dry suit zipper, hands, feet, lower arms and cuff seals.</i></p>
<p>6. Second potable water rinse</p>	<p>Diver is rinsed head-to-toe with potable water to remove Simple Green solution and remaining contaminants from scrubbing. Diver leaves the ladder or landing ramp and walks onto the vessel deck.</p> <p><i>Tenders will assist the diver as needed to prevent slips, trips and falls and will ensure the walkway remains clear of debris.</i></p>
<p>7. Helmet and dry suit removal</p>	<p>Tenders will help the diver remove the dive helmet, dry suit, dry gloves and nitrile under gloves.</p> <p><i>Nitrile under gloves will be disposed of in lined containers labeled “Contaminated Waste”. Dry gloves will be decontaminated, inspected for damage and repaired or replaced as needed.</i></p>

After removing the dry suit, divers will wash their hands or will use antibacterial gel sanitizer and will enter the support zone to dress back into their work clothes and don jobsite required PPE. Tenders will complete decon on

remaining dive gear (including definitive decon on diving helmets, dry suit exhaust valves and bail out QD's), tools and equipment and will decontaminate themselves before entering the support zone.

Decon Best Work Practices:

- Direct water flow away from potential leak points (e.g. exhaust valves, seal junctions, etc.)
- Direct spray away from the support zone – particularly during moderate to high wind events
- Assist the diver to prevent slips, trips and falls
- Contain waste water
- Make sure any seal that may come into contact with the diver when gear is removed is completely decontaminated before moving on to the next step

Q. Procedures for Leaks in Dive Gear or Gloves: Divers will immediately report any known or suspected leaks or damage to their gloves or dive gear. Supervisors will alert the tenders that the diver will be surfacing and will inform them which procedure they will need to perform.

Divers can elect to abort the dive after exposure if they are uncomfortable with the following exposure procedures.

Damage to Outer Glove:

Tenders will remove the damaged glove and inspect the integrity of the inner glove. If the inner glove is intact, the diver's hand will be decontaminated with Simple Green solution, dried and a new outer glove will be sealed to the cuff ring.

Damage to Inner and Outer Glove:

The diver will have both gloves removed, their skin will be washed with antibacterial soap, and their cuff will be inspected for further leaks. If no further leaks are found, the diver will receive a new inner and outer glove.

Dry Suit Leak:

The dive will be aborted and the suit will be repaired and leak tested before being used again. The diver will remove all contaminated undergarments and will wash all exposed skin with antibacterial soap and potable water.

Helmet or Neck Seal Leak:

The dive will be aborted and the hat/neck seal will be repaired and tested before being used again. The diver will remove all contaminated undergarments and will wash all exposed skin with antibacterial soap and potable water. If the diver has ingested contaminated water, they will immediately be examined by a medical professional.

R. Anticipated Topside & Underwater Conditions:

- *Air Temperature:* Estimated 45°F to 85°F (based on historical averages)
- *Wind Velocity:* TBD closer to start date
- *Water Temperature:* Anticipated 50°F to 55°F
- *Current:* Estimated to be less than 2 knots
- *Underwater Visibility:* 0 feet to 5 feet
- *Bottom Type:* Silt and/or Mud
- *Site Elevation:* Approx. 32 feet above sea level

- *Planned Dive Depth:* ≤50 feet
- *Maximum Dive Depth:* 50 feet

S. Maximum Bottom Time at Planned Depth: Divers will not exceed a deepest depth of 50 feet for a bottom time longer than 92 minutes. All dive operations will not exceed a table/schedule of 50/:92, repet group M. Dive tables do not require correction, dive site is less than 1,000 feet above sea level.

T. Planned Recompression Schedule: Recompression is not required for this diving evolution. There are no required or planned decompression/safety stops for this diving evolution. Information and contact numbers for the nearest emergency recompression facilities are provided in the site-specific Emergency Management Plan (EMP), which will remain onsite and available to all diving personnel.

U. Planned Rotation of Dive Team Members: Divers will be rotated as required by the Diving Supervisor to ensure they stay within decompression limits and maintain a margin of safety while completing the required tasks. The standby diver will be rested and capable of performing emergency rescue assistance. Because work is limited to no-decompression limits, the standby must be sufficiently free of residual nitrogen to allow for 25 minutes of bottom time at the working depth without exceeding “No Decompression Limits”.

V. Post Dive Procedures: At the completion of a dive, the Diving Supervisor will observe the physical condition of the diver, question the diver as to any symptoms, physical problems or adverse physiological reactions (including decompression sickness symptoms), advise the diver of the location of the nearest decompression chamber and alert the diver to the hazards of flying too soon after the dive. Divers will log their dive and have it signed by the Dive Supervisor.

Divers will wait at least 12 hours before flying after any dive; this interval should be extended to 24 hours following multiple days of repetitive dives.

W. Personnel Directly Involved in Topside Assistance/Support: Every member of the dive crew will provide topside assistance and support and will be rotated at the supervisor’s discretion based on their certifications, level of experience, skills and place in the dive rotation.

X. Means of Direct Communication: VHF Radios (as required) programmed to a pre-determined channel and/or mobile phones will be used to communicate directly with project personnel. Line pull signals and/or flashing the camera light will be used as a back-up communication method should the diver communications fail. Loss of diver communications will require that the diver abort and surface until communications can be repaired.

Y. Project Contacts:

PROJECT CONTACTS		
Name	Mobile No.	Job Title
Jesse Hutton	(360) 518-3641	Chief Executive Officer / Project Estimator
Dean Reynolds	(360) 609-8330	Chief Operations Officer
Drew Christensen	(360) 518-6691	Operations Manager
George Birch	(206) 604-7388	Operations & Staffing
Troy Nylander	(360) 989-0262	Equipment Manager
Rebekah Feasel	(360) 989-0920	Safety Manager
Justin Siewert	(360) 772-3126	Dive Supervisor
Paul Fuglevand	(206) 660-3079	Prime Contractor POC
Tim Thompson	206 619-4109	Onsite Prime Contractor POC
EMERGENCY CONTACTS		
Name	Mobile No.	Job Title
Rebekah Feasel	(360) 989-0920	Safety Manager
Dean Reynolds	(360) 609-8330	Chief Operations Officer
Drew Christensen	(360) 518-6691	Operations Manager
Dana Gordon	(206) 947-8810	Dive Medical Technician
Edmond Kay, M.D.	(206) 954-3750	24/7 Hyperbaric & Occupational Physician
OSHA	(800) 321-6742	Report a fatality or life threatening situation
See the site-specific Emergency Management Plan for additional emergency information		

***ALL EMERGENCY NUMBERS VERIFIED JUNE 17, 2014 BY REBEKAH FEASEL**

It is requested that any questions and/or comments regarding this DOP be directed to Rebekah Feasel, Safety Manager; Mobile (360) 989-0920; Rebekah.Feasel@BallardMC.com.

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ATTACHMENT 5

LABORATORY SOPs

Ultra Trace Air Toxics SOP BRL SOP-00405 /
11

Campobello

CLEAN-UP OF SAMPLE EXTRACTS FOR PCDD AND PCDF ANALYSIS

Maxxam Analytics International Corporation
6740 Campobello Road
Mississauga, Ontario
905-817-5700

Document Identity**Document Categorization****Invalid Application Parameter selection**

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Release and Audit Schedule**Release Schedule**

When Approved

 Allow Administrator to Release Document Early**Expiration Schedule**

When Superseded or Obsoleted

Audit Schedule

12 Month(s)

Special Handling on Release **Update Completed Trainee Records****Insert Text** CTA BRL SOP-00405**Associated Documents****Associated External Documents** METHOD 23—DETERMINATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS FROM STATIONARY SOURCES Method 1613, Revision B METHOD 8290A Method TO-9A**Document Control Documents** Burlington SOP BRL SOP-00404 : Dioxins and Furans by HRGC HRMS in Air Samples Burlington SOP BRL SOP-00406 : Dioxins and Furans by HRGC HRMS in Water and Soil (EPA 8290) Burlington SOP BRL SOP-00408 : PCB Congeners Analysis by HRGC HRMS in Water, Soil and Air Burlington SOP BRL SOP-00410 : Dioxins and Furans in Water and Soil by HRGC HRMS (EPA 1613) Burlington FCD BRL FCD-00015 : All Parameter Hi-Res Sample Tracking Sheet Burlington FCD BRL FCD-00023 : Hi Res/ Low Res Sample Tracking Sheet Corporate WI Publish to All COR WI-00012 : Definitions Corporate WI Publish to All COR WI-00040 : Corporate Procedure for Policy Deviation Forms Campobello WI CAM WI-00095 : Environmental Method Validation (NELAC + DOD requirements) Campobello WI CAM WI-00121 : Maxxam Lab QM Supplement to Meet Requirements of DoD QSM Version

4.1

-   Campobello FCD CAM FCD-00903 : FMS Proofing Information Form
-   Campobello FCD CAM FCD-00904 : FMS Clean-up Form
-   Campobello Method Summary Sheet CAM MS-00010 : BRL SOP-00405 Method Summary for DFs Sample Clean-up
-   Campobello WI CAM WI-00010 : Receipt, Handling and Labeling of Analytical Standards and Chemicals
-  Ultra Trace Air Toxics SOP BRL SOP-00407 : Dioxin and Furan Extraction in Water and Soil Samples

Reason for Change

Date of Change July 14, 2009	Version 2
Section Changed Header, 1.0, 4.0.1, 4.3, 7.A-7.B, 10.1, 10.2.2, 12.0	
Change Made Header updated Maxxam's name 1.0 updated current lab location 4.0.1 updated reference method 8290 to current revision 4.3 replaced SOP list with the reference to Associated Documents 7.A renumbered section by adding a prefix "A" differentiate from added option 7.B. 7.B added option "B" for Automated Sample Clean-up using POWERPREP™ 10.1 updated lab's location 10.2.2. updated procedure to reflect current practice 12.0 added FCD#	
Date of Change January 6, 2012	Version 3
Section Changed 6.3.1, 7.A.1.1, 7.A.3, 7.A.4, 7.B.1.3, 7.B.1.6, 12.0	
Change Made section 6.3.1 added - listing disposable FMS columns and their part numbers. section 7.A.1.1 - corrected reference to section 7.A.2 section 7.A.3 - added NOTE: Carbon cleanup is required for ALL Soil samples section 7.A.4 step 14 - corrected information - changed 2mL to 1mL and changed benzene to toluene section 7.B.1.3 - added "Example of POWERPREP setting when "Jumbo" silica column is used " and changed some of the values for the solvents section 7.B.1.6 added "Example of Wash program for POWERPREP unit, this can vary dependent on how much cleanup is required" section 12.0 added "BRL FCD-00023 Tracking Sheet"	
Date of Change January 10, 2012	Version 4
Section Changed 7.A.1.2.1	
Change Made Sulphuric Acid Extraction: change all references to hexane to DCM	
Date of Change January 10, 2012	Version 5
Section Changed 1 page Header	
Change Made 1 page of the Word doc was formatted as a separate page, inadvertently rev. 4 was not reflected on 1st page, but all other pages. Rev 5 corrected for the formatting of this SOP.	
Date of Change September 17, 2012	Version 6
Section Changed 7.A.2	
Change Made Section 7.A.2 - Step 4 - added iso-octane as a keeper	
Date of Change December 5, 2012	Version 7
Section Changed 4.0.3-4.0.5, 7.A.3	
Change Made 4.0.3-4.0.5 added relevant reference methods to this section &.A.3 added the addition of carbon clean-up to all air samples	
Optional Field A Associated documents have been reviewed, and where required the CPro links were updated to reflect most current procedures in use by the HRMS laboratory	
Date of Change May 8, 2013	Version 8
Section Changed 10.1, 10.3, 10.4	
Change Made 10.1 - added BRL FCD-00023 10.3 - Added reference to CAM WI-00010 10.4 - fixed numbering Associated documents have been reviewed, and where required the CPro links were updated to reflect most current procedures in use by the HRMS laboratory	
Date of Change September 30, 2013	Version 9
Section Changed various	
Change Made added info to section 6.1.6 re teflon tubes	
Optional Field A updated preparation of raw silica gel section 6.2.12 Also added expiry dates to prepared adsorbants	
Optional Field B 7.A.2 updated to reflect that adsorbants used to prepare the mixed bed silica column are now weighed. Also	

added the eluant is to be collected as soon as the extract is added to the column	
Date of Change March 11, 2014	Version 10
Section Changed 6.2.4.1	
Change Made changed carbon and celite mixture to current practice - 18g carbon & 82 g celite	
Optional Field A Note: associated documents have been reviewed, and no changes to them are required.	
Date of Change February 18, 2015	Version 11
Section Changed Section 7.A.1, 7.A.1.2.1, 7.A.2, 7.A.2.1, 7.A.3, 7.A.4, 7.A.5	
Change Made section 7.A.1 - revised to reflect current practice	
7.A.1.2.1 - added details for Sulphuric Acid Extraction	
7.A.2 - added hexane details to step 8 and keeper to step 9	
7.A.2.1 - added conditions for column preparation; updated steps 3 and 4; updated steps 1,3 and 4 for Sulphur clean-up	
7.A.3 - added details to steps 1, 5,7,11,12,13,14 and 15	
7.A.4 - added details to steps 8,10,11,12,15 and 16; added rinses	
7.A.5 - added details to steps 2,5 and 6	
added CTA	
Optional Field A Note: associated documents have been reviewed; added BRL SOP-00407 and removed redundant links.	

Approval Status Table			
Approver	Source	Role for Approvers	Parallel-Everybody Segment
Approver	Action	Date	Comment
Betsy Cliffe	Approve	February 18, 2015 4:48 PM GMT-5	
Karen Nicol	Approve	February 18, 2015 2:39 PM GMT-5	
Salima Haniff	Approve	February 18, 2015 6:41 PM GMT-5	

CLEAN-UP OF SAMPLE EXTRACTS FOR PCDD AND PCDF ANALYSIS

1.0 LOCATION:

Clean-up procedures are performed in the HRMS Preparation Laboratory.

2.0 PURPOSE:

This method is used to prepare and clean up extracts for the determination of PCDD/DF.

2.1 Principle of the Method: extracts for the determination of PCDDs and PCDFs are cleaned up and passed through a series of columns which remove, by reaction and/or selective adsorption, the bulk of the organic matrix co-extracted with the PCDDs and PCDFs.

A mixed bed column of 44% H₂SO₄/Silica gel, 33% 1M KOH/Silica gel, 10% AgNO₃/Silica gel is the first column the sample extract is passed through. The acid silica gel removes any oxidizable contaminants including PAHs and some organochlorine pesticides, many of which are oxidized to acids. This layer becomes highly coloured if a sample extract contains a high concentration of oxidizable material. The basic silica gel removes any acids and phenols. The high water content of the acid and base silica gel deactivates the silica to the point where the silica gel acts only as a support for the acid and base. The AgNO₃/Silica gel reacts with organic thio-compounds, molecular sulphur and olefins, complexing them and retaining them on the column. If the sample extract contains high concentrations of these compounds, the AgNO₃/Silica layer will be highly coloured.

Silica gel is used between the layers of acid, base and AgNO₃ silica gel. These layers hold on to polar compounds. If hexane, used as the eluting solvent, is contaminated with even a small amount of a polar solvent, the polar compounds expected to remain on the column may be eluted. If the silica gel is too active, i.e. not deactivated with at least 3% water, some of the more polar of the dioxins and furans may elute later and not within the expected elution window.

The elution order is generally based on polarity. The higher chlorinated dibenzo-p-dioxins are the least polar and elute first, followed by the less chlorinated dibenzo-p-dioxins. The dibenzofurans are more polar than the dibenzo-p-dioxins and will start eluting later and in the same general order as the dibenzo-p-dioxins based on their degree of chlorination. Overlap occurs in the elution of the dioxins and the furans. The position of chlorine atoms may increase the polarity causing it to elute later. This results in some inconsistencies in the general rule that the higher chlorinated compounds elute first. Solubility also affects the elution order. Less chlorinated, smaller molecular weight compounds are more soluble and causes the lower chlorinated PCDD and PCDF to elute earlier.

The eluent from the mixed-bed column is concentrated and passed through a column of activated alumina. This column also separates compounds based on polarity and is mainly used to separate

the dioxins and furans from PCBs. PCBs do not contain oxygen atoms and thus are less polar. They will pass through the column in the first fraction. The dioxins and furans are collected in a second fraction which eluted with dichloromethane, a highly polar solvent used to strip any polar compounds held by the column. This vigorous stripping of polar compounds is possible at this point since most of the unwanted polar compounds were removed with the initial mixed bed column.

If further cleaning of the extract is required an activated charcoal column is used. The extract is loaded onto a column of charcoal supported on Celite. Dioxins and furans are removed from the column using toluene. The activated charcoal column separates the dioxins and furans from interfering compounds based on planarity. The dioxins, furans are planar and elute with the toluene. Co-planar PCBs also elute with the toluene.

2.2 Safety:

2.3.1 General Considerations: each reagent, analyte and sample should be treated as a potential health hazard and exposure should be reduced to the lowest possible level. On the basis of the available toxicological and physical properties of the PCDDs and PCDFs, these compounds should only be handled by highly trained personnel familiar with handling and cautionary procedures, and who understand the associated risks. All work related to the analysis of PCDDs and PCDFs should be carried out within a specially designed laboratory. Refer to the appropriate MSDS for further information.

2.2.2 PCDDs and PCDFs: the 2,3,7,8-tetrachlorodibenzo-p-dioxin isomer has been found to be acneogenic, carcinogenic and teratogenic in laboratory animal studies. It is soluble in water to ~200 ppt, (ng/L), and in organic solvents to ~0.14%. At room temperature it is a solid and has a relatively low vapour pressure. The physical properties of the 135 other tetra to octa chlorinated PCDDs/PCDFs have not been well established. It is presumed that the physical properties of these congeners are generally similar to those of the 2,3,7,8-TCDD isomer.

All labware, safety clothing, and other items known to have been contaminated with PCDD/PCDF must be carefully secured and subjected to proper disposal. In the unlikely event that analytical personnel experience skin contact with PCDD/PCDF or samples containing these, the contaminated area should be immediately and thoroughly scrubbed using mild soap and water. Personnel involved in any such accident should seek medical advice.

3.0 SCOPE:

This procedure is applicable to all extracts of soil, water, air and biota for the determination of PCDDs and PCDFs at low picogram to nanogram levels by HRGC/HRMS or HRGC/LRMS.

3.1 Interferences: solvents, adsorbents, reagents, glassware and other sample processing hardware may yield artifacts or elevated baselines that may cause misinterpretation of the data. Proper cleaning of glassware is extremely important. Note that glassware may not only contaminate the

samples, but may also remove the analytes of interest by adsorption on the glass surface. Method blanks are analyzed to demonstrate that all laboratory materials are free from interferences under the conditions of the analysis. The use of high purity reagents minimizes interferences.

The sensitivity of this method is dependent upon the level of interferences within a given matrix. Interferents co-extracted from the sample material will vary considerably with the matrix and the diversity of the site being sampled. PCDDs and PCDFs are often associated with other chlorinated organics, which may potentially interfere with the analysis. These include PCBs, polychlorinated methoxybiphenyls, polychlorinated hydroxy diphenylethers, polychlorinated benzylphenyl ethers, polychlorinated diphenyl ethers, polychlorinated naphthalenes, polychlorinated xanthenes, polynuclear aromatics, and pesticides.

The interfering compounds may be present at concentration levels several orders of magnitude higher than any PCDDs and PCDFs in the sample. This cleanup procedure reduces or eliminates these interferences to the maximum extent practicable in order to ensure reliable quantitation of PCDDs and PCDFs at trace levels. Despite rigorous cleanup procedures, the possibility of matrix interference will still exist. If detection limits are seriously elevated by excessive background, the sample extract may have to be re-processed or re-extracted with modified cleanup techniques.

4.0 REFERENCES:

4.0.1 US EPA SW846 8290A, Revision A, February 2007

4.0.2 Reference Method for the Determination of PCDDs and PCDFs in Pulp and Paper Mill Effluents, 4th Draft April 1991, Chemistry Division, River Road Environmental Technology Centre, Conservation and Protection, Environment Canada.

4.0.3 US EPA Method 1613, Revision B, Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS

4.0.4 US EPA SW846 Method 23A Version 1, Dec. 1, 1996. "Sampling Method for Polychlorinated Dibenzo-p-dioxin and Polychlorinated Dibenzofuran Emissions from Stationary Sources.

4.0.5 US EPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-9, Method for the Determination of Polychlorinated Dibenzo-p-dioxins In Ambient Air Using High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS)

4.1 Analytical Testcodes:

Test codes may be created as necessary

4.2 Other Relevant SOPs – refer to Associated Documents in CPro section of this SOP

4.3 Modifications and/or Improvements from Referenced Methods:

4.3.1 EPA SW846 Method 8290A & 1613B:

- Maxxam does not partition the sample with NaCl
- Reference uses NaOH Si Gel, Maxxam uses KOH Si Gel
- Reference uses acidic alumina, Maxxam uses basic alumina
- Reference elutes alumina with 20%DCM in Hexane/DCM, Maxxam uses: 4%DCM in hexane/hexane

4.3.2 Environment Canada River Road Protocol:

- Reference uses 2% DCM in hexane, Maxxam uses 4% DCM in hexane
- Reference uses 50% DCM in Hexane, Maxxam uses straight DCM

5.0 SAMPLE HANDLING AND PRESERVATION:

Maintain the volume of any extracts to at least 2 ml in glass containers prior to cleanup by this procedure. If the cleanup is to be performed >5 days after extraction, store the extracts in teflon-sealed glass containers at 2-6 °C until clean-up.

6.0 APPARATUS AND MATERIALS:

6.1 Apparatus: equivalent labware and equipment may be purchased from other suppliers as available.

6.1.1 Pasteur Pipettes: 5¾" from VWR, Cat. No. 14673-010 and 9" Cat. No. 14673-043 or equivalent

6.1.2 Chromatography Columns: borosilicate glass, 15 mm ID, ~40 cm long with tapered ends for preparing mixed bed silica columns. Obtained from a commercial glass blower.

6.1.3 Borosilicate Glass Tubing: 14 cm long x 5.5 mm ID, for the preparation of carbon/Celite columns. Custom made by a commercial glass-blower.

6.1.4 Borosilicate Glass Vials (16 ml): with closures, used for the collection of fractions from the alumina and carbon/celite columns, rinsed with DCM prior to use. (VWR 66011-121) or equivalent

6.1.5 Borosilicate Glass Vials (40ml): with closures, used for the collection from the mixed bed silica column, rinsed with dichloromethane prior to use. (VWR Catalogue No. 66012-066) or equivalent

6.1.6 Teflon Tubing: to fit tightly over wide end of pasteur pipettes to facilitate the addition of solvent for alumina cleanup. 6.4 mm. ID, 7.9 mm. OD, cut to ~30 cm lengths. (Canlab, Cat No. R5354-3, Nalgene 890 Teflon FEP 8050-0310 or equivalent). **Note:** The teflon tubing is reusable and as a minimum should be rinsed with DCM between sets of samples. The teflon tubes are stored in a 500mL cylinder filled with DCM when not in use.

6.1.7 Reacti-vials: clear glass, 1 ml, rinsed with DCM prior to use. (Kimble 60700-1) or equivalent. 5mL disposable centrifuge tubes may also be used.

6.1.8 Nitrogen Evaporator/Concentrator: Meyer N-EVAP Organomation Model 111

6.1.9 Balance: capable of measuring to within 0.1 gram

6.1.10 Bottles: 500 ml a/g wide mouth and 1 L c/g bottles with teflon lined closures for the preparation and storage of column packing materials. Rinse with DCM and air dry prior to use.

6.1.11 Glass Wool: 8 μ fiberglass

6.2 Reagents: equivalent reagents may be purchased from other suppliers as available. Other volumes of a reagent may be prepared as necessary by modifying the amount of stock used appropriate to the final volume required.

6.2.1 Activated Carbon/Charcoal: activated charcoal from Anderson Development Company, Cat. No. AX-21 or equivalent.

6.2.2 Basic Alumina: aluminum oxide basic powder, Brockmann Activity Grade 1, 50-200 μ m (Baker no. 0539-05) or equivalent. Activated by heating for at least 18 hours at ~ 225 °C. Store at ~ 225 °C.

6.2.3 Copper Powder: reagent grade, from Anachemia, Cat. No. AC 2577 or equivalent

6.2.3.1 Activated Copper Powder: add ~ 1 ml of reagent grade copper powder to a 40 ml vial and add ~ 20 ml of concentrated HCl. Shake for ~ 1 min. After settling remove the HCl with the pipette. Rinse 3 times with RODI water, followed by 3 sequential rinses each of acetone and hexane. Dry using a stream of N_2 . Prepare this fresh daily.

6.2.4 Celite: Celite 545 from Fisher Scientific or equivalent

6.2.4.1 Carbon/Celite Mixture: mix 18.0 ± 0.01 g of activated carbon and 82.0 ± 0.01 g of Celite in a 250 ml bottle with a Teflon-lined screw cap. Tumble overnight, minimum 16 hr. Label with the batch number, prep date and analyst ID.

6.2.5 Nitrogen: UHP Grade from Linde or equivalent

6.2.6 RODI: Reverse Osmosis Deionized Water, (RODI), $>16M\Omega$ purity.

6.2.7 Hydrochloric Acid (HCl): reagent grade, from Anachemia, Cat. No. EG 4955 or equivalent

6.2.8 Potassium Hydroxide (KOH): reagent grade, from Caledon, Cat. No. 6160-1 or equivalent

6.2.9 Potassium Hydroxide (1.0 M KOH): weigh 56.00 ±0.01 g of KOH into a 1L volumetric flask and dilute to volume with RODI. Store in a 1L amber bottle at room temperature. Prepare as needed.

6.2.10 Solvents: dichloromethane (DCM), ethylene chloride, toluene, hexane, cyclohexane, ethyl acetate, iso-octane from Caledon or equivalent, Distilled in Glass quality

6.2.10.14% DCM in Hexane: using the 4% DCM in hexane labeled Oxford dispenser or equivalent, add 40 ml of DCM to the dispenser and make up to 1 L with hexane

6.2.11 Silver Nitrate: reagent grade, from Caledon, Cat. No. 7020-1 or equivalent

6.2.12 Silica Gel: 100-200 mesh, 60 A. from ICN Biomedicals, Cat. No. 02761 or equivalent

The Silica gel must be washed as follows before use:

1. Place approx. 300mL of ICN Silica Gel into a 600mL Buchner funnel and connect to a vacuum pump
2. Cover the silica gel with approx. 300mL of hexane
3. Stir the silica with a spatula or glass rod and let it settle for 2 minutes
4. Turn on the vacuum pump to remove the solvent
5. Repeat steps 2,3 & 4 2 more times using hexane – total washing with hexane = 3
6. Repeat steps 2,3 & 4 using DCM – this is also repeated 3 times
7. Transfer the washed Silica gel into a pyrex dish lined with foil (rinsed with DCM)
8. Cover pyrex dish with rinsed foil (put some vent holes in the foil cover)
9. Allow to dry in a fumehood overnight to remove solvent
10. Once the solvent is removed, place the silica in the pyrex dish in the oven at 200°C overnight

The washed silica gel is to be used for the preparation of all adsorbants used for D/F cleanups

6.2.12.1 Acid Silica Gel (44% H₂SO₄): tare an empty 1 L clear glass bottle, marked for 44% H₂SO₄. Add ~270-300 g silica gel. The amount of H₂SO₄ needed is calculated by:

$$\text{Wt. H}_2\text{SO}_4 \text{ needed (g)} = \text{wt. Silica Gel (g)} \times (44/56)$$

Carefully add the H₂SO₄ to the bottle, on the balance, and allow it to be absorbed. Shake by hand to loosen up the silica gel before placing on the tumbler. Record the prep date, expiry date and prep person's name on the bottle and in the Adsorbent Logbook. Tumble overnight, minimum 16hrs. Store at room temperature, prepare as needed. Expiry date is 1 month from preparation date.

6.2.12.2 Basic Silica Gel (33% KOH): tare an empty 1 L c/g bottle labeled 33% KOH. Add ~270-300 g silica gel. The amount of 1M KOH needed is calculated by:

$$\text{Wt. 0.1 M KOH needed (g)} = \text{Wt. silica gel (g)} * (33/67)$$

Carefully add 1M KOH to the bottle, on the balance, and allow it to be absorbed. Shake by hand to loosen up the silica gel before placing the bottle on the tumbler. Record prep date, expiry date and prep person's name on the bottle and in the Adsorbent Logbook. Tumble overnight, minimum 16hrs. Store at room temperature, prepare as needed. Expiry date is 1 month from preparation date.

6.2.12.3 AgNO₃/Silica Gel (10% AgNO₃): dissolve 30.00 ±0.01 g of AgNO₃ in a minimum amount of water in a wide mouth glass container with a Teflon-lined closure. Add 270 g of silica gel, cap and shake by hand for ~2 min. to distribute the AgNO₃. Cover the bottle with a suitable material to prevent light penetration. Tumble overnight, minimum 16hours. The mixture is placed in the oven at 200°C for 30 minutes. Store in a dessicator and prepare as needed. Record weights, dates, prep person and supplier/lot # in the Adsorbent Logbook. Avoid light penetration of the bottle. Expiry date is 1 month from date of preparation.

6.2.13 Sodium Sulfate (Na₂SO₄): granulated, reagent grade, from Caledon, Cat. No. 8220 or equivalent

6.2.14 Sulfuric Acid (H₂SO₄): reagent grade, from Anachemia, Cat. No. EG 8750 or equivalent

6.3.1 Disposable FMS (Fluid Management Systems) Columns:

- PCB Free High Capacity with Teflon Chips (Jumbo Silica column) part # PCB-HCDS-ACD-TFC
- PCB Free Classical Silica ABN Column part # PCB-ABN-STD
- PCB Free Disposable Basic Alumina (11g) column part # PCBA-BAS-011
- PCB Free Disposable Carbon/Celite (34g_ Column part # PCBC-CCE-034

7.0 ANALYTICAL PROCEDURE:

Note: for drinking water samples logged in for DFT4CDD-W – cleanup is optional.

7.A.1 Extract Preparation: The 2 ml sample extracts from BRL SOP-00407 are transferred to the first clean up Mixed Bed Silica Gel Column Clean-Up column directly from the flask, adding a clean up spike if applicable, if no splits are required and if samples have not been double spiked.

If samples have been double spiked perform the following:

- Step 1* Using a DCM dispenser calibrate a 10 mL centrifuge vial at ~2mL and ~4 mL position. This will allow a 2 mL clean up portion and 2 mL archive portion.
- Step 2* Label the centrifuge tubes and transfer the sample into the centrifuge tube.
- Step 3* Rinse the flask **3 times** with DCM. **Each time add the rinsate to the centrifuge tube.**
- Step 4* Concentrate on N2-Evap to the 4mL calibration point. **If a clean-up spike needs to be added, transfer 2mL split of the extract to a pre-rinsed 5mL centrifuge tube.**

Proceed to Section 7.A.2 if extract is normally coloured, or 7.A.1.2 if they are colored. Note: Based on analyst experience, the extract used for clean up may be split into multiple mixed bed silica gel columns rather than performing sulfuric acid extraction.

- Step 5* Store the archive portion in a flammable cabinet for future use if required.
Note: Archived portions will be disposed of after a 45 day period of time.

7.A.1.1 Normally Coloured Extracts: Proceed to Section 7.A.2 if the following are applicable

- concentrated extract is not highly coloured
- does not contain a high concentration of lipids
- not expected to overload the acid silica column, i.e. based on the experience of the analyst

7.A.1.2 Highly Coloured Extracts: A further sulfuric acid extraction may be required if

- the concentrated extract is highly coloured
- the sample is known to contain a high concentration of lipids
- the sample is expected to overload the acid silica, i.e. based on the analyst's experience
- Due to the nature of the sample after extraction a dilution may be required prior to cleanup. This must be noted on the worksheet including the reason for this

7.A.1.2.1 Sulphuric Acid Extraction:

- Step 1* Quantitatively transfer the 2mL extract from the flask to a pre-rinsed 40mL vial labeled 'A' and rinse the flask 4 times with ~2mL of DCM –add each rinse to vial 'A'
- Step 2* Concentrate the extract to ~ 10mL.
- Step 3* Add ~10 ml of concentrated H₂SO₄ to the extract in vial 'A'. Shake and vent several times to release the pressure. Then shake vigorously for ~2minutes. Allow the vial 'A' to stand for ~10minutes.
Note: Using a centrifuge after shaking for ~2 minutes at a setting of 3000rpm for ~ 4minutes will speed up the process.
- Step 4* When 2 distinct layers are formed, transfer the DCM layer (top layer) using a Pasteur pipet into another pre-rinsed 40mL vial labeled as 'B'. If the H₂SO₄ portion in vial 'A' is highly coloured, add ~10mL of H₂SO₄ to vial 'B' and repeat step 3.
Note: If an emulsion forms and 2 distinct layers are not observed, transfer the entire contents of the vial to a 250mL jar or a small separatory funnel and increase the volume of H₂SO₄ to ~50mL and DCM to ~75mL.
- Step 5* If colour is still present in the acid portion, repeat steps 3 and 4. The DCM portion to be transferred to another pre-rinsed vial labeled 'C'. Repeat the extractions with H₂SO₄ until no further colour is noticed. Label the last re-rinsed vial as 'F' (Final)
- Step 6* For vial 'A' acid portion, rinse 2 times with ~ 10mL of DCM and shake each time for ~ 2 minutes. Add the rinsate to vial 'B', then the rinsates from 'B' should be added to vial 'C' and the rinsate from vial 'C' will be transferred to vial 'F'
- Step 7* Concentrate the extract, vial 'F' under a gentle stream of N₂ to ~ 2mL
- Step 8* Process the extract as per 7.A.2

7.A.2 Mixed Bed Silica Gel Column Clean-Up: Prepare these columns just prior to use

Step 1 Pack the tapered end of a 15 mm ID x 40 cm glass column with a small piece of glass wool and add in the following sequence:

- Glass wool plug in bottom of column
- 2.5g of Na₂SO₄
- 1.0g of 10% Silver nitrate/Silica gel
- 1.0g washed Silica gel
- 3g of 33% KOH/Silica gel
- 1g of washed Silica gel
- 8g 44% Sulphuric acid/ Silica gel
- 1g washed Silica gel
- 2.5g Na₂SO₄

Step 2 Rinse the packed column with 30 ml Hexane.

Step 3 Using a Pasteur pipette, load the 2mL extract on the column just as the solvent reaches the top of the column bed.

Transfer steps are critical. Loss of any of the extract will seriously affect recoveries.

Step 4 Rinse the centrifuge tube/vial with ~2mL of hexane then transfer the rinsate to the column. Once the solvent reaches the column bed, discard the eluent from the waste vial and switch to a pre-rinsed 40mL collection vial that has been labeled appropriately

Step 5 Quantitatively rinse the centrifuge tube/vial 2 more times, adding each rinse to the column just as the previous rinse reaches the top of the column bed.

Step 6 Add additional Hexane in small amounts to rinse down the sides of the column.

Step 7 When the vial is approximately half full, the Hexane can be added in larger amount. (~10 ml)

Step 8 Continue addition of Hexane to the point where the vial is filled to the top.

Step 9 Concentrate the total eluent to a ~2 ml final volume under a gentle stream of N₂, adding ~1mL of iso-octane as a keeper during the concentration.

Step 10 Cover the eluent with a teflon-lined cap if the extract will not be processed immediately.

Note: If the entire sulphuric acid-silica gel layer is coloured, the column has been overloaded. Reprocess the concentrated eluent on a fresh column. Based on the experience of the analyst, the sample may be passed through a column of 44% H₂SO₄ described below.

7.A.2.1 Secondary H₂SO₄ Acid/Silica Gel Clean-Up: Prepare these columns just prior to use

Step 1 Pack the tapered end of a 15 mm ID x 40 cm glass column with glass wool and add the following in sequence;

- 2.5g sodium sulfate (Na₂SO₄)

- **1.0g AgNO₃/SiO₂ – this layer is added only if this layer was coloured in the mixed bed column**
- 1.0g washed silica gel (SiO₂)
- 8.0g of 44% sulphuric acid silica gel
- 1.0g washed silica gel (SiO₂)
- 2.5g sodium sulfate (Na₂SO₄)

Step 2 The sample may also be split and passed through multiple columns and then recombined when acid layer is clean. (This decision is based on the experience of the analyst and will depend on the appearance of the “mixed bed column)

Step 3 Rinse the packed column with 30 ml Hexane

Step 4 Load the 2mL of the extract that has been cleaned up on the mixed bed column and collect the eluent in the same manner as in Section 7.A.2.

Step 5 Rinse the centrifuge tube/vial with ~2mL of hexane then transfer the rinsate to the column. Discard the eluent from the waste vial and switch to a pre-rinsed 40mL collection vial that has been labeled appropriately

Step 6 Quantitatively rinse the centrifuge tube/vial 2 more times, adding each rinse to the column just as the previous rinse reaches the top of the column bed

Note: If the AgNO₃ column is highly coloured (yellow), clean it further with fresh activated copper powder prior to another column cleanup by performing the following, (see BRL SOP-00008)
Sulphur Clean-up:

Step 1 Add ~0.5 ml of the active copper powder to the ~2 ml concentrated extract in the vial requiring copper clean-up.

Step 2 Mix for a few seconds

Step 3 Add more copper powder until the copper powder stays a pink shade and no longer turns black.

Step 4 The extract can now be passed through the Secondary H₂SO₄ Acid/Silica Gel column as described in 7.A.2.1.

7.A.3. Basic Alumina Column Clean-Up:

Step 1 Pre-rinse the Teflon tubing required with ~5-10 ml DCM and set aside to dry.

Step 2 Prepare 15 ml vials by rinsing 3 times with DCM. Print labels for the worksheet and use these to label the vials for Fraction A. Label additional vials for the samples by hand for Fraction B so as to be visually distinct from Fraction A. Add ~1 mL of iso-octane to Fraction B vials.

Step 3 Pack the tapered end of a 9" Pasteur pipette with glass wool and add the following in sequence;

- Add ~0.5 cm sodium sulfate
- Fill to within 1 cm of the top with hot basic alumina
- Add ~0.5 cm of sodium sulfate

Step 4 Fit the top of the pipette with a piece of Teflon tubing.

- Step 5* Place column in a stand and rinse with ~7 ml of Hexane quickly after preparation of the column so that the alumina is still warm. The Hexane eluent is discarded.
- Step 6* Place the labelled Fraction A 15 ml borosilicate glass vial under the column.
- Step 7* Add the sample extract to the column with a Pasteur pipette just as the Hexane rinse reaches the top of the column bed and columns are no longer dripping.
- Step 8* Quantitatively rinse the vial with ~2 ml of 4% DCM/Hexane 2 times.
- Step 9* Add each rinse to the column when the previous rinse just reaches the top of the column bed.
- Step 10* Add a further and final ~4 ml of 4% DCM/Hexane for a total eluent volume of ~10 ml.
- Step 11* Once the eluent is collected, cap the fraction A and archive.
- Step 12* Place the second labelled Fraction B 15 ml vial under the column just as the last of the ~4 ml 4% DCM/Hexane rinse reaches the top of the column bed.
- Step 13* Add a total of ~12 ml of DCM to the column using the solvent dispenser. This DCM "Fraction B" contains PCDD/DF.
- Step 14* If carbon cleanup isn't required, concentrate the extract as in Section. 7.A.5.
- Step 15* If carbon cleanup is required, concentrate the eluent to ~1 ml under a gentle stream of N₂ and proceed to 7.A.4.

NOTE: Carbon cleanup is required for ALL soil samples, with the exception of DFCDN-S and ALL air samples

7.A.4 Carbon/Celite Column Clean-Up:

- Step 1* Mark a 14 cm long piece of 5 mm ID glass tubing with a permanent marker at 7cm and 11 cm.
- Step 2* Form a plug of glass wool at the 7 cm mark.
- Step 3* Fill to ~half way between the 11 cm mark and the end with Carbon/Celite mixture.
- Step 4* Gently tap on the counter to bring the Carbon/Celite down to the 11 cm mark.
- Step 5* Add glass wool to form another plug for the other end.
- Step 6* Place the columns in the stand with the larger reservoir end up.
- Step 7* Place a 15 ml vial under the column to collect waste from the rinses that will be added.

Add rinses as follows (Note: Rinses can be pushed through the column using a bulb):

- Step 8* Add ~5 ml of toluene in ~1 ml aliquots at a time, adding each rinse to the column just as the previous rinse reaches the top of the column bed.
- Step 9* Add ~1 ml of 50:50 DCM/Cyclohexane.
- Step 10* Add ~5 ml hexane in ~1 ml aliquots at a time, adding each rinse to the column just as the previous rinse reaches the top of the column bed.
- Step 11* Add the sample, (concentrated Fraction B eluent from alumina cleanup), to the column using a Pasteur pipette just as the final Hexane wash solvent reaches the top of the column bed.
- Step 12* Transfer the extract, rinsing twice with ~0.5 ml Hexane, adding each rinse to the column just as the previous rinse reaches the top of the column bed. Keep this vial to collect the sample portion of the eluent after column is inverted.
- Step 13* Add ~2 ml 50:50 DCM/Hexane in ~1 ml aliquots at a time, adding each rinse to the column just as the previous rinse reaches the top of the column bed.

- Step 14* Add ~1 ml of 50:50 Toluene/Ethyl acetate.
- Step 15* Discard the waste vial once the Toluene/Ethyl acetate rinse has completed dripping.
- Step 16* ****Invert column and place a piece of Teflon tubing on the column**** (Note: Teflon tubing used for Alumina clean up can be used at this time or new Teflon tubing that has been rinsed with DCM)
- Step 17* Place the sample vial saved from Step 12 back under the column and add ~14 ml of toluene, in two ~7 ml portions.
- Step 18* This rinse contains the PCDD/DFs and is then concentrated and transferred as in Section 7.A5.

7.A.5 Concentration of Cleaned Extract:

- Step 1* Concentrate the eluent containing PCDD/DF from the Alumina column, or the eluent containing PCDD/DF from the Carbon/Celite column, to ~0.5-1 ml with a gentle stream of N₂.
- Step 2* Transfer the concentrated extract to a DCM rinsed Reacti-vial/5mL centrifuge tube ensuring that the vial is not filled to greater than half full.
- Step 3* Concentrate the extract under a gentle stream of N₂ while transferring Hexane to the sample vial for rinsing.
- Step 4* Rinse the vial at least three times with ~0.5ml of Hexane each time.
- Step 5* Concentrate the extract almost to dryness.
- Step 6* Samples are ready for instrument analysis. The method spike, consisting of all the spiking solutions added to the blank spike, that is prepared with each batch of samples is retrieved and delivered to the instrument lab with the worksheet and tracking sheets prepared.

NOTE: Adding the rinses to the extract, at a point when the total volume in the vial is less than half full, ensures that the sides of the vial are rinsed and that the final extract will be in the bottom of the vial.

7.B.1 Automated Sample Clean-up using POWERPREP™ (Optional)

Expiry date of elution solvents is assigned according to CAM WI-00010 unless otherwise stated in this SOP.

- 7.B.1.1** The elution solvents are placed at the right of the units and are installed as follows:
Position 1, hexane, Position 2, 2%DCM in hexane, Position 3, 50% DCM in hexane, Position 4, 50% EtAC in toluene and Position 5, toluene.
- 7.B.1.2.** 2%DCM in hexane and 50% DCM in hexane should be made daily or every other day at the most. The 50% EtAC in toluene is prepared, at a minimum every month depending on consumption.
- 7.B.1.3.** Assuming that the lines have been flushed already, connect the columns and place the sample into position according to the diagram at the front of the POWERPREP™.

Note that the silica columns can only be installed only way with the red arrow pointing upwards.

NOTE: IF THE BACK PRESURE BUILDS TO 30psi, THE UNIT WILL STOP. SHUT OF THE POWERPREP AND TURN ON AGAIN, THEN FOLLOW THE PROCEDURE IN THE MANUAL.

DF CLEANUP PROGRAM FOR POWERPREP™

Example of POWERPREP setting when “Jumbo” silica column is used

No	Flow ml/min	Volume (mL)	Description
1	10	80	Wet Si column with hexane
2	12	12.5	Flush hexane through by-pass
3	10	24	Wet Alumina Col. With hexane
4	10	24	Wet carbon Col. With hexane
5	10	240	Condition Si Column with hexane
6	12	14	Change to Toluene through by-pass
7	10	47	Pre-elute carbon with Toluene
8	12	14	Change to Et/Ac Through by pass
9	10	12	Pre-elute carbon with EtAc/Toluene
10	12	14	Change to 50% DCM/Hex Through by pass
11	10	24	Pre-elute carbon with 50% DCM/Hex
12	12	14	Change to Hex Through by pass
13	10	36	Pre-elute carbon with Hexane
14	5.0	18	Add sample Extract in Hexane
15	10	240	Elute Si Column with hexane
16	12	12	Change to 2% DCM/Hex Through by pass
17	10	72	Elute Al and Carbon column with 2% DCM/Hex
18	12	14	Change to 50% DCM/Hex Through by pass
19	10	143	Elute with 50% DCM/Hex
20	12	12	Change to Et/Ac Through by pass
21	10	4.0	Elute with EtAc/Toluene
22	10	14	Change to hexane through by-pass
23	10	12	Flush Carb col with hexane
24	12	14	Change to Toluene through by-pass
25	5.0	156	Collect PCDD/PCDF through reverse carbon Column

7.B.1.4 When the high capacity or “jumbo” silica column is employed the following steps are affected: Step 1, 70mL instead of 20mL, Step 5, 200mL, Step 14, depends on desired sample dilution and Step 15, 200mL. The same volumes here are used when both silica columns are employed as well.

When the clean up is done remove the spent columns and discard. Place the couples and connect the lines where the columns once were.

7.B.1.5 Remove the samples tube and replace with a vessel containing clean hexane.

7.B.1.6 Run the clean power prep program in order to clean out the back lines. See the following:

INTERNAL LINE WASH PROGRAM FOR POWERPREP™

Example of Wash program for POWERPREP unit, this can vary dependent on how much cleanup is required

No	Flow ml/min	Volume (mL)	Description
1	15	40	Wash lines with 50%DCM/hexane
2	15	40	Wash carbon column lines with 50%DCM/hexane
3	15	40	Wash sample lines with 50%DCM/hexane
4	15	40	Wash PCB lines with 50%DCM/hexane
5	15	40	Wash lines with hexane
6	15	40	Wash carbon column lines with hexane
7	15	40	Wash lines with hexane
8	15	40	Wash PCB lines with hexane

Note that the final steps of the line wash are in hexane as DCM can attack the internal valve structures.

8.0 QUALITY CONTROL:

8.1 Internal Standards: Refer to the appropriate analytical SOP for details.

8.2 Method Blanks: For water samples, process a method blank of RODI water with each batch of 20 samples. Process a method blank of sodium sulfate for each batch of 20 solid samples.

8.3 Blank Matrix Spikes: An aliquot, equal to or as close as possible to the method blank aliquot size is spiked with the matrix spiking solution. Refer to the analytical SOP for details on the spiking solution to use. Extract the blank spike with the samples in the batch. One blank matrix spike is analyzed for every 20 samples unless regulations or contracts require or allow a different frequency.

8.4 Matrix Duplicate: Process a matrix duplicate from a random sample as required by the specific method or client's request. If possible, use a sample in which positives are expected i.e. site history indicates positives.

8.5 Matrix Spike/Matrix Spike Duplicates: Spike a random aliquot, equal to or as close as possible to the sample aliquot size, with the matrix spiking solution. Refer to the analytical SOP for details on the spiking solution to use. Extract the sample matrix spike with the batch of samples. A sample

matrix spike is analyzed at a frequency of 1 in 20 samples unless regulations or contracts require otherwise.

8.6 Additional Quality Control: Blind duplicates, audit and performance evaluation samples may have specific instructions to be followed. They are to be treated the same as any other sample.

9.0 DATA CALCULATIONS:

9.1 Data Entry:

All lot numbers of adsorbents, solvents, spiking solutions etc. are recorded on the Job Work/tracking sheet, generated using MaxxLIMS when work on a batch of samples commences. Data is entered in MaxxLIMS for each test or group of tests logged for a set of samples ie.,Lipid determination, moisture determination etc. This information is retrievable for reporting by the Project Manager to the client and is linked by Job number, worksheet number, sample number, client id, and analytical test results.

10.0 DOCUMENTATION:

10.1 A tracking sheet is completed (see BRL FCD-00015 and BRL FCD-00023 forms) for each batch of samples. It must contain complete information i.e.; Job number, extraction date, clean up date, sample number, client name, client sample id, sample weight/volume, number of splits, amount and type of spike added, solvent lots, reagent lots, preparation dates and any additional information pertaining to the extraction or cleanup. A photocopy is given to the instrument technician with the completed samples and the original is kept in a binder in the HRMS Prep Lab.

10.2 Analyst Logbook: Maintain a logbook which contains, at a minimum, the following information.

- deviations from normal procedures required for problematic samples, (these deviations must be discussed and signed off by the appropriate Supervisor or Operations Manager. Deviations can alternatively be recorded on the sample tracking/worksheet or other approved media.

10.2.1 Sample Deviation Records: Deviations must be recorded in the Job report remarks section in Maxxlms and appear on the Certificate of Analysis. Examples are as follows:

- analyzed past hold time
- sample is not homogeneous

10.2.2 Method Deviation Records: If instances arise in which the SOP may not be applicable to the nature of the sample and may require modifications to the normal methodology.

- prior to use, discuss proposed deviation with the Supervisor or Operations Manager
- if deviation is deemed appropriate, record the deviation in the QSI Policy Deviation Form and submit to the Supervisor or Operations Manager for approval. Deviation must be approved prior to its implementation.
- record the deviations for each sample in the Sample report remarks area in Maxxlms.

10.3 Standard and Reagent Preparation Tracking: Record all preparations of standards and reagents in the Standard Preparation and the Reagent Preparation Logbooks. Refer to CAM WI-00010 for the required information.

10.4 Certificates of Analysis for Standards and Reagents: Certificate of analyses are kept for all inorganic salts and solutions utilized in this SOP. These records will contain at a minimum the following information.

- Source of the inorganic salt or solution
- supplier information and Lot Number
- date received

11.0 WASTE MANAGEMENT:

All efforts are taken to prevent or reduce to a minimum the effect of waste disposal on the environment. All solvents are collected for shipment to a recycling facility. All recyclable plastic, glass and paper products are shipped to an appropriate recycling facility. The disposal of waste materials and samples are to be carried out in accordance with protocols outlined in the SOP for the Preparation, Storage and Disposal of Reagents and Standards and the SOP for the Receipt, Handling and Disposal of Hazardous Wastes. All waste disposal will comply with the Ontario Ministry of the Environment and Energy's Sewer Guidelines and Regulation 558.

11.1 Specific Disposal Issues: Contaminated sample extracts are collected and sent for disposal to an approved hazardous waste subcontractor. Excess contaminated samples are either returned to the client or submitted for disposal as noted.

Ultra Trace Air Toxics SOP BRL SOP-00406 /
12

Ultra Trace Air Toxics

Dioxins and Furans by HRGC HRMS in Water and Soil (EPA 8290)



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Document Identity	
Document Categorization	
Ultra Trace Air Toxics Departments Hidden	Environmental HRMS

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Release and Audit Schedule	
Release Schedule	When Approved <input type="checkbox"/> Allow Administrator to Release Document Early
Expiration Schedule	When Superseded or Obsolete
Audit Schedule	12 Month(s)
Special Handling on Release	
<input checked="" type="checkbox"/> Update Completed Trainee Records	

Insert Text	
BRL SOP-00406 rev12	

Associated Documents
Document Control Documents
<ul style="list-style-type: none"> Burlington FCD BRL FCD-00002 : Data Review Checklist Burlington FCD BRL FCD-00003 : Organic Control Chart Out of Control Checklist Burlington FCD BRL FCD-00023 : Hi Res/ Low Res Sample Tracking Sheet Burlington SOP BRL SOP-00405 : Dioxin and Furan Extracts Cleanup Burlington SOP BRL SOP-00407 : Dioxin and Furan Extraction in Liquid and Solid Samples Burlington WI BRL WI-00011 : Review and Validation of Analytical Data Campobello MOC CAM MOC-00174 : Confirmation of 2,3,7,8-TCDF Corporate WI Publish to All COR WI-00010 : Corporate Procedure for Nonconformances Corporate WI Publish to All COR WI-00011 : Corporate Procedure for Corrective and Preventative Actions Corporate WI Publish to All COR WI-00012 : Definitions Corporate WI Publish to All COR WI-00018 : Determination of Estimation of Analytical Uncertainty of Measurement Corporate WI Publish to All COR WI-00040 : Corporate Procedure for Policy Deviation Forms Corporate WI Publish to All COR WI-00044 : Manual Integration of Chromatographic Peaks Corporate WI Publish to All COR WI-00049 : Continuing Calibration Verification (CCV) Acceptance Criteria Corporate WI Publish to All COR WI-00050 : Environmental Chemistry Method Validation

 Corporate WI Publish to All COR WI-00055 : Corporate Procedure for Control Charting
 Campobello WI CAM WI-00095 : Environmental Method Validation (NELAC + DOD requirements)
 Campobello WI CAM WI-00121 : Maxxam Lab QM Supplement to Meet Requirements of DoD QSM Version 4.2

Reason for Change

<p>Date of Change July 4, 2007</p> <p>Section Changed 2.0, 3.6, 3.7, 8.10, 9.3</p> <p>Change Made 2.0-clarified matrices 3.6-removed list of definitions 3.7-added reference to MU procedure 8.10-clarified control chart practice 9.3- clarified data validation practice</p>	Version 2
<p>Date of Change August 7, 2007</p> <p>Section Changed Re-formatting entire document due to right side truncation when this SOP was printed</p> <p>Change Made Tables 1-3 and Figure 1 were moved as attached files. Added WHO 2005 TEFFor Dioxins and Dioxin-like Compounds.</p>	Version 3
<p>Date of Change August 31, 2007</p> <p>Section Changed 3.1, 3.2.2, 4.1, 5.0, 6.2.1, 6.2.2, 6.2.3, 6.4, 6.4.1, 7.3, 7.7.4, 8.1, 8.2, 8.3, 8.7, 9.1, 9.4, 10.5, 10.6.2</p> <p>Change Made Throughout the document (i.e., 3.1, 3.2.2, 6.2.3, 6.4, 6.4.1, 7.3, 7.7.4, 8.1, 8.2, 8.3, 8.7, 9.1, 10.6.2) corrected units from pg/mL tp pg/uL. Section 4.0 added reference to PSEP 1997a,b, Ecology 2003. Added alternative method re: sample storage and holding time for soil/sludge and pulp samples Section 5.0, removed first sentence since it was only refering to water samples. Added Temperature storage column for listed matrices. Changed "Biological" to "Tissue" in matrix column. Section 6.2.2, added section for ODWS on determination of Drinking Water MDL, and referenced OMOE respective document. The SOP has been removed from embedded to detached document due to difficulties in document formatting . Section 9.1, for the non-detected 2,3,7,8-substituted congeners added calculation methods for reporting TEQ Section 9.4 and 10.5, updated sections to reflect current practice Section 12.0, added Table 4 as 2005 WHO List Minor corrections of typographical errors throughout the document</p>	Version 4
<p>Date of Change August 21, 2008</p> <p>Section Changed 8.2, Table 4</p> <p>Change Made Both sections corrected for typographical errors</p>	Version 5
<p>Date of Change February 26, 2009</p> <p>Section Changed Header, 4.0</p> <p>Change Made Header - reflect lab's current name 4.0 - changed to reflect current revision of EPA SW-846 8290A, Revision 1, February 2007.</p>	Version 6
<p>Date of Change July 13, 2009</p> <p>Section Changed 7.3, Associated Documents</p> <p>Change Made 7.3, Step 5, changed to: confirmation runs for 2,3,7,8-T4CDF are performed only if the primary result is greater than the RDL. Added reference to CAM MOC-00174 in Associated Documents 9.1 corrected typographical error "quantification"</p>	Version 7
<p>Date of Change June 1, 2010</p> <p>Section Changed 1.0, 3.2., 3.3, 3.4, 4.3, 8.5, 10.2, 10.6.1,</p> <p>Change Made 1.0 updated to lab's current location 3.2+3.3 redefined correlation between MDL and detection limit, as well as Maxxam's RDL and LOQ, added performance of quarterly LOD and LOQ 3.4 updated to reflect current PT program 4.3 replaced with reference to QSI Associated Documents 8.5 added DoD requirements for method blank criteria & corrective actions re: DoD related projects 10.2 updated to reflect current practice re: use of COR WI-00040, Corporate Procedure for Policy Deviation Forms 10.6.1. updated storage of records offsite to reflect current practice</p>	Version 8
<p>Date of Change September 6, 2010</p> <p>Section Changed 4.3, 6.1, 6.1.1, 7.3.4.1, 7.3.4.2, 8.3, 10.0</p> <p>Change Made 4.3 Deleted test-codes that were not applicable 6.1 Removed solvents that were not applicable 6.1.1 Added nonane and removed nitrogen from compressed gases list 7.3.4.1 Added optional solvents 7.3.4.2 Added OPRs and matrix spikes to analytical sequence table 8.3 Added action required if instrument malfunctions prior to injection of post CCV 10.0 Revised to reflect current practice</p>	Version 9
<p>Date of Change December 7, 2010</p> <p>Section Changed 3.2, 6.2.1</p> <p>Change Made 3.2; updated reference to CAM WI-00095 6.2.1; corrected typographical error in units from mL to uL.</p>	Version 10

Date of Change January 4, 2012	Version 11
Section Changed 6.4, 6.4.1, 7.4, 8.1, 8.2, 8.10,	
Change Made Section 6.4 - updated instrumentation Section 6.4.1 - updated capillary columns Section 7.4 - revised RT criteria to -1 to +3 Section 8.1 - removed reference to CARB428 Section 8.2 - RSD criteria for labeled standards changed to <20% Section 8.10 - included an additional analyte for control charting (23478-PeCDF)	
Date of Change November 13, 2012	Version 12
Section Changed 3.4, 4.2, 7.3.1, 7.3.2, 7.3.4.1, 7.3.4.2, 7.4, 8.1, 8.2, 8.5, 8.10	
Change Made 3.4 - updated to reflect CAM Wi-00095 for method validation and maintenance of method validation records 4.2 - Added modification to confirmation analysis 7.3.1 and 7.3.2 - Updated GC conditions 7.3.4.1 and 7.3.4.2 - Made solvents and MSPIKE optional 7.4 updated to reflect current practice, i.e: the signal to noise (S/N) for all monitored ions must be ≥ 2.5 and for PCDF identification, no peak having a $S/N \geq 2.5$ may be found in the corresponding PCDF channels 8.1 and 8.2 - Added = sign to < or > and changed column terminology 8.5 - Added additional method blank criteria for internal standard recovery exceedances 8.10 updated to reflect reference to COR WI-00055 for control charting procedure	
Optional Field A Associated documents have been reviewed, and where required the CPro links were updated to reflect most current procedures in use by the HRMS laboratory	

Approval Status Table			
Approver	Source	Role for Approvers	Parallel-Everybody Segment
Approver	Action	Date	Comment
Ewa Konieczna	Approve	November 13, 2012 12:45 PM GMT-5	
Owen Cosby	Approve	November 13, 2012 5:43 PM GMT-5	

DIOXINS AND FURANS BY HRGC HRMS IN WATER AND SOIL (based on EPA 8290A)

1.0 LOCATION:

This procedure is performed in the HRMS Prep Lab and the HRMS Instrument Laboratory.

2.0 PURPOSE:

This method is used to measure the concentration of polychlorinated dibenzo-p-dioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's), in water and soil samples.

NOTE: For the purpose of this procedure's clarity on matrices, use the following reference

Water Matrix - ground water, drinking waters, surface waters, wastewaters, etc.

Soil Matrix - solids, chemical materials, sludges, sediments and other solid wastes

Biota Matrix - biota (sample of a plant and/or animal)

2.1 Principle of the Method: PCDD's/DF's are extracted from solid samples with toluene and aqueous samples with methylene chloride. After extraction, the samples are cleaned up by passing through a series of columns that remove, by reaction and/or selective adsorption, the bulk of the organic matrix co-extracted with the PCDD's and PCDF's. The resulting fraction is concentrated to a known volume for analysis. Qualitative/quantitative analysis for PCDD's and PCDF's is performed using separation by Hi Resolution Capillary Gas Chromatography (HRGC) and measured by Hi Resolution Mass Spectrometry (HRMS). PCDD's/DF's are identified by comparing GC retention times and the ion abundance ratios of the m/z's with the corresponding values obtained for authentic standards.

The analyte concentration is determined using GC/MS and an isotope dilution technique. Quantitation is based on the use of internal standards and relative response factors (RRFs). Total PCDD's and PCDF's are reported as the sum of the individual isomers, corrected for internal standard recoveries. The toxic equivalence (TEQs) for the sample is the sum of the individual 2,3,7,8-Isomers found multiplied by its specific Toxic Equivalence Factor (TEF).

2.2 Nature of Samples: samples can be from many different sources including incinerator ashes, soils, sediments and effluents. The laboratory should be made aware of any past history involving the samples or the presence of potentially interfering substances at elevated levels (e.g. PCB). This can allow the preparation technician to take a smaller aliquot of sample so that internal standards are not diluted out during analysis.

2.3 Safety:

2.3.1 General Considerations: the toxicity or carcinogenicity of each compound or reagent used in this method has not been established precisely. Each compound should be treated as a potential health hazard and exposure should be reduced to the lowest possible level. On the basis of the available toxicological and physical properties of the PCDD's and PCDF's, these compounds should only be handled by highly trained personnel thoroughly familiar with handling and cautionary procedures, and who understand the associated risks. All work related to the analysis of PCDD's and PCDF's should be carried out within a specially designed laboratory. As a general guideline, PCDD's and PCDF's and samples suspected to contain these compounds should be handled using essentially the same techniques employed in handling radioactive or infectious materials.

2.3.2 Specific Warnings: the 2,3,7,8-tetrachlorodibenzo-p-dioxin isomer is acnegenic, carcinogenic, and teratogenic (laboratory animal studies). It is soluble in water to ~200 ppt and in organic solvents to 0.14%.

3.0 SCOPE:

This is a HRGC/HRMS method for the determination of PCDD's and PCDF's at low ppt (parts per trillion) to ppq (parts per quadrillion) levels in liquid and solid samples.

3.0.1 Chemical Abstracts No.

Analyte	Symbol	CAS No.
2,3,7,8-Tetrachlorodibenzo-p-dioxin	TCDD	1746-01-6
1,2,3,7,8-Pentachlorodibenzo-p-dioxin	PeCDD	40321-76-4
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	HxCDD	39227-28-6
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	HxCDD	57653-85-7
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	HxCDD	19408-74-3
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	HpCDD	35822-46-9
1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin	OCDD	3268-87-9
2,3,7,8-Tetrachlorodibenzofuran	TCDF	51207-31-9
1,2,3,7,8-Pentachlorodibenzofuran	PeCDF	57117-41-6
2,3,4,7,8-Pentachlorodibenzofuran	PeCDF	57117-31-4
1,2,3,4,7,8-Hexachlorodibenzofuran	HxCDF	70648-26-9
1,2,3,6,7,8-Hexachlorodibenzofuran	HxCDF	57117-44-9
1,2,3,7,8,9-Hexachlorodibenzofuran	HxCDF	72918-21-9
2,3,4,6,7,8-Hexachlorodibenzofuran	HxCDF	60851-34-5
1,2,3,4,6,7,8-Heptachlorodibenzofuran	HpCDF	67562-39-4
1,2,3,4,7,8,9-Heptachlorodibenzofuran	HpCDF	55673-89-7
1,2,3,4,6,7,8,9-Octachlorodibenzofuran	OCDF	39001-02-0

Note: Total TEQ is calculated as per Section 9.1.1.

Total Tetrachlorodibenzo-p-dioxin	TCDD	41903-57-5
Total Pentachlorodibenzo-p-dioxin	PeCDD	36088-22-9
Total Hexachlorodibenzo-p-dioxin	HxCDD	34465-46-8
Total Heptachlorodibenzo-p-dioxin	HpCDD	37871-00-4
Total Tetrachlorodibenzofuran	TCDF	55722-27-5
Total Pentachlorodibenzofuran	PeCDF	30402-15-4
Total Hexachlorodibenzofuran	HxCDF	55684-94-1
Total Heptachlorodibenzofuran	HpCDF	38998-75-3

3.1 Linear Range: the method is calibrated over the following linear ranges of calibration solutions.

Cl4 to Cl7: 1.0-500 pg/uL and Cl8: 5 to 1000 pg/uL

3.2 Detection Limit: Detection Limit is also referred to as Method Detection Limits (MDL): an MDL is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. MDLs are determined by the procedure outlined in CAM WI-00095, Environmental Chemistry Method Development Revision and Validation

Target MDLs are verified annually by spiking water/soil replicates at the CS2-CS3 levels. These samples are carried through the full extraction and cleanup procedure. MDLs are determined by multiplying the standard deviation of the results by the Student's t-Value for the number of replicates used. If Target Limits are not achieved, the exercise is repeated spiking at a lower level. An MDL study is used to determine if the target limits

outlined in test methods have been achieved. These are maintained on file in the QSI MDL Module as well as at the instrument. To meet DOD requirements, these limits are then used to determine spiking levels for the Limit of Detection (LOD) verification. Each matrix is spiked two to three times the target limit (derived above) for a single analyte test or one to four times the detection limit for a multi-analyte test.

NOTE: As per CAM WI-00121, section D.1.2.1, Maxxam HRMS Lab schedules quarterly LOD verifications for each respective matrix to meet DOD requirements.

Estimated Detection Limit (EDL): EDLs are sample specific and are calculated on a case specific basis for all levels of chlorination, tetra through octa, as well as for each 2,3,7,8-substituted isomers. If a signal produced is not at least 2.5 times the average background level at the expected retention time for specific isomers, the area response for the noise is calculated as follows:

$$2.5 \times \text{peak intensity of background noise} \times \frac{\text{area of internal standard}}{\text{height of internal standard}}$$

This is done for either the quantitation ion or the confirmation ion. Using theoretical ratios for the specific degree of chlorination an area for the second ion is generated. These areas are then totaled and applied to the same calculation scheme as for "positive" hits. (see Section 9). EMPCs (Estimated Maximum Possible Concentrations) are calculated whenever peaks are detected that meet all criteria except for ratios. The area in this case is recalculated (factored up or down) to meet the classical ratio and the result is flagged as an EMPC (NDR, not detected because of ratios, for Canadian Method).

NOTE: Maxxam HRMS lab schedules quarterly LOD verifications. They are analyzed with the next batch of samples for respective matrix.

3.3 Reporting Detection Limit (RDL): Reporting Detection Limit is also referred to as Limit of Quantitation (LOQ), equivalent to the Low Level Standard.

NOTE: As per CAM WI-00121, section D.1.2.1, Maxxam HRMS lab schedules quarterly LOQ verifications for each respective matrix to meet DOD requirements.

3.4 Other Method Validation: further method performance is evaluated/monitored by the participation in the Non Potable Water and Solid Waste Performance Testing Programs from Resource Technology Corporation (RTC). Results of these ongoing studies are maintained in the CPro database for method validation and the respective lab. Refer to CAM WI-00095 for Method Validation procedure.

3.5 Interferences: interferences co-extracted from the sample material will vary considerably with the matrix and the diversity of the site being sampled. PCDD's and PCDF's are often associated with other chlorinated organics that may potentially interfere with the analysis. These include polychlorinated biphenyls, polychlorinated methoxy biphenyls, polychlorinated hydroxy diphenyl ethers, polychlorinated benzylphenyl ethers, polychlorinated diphenyl ethers, polychlorinated naphthalenes, polychlorinated xanthenes, polynuclear aromatics, and pesticides.

Often the compounds responsible for interferences may be present at concentration levels several orders of magnitude higher than any PCDD's and PCDF's that may be present. Cleanup procedures can be used to reduce or eliminate these interferences to the maximum extent practicable in order to ensure reliable quantitation of PCDD's and PCDF's at trace levels. Despite rigorous cleanup procedures, the possibility of matrix interference will still exist. If detection limits are seriously elevated by the excessive background, the sample extract will have to be re-processed using alternative cleanup techniques.

3.6 Definitions: Refer to COR WI-00012 Corporate Definitions

3.7 Measurement Uncertainty: defines an interval about a sample result that would be expected to contain a large fraction of the distribution of values that would occur through repeated analysis of similar samples using the same methodology. Uncertainty is expressed as the standard deviation of the mean of a set of data (Blank Spikes/Laboratory Control Samples). Laboratory blunders or human errors are not incorporated into the calculations. Refer to COR WI-00018, Determination of Estimation of Analytical Uncertainty of Measurement.

The reported Expanded Uncertainty of an analyte is specific to the laboratory method used and incorporates laboratory procedures; physical measurements, (volume, temperature and mass), environmental variation, reagent and standard purity, sample preparation procedures (if applicable), personnel and instrumental parameters.

The most significant factors affecting the uncertainty of a measurement arise from the field-sampling program. They involve field site sample homogeneity; sampling technique; cleanliness of sampling equipment/containers; cross contamination of samples; environmental conditions; subsampling techniques; preservation techniques; sample storage; time to submit to laboratory. These variations are not incorporated into Maxxam's uncertainty calculations.

Maxxam uses a coverage factor "k" (multiplier of the combined standard uncertainty) to obtain an Expanded Uncertainty. Maxxam reports to a confidence level of 95% (k=2).

Maxxam does not correct sample data for bias or recoveries (except surrogate recoveries in Isotope Dilution methods). The final decision on the acceptability and application of the reported data is the responsibility of the client.

4.0 REFERENCES:

U. S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, SW-846 8290A, Revision 1, February 2007

4.1 Other Information Sources:

- U. S. Environmental Protection Agency, Tetra through Octa-chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, Revision B, October 1994.
- Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples, Section 3A [required for cleaning glass components of the sampling train].
- For further information contact Gary McAlister or Roger Shigehara, Emission Measurement Branch (MD-19), Technical Support Division, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, USA 27711, telephone (919)-541-1062.

4.2 Modifications and/or Improvements from Referenced Methods: Maxxam meets or exceeds all requirements of the referenced methods. For the two column confirmation analysis, Maxxam monitors only one descriptor (for tetras), not three (for tetras, pentas, hexas) as per Section 11.9.8.2 of Method 8290A.

4.3 Analytical Test Codes:

Waters:

Analysis:

DF8290-W Method 8290 2378-substituted Isomers and PCDD/DF congeners
(Tetra to Octa Homologue Groups) in water samples

DF8290S-LC Method 8290 2378-substituted Isomers and PCDD/DF congeners
(Tetra to Octa Homologue Groups) in TCLP leachate samples

Solids:	Analysis:
DF8290-S	Method 8290 2378-substituted Isomers and PCDD/DF congeners (Tetra to Octa Homologue Groups) in solid samples
DF8290-SB	Method 8290 2,3,7,8-substituted isomers and PCDD/DF congeners (Tetra to Octa Homologue Groups) in swab samples

Other test codes may be created as necessary

5.0 SAMPLE HANDLING AND PRESERVATION:

During transit, the samples should be packed in rigid-body coolers in an upright position and kept chilled at all times. Due to the fragile nature of the containers, the samples should be well wrapped with protective packaging during shipment from the field site to the laboratory. Samples that exceed the hold time will be flagged on the Certificate of Analysis. Different hold times may be imposed by other regulating agencies or as determined by client specific projects. Project specific and regulatory requirements for preservation method and reporting criteria (required detection limit, dry or wet weight basis) must be examined and made clear prior to sample analysis. All containers should have Teflon liners in the caps.

Matrix	Container	Min. Vol.	Time to Extract	Time to Analysis	Temperature Storage
Waters	4 x 1L amber glass	800 ml	30 days	45 days	4°C ±2°C
Soils/Sludge	100 ml amber glass	2 x 5 gram	30 days	45 days	4°C ±2°C
Pulp	100 ml amber glass	2 x 15 gram	30 days	45 days	4°C ±2°C
Tissue	100 ml amber glass	2 x 20 gram	30 days	45 days	< -10°C

6.0 APPARATUS AND MATERIALS:

6.1 Reagent Preparation: all reagent preparation information, Lot Nos., supplier, are documented in the Reagent Preparation Logbook kept in the sample preparation laboratory. Equivalent quality reagents and standards may be purchased from other suppliers as appropriate.

6.1.1 Solvents: nonane is purchased from Aldrich, Distilled in Glass quality or better and transferred to a 1L amber glass dispensette. This is stored at ambient temperature for up to 2 years.

- RODI Water: reverse osmosis deionized water produced in house
- Compressed Gases: UHP Grade helium. Air is provided by an on-site compressor.

6.2 Standard Preparations: all standards preparations, Lot Nos., supplier information, pertinent dates are documented by the analyst in the Standard Preparation Log Book located in the instrumentation laboratory. Stock standards are stored as per manufacturer's directions. Once prepared, the standards are transferred to amber glass vials with teflon-lined caps and refrigerated at 2-6 °C. They are equilibrated to room temperature and are then sonicated prior to use. Intermediate and Working level standards are stored for up to 2 years. Alternatively, commercially prepared "ready to inject" Calibration Standard mixes may be used.

6.2.1 Calibration Standards: refer to Appendix: Table 3 for the volumes of the stock standards to use for preparing Calibration Standards. Current Suppliers and Lot Numbers are in the Standards Prep Logbook in the Instrument Lab.

Intermediate Calibration Standards: add the volumes of stocks to 660 uL of nonane in a 2 ml vial

Component	Stock Conc. (ng/uL)	Final Conc. (ng/uL)	Vol. Added (uL)
2,3,7,8-T4CDD	50	1	20
2,3,7,8-T4CDF	50	1	20
P5-H7CDD/CDF	25	2.5	100
1,2,3,4,6,7,8,9-O8CDD	50	5	100
1,2,3,4,6,7,8,9-O8CDF	50	5	100

Initial Calibration Verification Standard (ICV): purchased as an injection ready standard from a second source supplier. The Standards Prep Logbook lists current information on the supplier and Lot No. This standard contains the following analytes at the indicated concentrations.

Native Analytes:	Conc. (pg/ul)	Internal Standards:	Conc. (pg/ul)
2,3,7,8-T4CDD	10	2,3,7,8-T4CDD ¹³ C ₁₂	50
2,3,7,8-T4CDF	10	2,3,7,8-T4CDF ¹³ C ₁₂	50
1,2,3,7,8-P5CDD	25	1,2,3,7,8-P5CDD ¹³ C ₁₂	50
1,2,3,7,8-P5CDF	25	1,2,3,7,8-P5CDF ¹³ C ₁₂	50
2,3,4,7,8-P5CDF	25	1,2,3,6,7,8-H6CDD ¹³ C ₁₂	125
1,2,3,4,7,8-H6CDD	25	1,2,3,4,7,8-H6CDF ¹³ C ₁₂	125
1,2,3,6,7,8-H6CDD	25	1,2,3,4,6,7,8-H7CDD ¹³ C ₁₂	125
1,2,3,7,8,9-H6CDD	25	1,2,3,4,6,7,8-H7CDF ¹³ C ₁₂	125
1,2,3,4,7,8-H6CDF	25	O8CDD ¹³ C ₁₂	250
1,2,3,6,7,8-H6CDF	25		
2,3,4,6,7,8-H6CDF	25	Recovery Standards:	Conc. (pg/ul)
1,2,3,7,8,9-H6CDF	25	1,2,3,4-T4CDD ¹³ C ₁₂	50
1,2,3,4,6,7,8-H7CDD	25	1,2,3,7,8,9-H6CDD ¹³ C ₁₂	125
1,2,3,4,6,7,8-H7CDF	25		
1,2,3,4,7,8,9-H7CDF	25		
O8CDD	50		
O8CDF	50		

6.2.2 Method Spiking Solution (Internal Standard): a 10 ml nonane working level internal standard solution, is prepared once per year or as required containing isotopically labeled PCDD's and PCDF's stock solutions. The volume of stock standards used is recorded in the Standard Preparation Log Book, located in the Instrument laboratory. Manufacturer Certified Stock standards are purchased from Cambridge Isotope Laboratories, Woburn, Massachusetts USA or Wellington Labs (Chemsyn Science Labs) in Guelph, Ontario, Canada.

Component	Stock Conc. (ng/uL)	Final Conc. (pg/uL)	Vol. Added (uL)
2,3,7,8-T4CDD ¹³ C ₁₂	50	100	20
1,2,3,7,8-P5CDD ¹³ C ₁₂	50	100	20
1,2,3,6,7,8-H6CDD ¹³ C ₁₂	50	250	50
1,2,3,4,6,7,8-H7CDD ¹³ C ₁₂	50	250	50
1,2,3,4,6,7,8,9-O8CDD ¹³ C ₁₂	50	500	100
2,3,7,8-T4CDF ¹³ C ₁₂	50	100	20
1,2,3,7,8-P5CDF ¹³ C ₁₂	50	100	20
1,2,3,4,7,8-H6CDF ¹³ C ₁₂	50	250	50
1,2,3,4,6,7,8-H7CDF ¹³ C ₁₂	50	250	50

6.2.3 Recovery Standard (Injection Std.): prepare a 10 ml final volume, nonane working level solution, once per year or as needed. Concentrations may vary with suppliers and with the same supplier. Volumes of stock standard used for the current standards are listed in the Standard Prep Book. The following are used for 50 ng/uL stocks.

Component	Stock Conc. (ng/uL)	Final Conc. (pg/uL)	Vol. Added (uL)
1,2,3,4-T4CDD ¹³ C ₁₂	50	50	10
1,2,3,7,8,9-H6CDD ¹³ C ₁₂	50	50	10

6.3 Apparatus: autosampler vials; assorted gas-tight micro syringes; assorted screw-cap amber vials with teflon-lined caps

6.3.1 Glassware Quality Control: all extraction glassware is engraved with a specific serial number. Glassware used for processing samples is tracked using this number. All glassware is subjected to a proven, rigorous cleaning procedure after which it is acceptable for reuse. The analysis of Method Blanks confirms the acceptability of this procedure.

- Soxhlet apparatus that were exposed to samples resulting in highly-coloured extracts are soaked in a soap solution (Extran) overnight
- after soaking they are rinsed thoroughly with successive rinses of RODI water and acetone
- all Soxhlets are then cycled with toluene overnight
- Rotovap glassware is rinsed thoroughly with appropriate solvents after each use

6.4 Instrumentation: High Resolution GCs coupled to High Resolution Mass Spectrometers

HR GC: **Associated HR MS:**

HP6890 Plus	(S/N US00021197)	Micromass Autospec Ultima	(S/N M278)
HP6890	(S/N US000034029)	Micromass Autospec Ultima	(S/N M384)
HP6890	(S/N US00029754)	Micromass Autospec Ultima	(S/N M230)
HP6890D	(S/N US00030341)	Micromass Autospec Ultima	(S/N M449)
HP6890N	(S/N US10131086)	Micromass Autospec Ultima	(S/N M536)
HP6890A Plus	(S/N US00038736)	Micromass Autospec Ultima	(S/N M526)

6.4.1 Gas Chromatographs: gas chromatographs consist of the following components

- Oven: must maintain a temp. $\pm 1^{\circ}\text{C}$ and perform programmed increases in temp. at rates of $3^{\circ}\text{C}/\text{min}$
- Temperature Gauge: to monitor column oven, detector, & exhaust temperature $\pm 1^{\circ}\text{C}$
- Gas Flow Metering System: to measure sample, fuel, combustion gas, & carrier gas flows
- Capillary Columns: the primary column is a fused silica column, Varian CP-Sil 8 CB, 60 m x 0.25 mm inside diameter (ID), or equivalent, and the confirmation column is a fused silica column, Restek, Rtx-Dioxin2, 60 m x 0.25 mm ID, or J&W DB225, 30m x 0.25mmID, or equivalent.

6.4.2 Mass Spectrometers: capable of routine operation at 1:10000 resolution with $\pm 5\text{ppm}$ stability with a compatible data system capable of monitoring at least five groups of 25 ions

6.5 Miscellaneous Equipment: analytical balance capable of measuring within 0.1 mg

7.0 ANALYTICAL PROCEDURE:

7.1 Sample Extraction: refer to "BRL SOP-00407 for the Extraction of Liquid and Solid Samples for PCDD's and PCDF's."

7.2 Sample Clean Up and Fractionation: refer to "BRL SOP-00405 Clean Up of Sample Extracts for PCDD/DF Analysis."

7.3 Analysis: analyze the sample extract by HRGC/HRMS using the instrumental parameters in section 7.3.1 and 7.3.2.

Step 1 add 20 uL of Recovery Standard to the dry sample extract in the 1 mL Reacti-vial

Step 2 vortex for ~30 seconds and allow to equilibrate for at least 3 minutes

Step 3 transfer to an amber autosampler vial using a micropipettor

Step 4 seal with an aluminum teflon lined crimp cap

Step 5 inject 1 or 2 uL of the extract into the GC

Analyze the sample using a GC/MS with the instrument parameters given in Section 7.3.1 and 7.3.2. A 1-2 uL aliquot of the extract is injected into the GC. Sample extracts are first analyzed using the DB-5 type capillary column to determine the concentration of each isomer of PCDD's and PCDF's (tetra through octa). On a DB5 type column 2,3,7,8-T4CDF is not uniquely separated from 2,3,4,7-T4CDF and 1,2,3,9-T4CDF. Therefore, confirmatory runs for 2,3,7,8-T4CDF are performed only if the primary result is greater than the RDL. In either case the separation criteria in Figure 1 must be met and demonstrated.

7.3.1 Typical GC Operating Conditions (DB5 'type' 60 meter column): these are typical conditions and are optimized for each individual column to maximize performance.

- Injector: configured for capillary column, splitless, 290 °C
- Carrier Gas: helium at 1-2 ml/min
- Initial Temperature 150 °C for 2 minute
- 20 °C/minute to 200 °C
- 2.0 °C/min to 235 °C
- 8 °C/min to 310 °C
- hold at 310 °C for 7 minutes

7.3.2 Typical GC Operating Conditions (DB225/Rtx-Dioxin2 'type' column): these are typical conditions and are optimized for each individual column to maximize performance.

- Injector: configured for capillary column, splitless, 290 °C
- Carrier Gas: helium at 1-2 ml/min
- Initial Temperature 180 °C for 1 minute
- 45 °C/minute to 235 °C for 1 minute
- 3 °C/min to 250 °C for 10 minutes
- 50°C/min to 300 °C for 5 minutes

7.3.3 High Resolution Mass Spectrometer

- Resolution of 10,000 minimum
- Ionization Mode: Electron impact, 35-40 eV (optimize)
- Source Temperature: 290 °C (optimize)
- Monitoring mode: Selected ion recording - see Table 1 for a list of the ions to be monitored

7.3.4 Typical Run Sequence: at the beginning and the end of a run sequence, a hardcopy of the resolution check is printed out. The operator manually verifies that a minimum resolution of 1:10,000 has been achieved for each multi-group experiment (see the descriptor groups in see Table 1).

7.3.4.1 Initial Calibration: (process takes ~12 hours to perform)

- DB5 Window Performance Check
- Solvent
- Solvent (optional)
- CS1_8290
- CS2_8290
- CS3_8290
- CS4_8290
- CS5_8290
- Solvent (optional)
- NBS 1614
- Solvent (optional)
- CS3_8290 (second source check)
- Solvent (optional)

7.3.4.2 Typical Sample Analysis Sequence: (process takes ~12 hours to perform). At the beginning and the end of a run sequence a hardcopy of the resolution check is printed out. The operator manually verifies that a minimum resolution of 1:10,000 has been achieved for each multi group experiment, see the descriptor groups in Table 1. After this verification is complete the run can proceed as follows:

- DB5 Window Performance Check
- Solvent (optional)
- CS3_8290
- OPR
- OPR Dup (if available)
- Matrix Spike (if available)
- Matrix Spike Dup (if available)
- Solvent
- Solvent (optional)
- Method Blank
- Sample 1
- Sample 2
- Sample 3
- Sample 4
- Sample 5
- Sample 6
- Sample 7
- Sample 8
- Solvent (optional)
- CS3_8290 (post analysis calibration verification)
- Method Spike (optional, not used in any calculations, serves only as an aid to determine the source of potential problems for internal and matrix recoveries).

7.4 Identification Criteria: the following identification criteria shall be used for characterization of PCDD's and PCDF's.

- the integrated ion-abundance ratio shall be within ± 15 percent of the theoretical value. Table 2 gives acceptable ion abundance ratio ranges for identification of chlorine-containing compounds
- analyte retention time must be within -1 to $+3$ seconds for the corresponding labeled internal, surrogate or alternate standard.
- the monitored ions shown in Table 1 for a given analyte shall reach their maximum within 2 seconds of each other
- the identification of specific isomers that do not have corresponding labeled standards is done by comparing the relative retention time (RRT) of the analyte to the nearest internal standard retention time with reference (i.e. within 0.005 RRT units), to the comparable RRT's found in the continuing calibration
- the signal to noise (S/N) for all monitored ions must be ≥ 2.5
- confirmation of 2,3,7,8-T4CDF shall satisfy all of the above criteria
- for PCDF identification, no peak having a $S/N \geq 2.5$ may be found in the corresponding PCDPE channels

7.5 Quantification: the peak areas for the two ions monitored for each analyte are summed to yield the total response for each analyte. Each internal standard is used to quantify the indigenous PCDD's or PCDF's in its homologous series. For example, the 2,3,7,8-T4CDD¹³C₁₂ is used to calculate the concentrations of all other tetra chlorinated dioxin isomers.

Recoveries of the tetra- and penta- internal standards are calculated using the 1,2,3,4-T4CDD¹³C₁₂. Recoveries of the hexa through octa internal standards are calculated using the 1,2,3,7,8,9-H6CDD¹³C₁₂.

7.6 Maintenance: emergency maintenance is performed by either Maxxam staff or the manufacturer's Service Engineer. Preventative maintenance is performed annually through a service contract.

7.7 Troubleshooting and Common Problems: the analyst may perform the following checks if he/she is capable. Otherwise call a Manufacturer's Service Engineer. Check for the following conditions:

- system is fully powered on and is in the Operate mode
- vacuum is in acceptable range, i.e. 10⁻⁶ mbar or better, if not check for leaks
- filament is "ON" and the trap is regulating
- source and transfer line heaters are at the proper operating temperature, the source temperature affects the fragmentation of the sample
- GC in good working order, adequate supply of carrier gas with respect to oven heater and temperature regulation
- Injector system is clean with a properly installed column, liner and septum. Leaks and contamination may cause performance problems
- capillary column Helium head pressure is adjusted to proper setting, i.e. ~25 psi for a 60 m x 0.25 mm ID column
- autosampler syringe is in good condition, not leaking nor plugged
- data system is running and is controlling and communicating with the instrument

7.7.1 Loss of Beam: may be caused by any of the following

- a defective source, collector or alpha slit may be obstructing the beam
- the isolation valve may not be completely open, check the pneumatic valve
- check the compressed air tank line pressure
- broken or blocked PFK jet or capillary line, replace if necessary

7.7.2 Loss of Filament Current, Trap Current and Electron Energy: may be caused by any of the following

- remove the source, check for short circuits, dirty or defective parts. Clean or replace if needed
- check the filament alignment in the source when replacing it
- if the filament comes on and there is no trap current, this could indicate that a trap contact problem has occurred
- check the electrical contacts and the alignment of the source magnets

7.7.3 Loss of Magnet: may be caused by any of the following

- high voltage breaker switch tripped due to a power interruption or surge
- high voltage breaker switch tripped due to a loss of the cooling water supply. When cooling water supply is lost or is too warm the magnet unit and the diffusion pumps overheat. The heat sinks on the power supply board cause the power to shut down and may trip the breaker on the power distribution panel on the front of the instrument. These must all be reset before the magnet can be turned back on

7.7.4 Loss of High Voltage: may be caused by any of the following

- an electronic fault and may be brought on by a discharge of a dirty lens or ceramics or arcing on the flight tube
- these regions must be cleaned to restore voltages and to re-establish control of the beam electronics and SIOS interface will also have to be reset to restore communications and control of the beam control and source control PCBs.

8.0 QUALITY CONTROL:

8.1 Column Separation and Performance Check: inject 1 uL of the DB5 Window Performance Mix, which documents resolution between 2,3,7,8-T4CDD and other T4CDD isomers for DB5. Resolution is acceptable if the result of the following equation:

$$\frac{\text{Height of valley between 2,3,7,8-T4CDD and the closest eluting peak}}{\text{Height of 2,3,7,8-T4CDD peak}}$$

Result must be $\leq 25\%$ for DB-5 (2,3,7,8-T4CDD) or $\leq 25\%$ for DB-225 (2,3,7,8-T4CDF)

See Figure 1. Sample analysis is not started until the above performance criterion is achieved.

8.2 Initial Calibration: calibrate the GC/MS system using the set of five standards (Table 3). These working level standards are used for a period of up to 2 years. If available, an “injection ready” standard from a second source supplier and an NBS 1614 standard reference material is also run as part of the Initial Calibration. Instrument parameters are adjusted and standards are analyzed until the following QC criteria are achieved.

- relative standard deviation (RSD) of the mean response factor for each unlabeled analytes must be $\leq 20\%$
- RSD of the mean response factor for each of the labeled standards must be $\leq 20\%$
- S/N ratio for the GC signal present in every selected ion current profile shall be ≥ 10 for both labeled and unlabeled analytes
- the ion abundance ratios shall be within the control limits in Table 2
- absolute retention time of 13C12-1,2,3,4-TCDD shall exceed 25.0 minutes on a DB5 type column and 15.0 minutes on the DB225 type column.
- 2nd Source standard should be $\leq 50\%$ for both labeled / unlabeled analytes.

8.3 Continuing Calibration Verification: inject 1 uL of solution CS3 (see Table 3). At the beginning of each 12 hour sequence, calculate the relative response factors (RRFs) for each compound and compare each of them to the corresponding mean RRF obtained during the initial multi-point calibration. The following requirements must be met before sample analysis can begin.

- the measured %RSD of the RRF for the labeled analytes for the daily run must be $\leq 30\%$
- the measured %RSD of the RRF for the unlabeled analytes for the daily run must be $\leq 20\%$
- the ion abundance ratios must be within the limits given in Table 2

The CS3 standard is analyzed at the end of the run sequence. The %RSD of the RRFs are again compared to the initial calibration and must satisfy the above criteria to validate the analytical run.

NOTE: if the sample analysis sequence was unable to be completed due to instrument failure, immediately run a CS3 continuing calibration standard to validate the sample data. If this fails to meet criteria, all samples **must** be re-injected.

8.4 Internal Standards: are added to all samples and QC samples.

Recoveries must be 40-135% for the tetra through octa-chlorinated compounds

8.4.1 Corrective Actions: if the above criterion is not achieved

- the data will still be acceptable provided that the signal is equal to or greater than ten times the noise level
- this will be flagged in the Case Narrative section of the final report
- the sample may be re-extracted if nothing can be found to explain the low or high recoveries and no obvious interference is causing the problem.

8.5 Method Blanks: a method blank is run in every batch, and a minimum of one for every 20 samples. For any 2,3,7,8-substituted chlorinated dibenzo-p-dioxin or chlorinated dibenzofuran, the method blank must be less than the minimum levels (less than the CS1) as documented in EPA Method 8290.

NOTE : A low or high internal standard percent recovery for the method blank does not require discarding the analytical data as per Section 9.7 of EPA Method 8290A

<20 pg of T4CDD/DF

<50 pg of P5/H6/H7CDD/DF

<100 pg O8CDD/DF

NOTE: for DoD samples, the method blank will be considered to be contaminated if:

- The concentration of any target analyte in the blank exceeds 1/2 the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater);
- The concentration of any common laboratory contaminant in the blank exceeds the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater); or
- The blank result otherwise affects the samples results as per the test method requirements or the project-specific objectives

8.5.1 Corrective Actions: if the above criteria are not met then

- investigate possible source of contamination by checking at a minimum: Instrument Spike Standard Solutions, Recovery Standards, proofing of glassware, proofing of solvent and absorbents used in clean-up
- all of the samples must be re-prepared and reanalyzed
- if sufficient sample is not available then any positive sample data must be flagged as possibly contaminated to the level found in the Method Blank

8.6 Blank Matrix Spike: must be prepared and analyzed at a frequency of 1 Blank Spike for every batch of samples up to a maximum batch size of 20 samples. Calculate the recovery as:

$$\text{Spike Recovery (\%)} = \frac{\text{Spiked Blank Result}}{\text{Spike Added}} \times 100$$

Native analyte recoveries must be 80-140%

Internal Standard recoveries must be 40-135%

8.6.1 Corrective Actions:

- check calculations and reanalyse if recoveries are outside of these limits
- if the blank spike is outside of limits but the matrix spike is acceptable then the blank spike may have been spiked incorrectly. Review the data with the Supervisor or Operation Manager. All data may be accepted but must be flagged as exceeding acceptance criteria
- if both the blank spike and the matrix spikes exceed their respective limits re-prepare and reanalyze the samples providing sufficient sample is available
- if sufficient sample is not available the data must be flagged in the Sample report remarks section in Maxxlims

8.7 Matrix Duplicate: must be prepared and analyzed using randomly selected samples, at a frequency of 1 matrix duplicate for every batch of samples up to a maximum batch size of 20 samples. The RPD is calculated as:

$$\% \text{ RPD} = \frac{\text{first sample result} - \text{duplicate sample result}}{(\text{first sample result} + \text{duplicate sample result})/2} \times 100$$

RPD between duplicates should be $\leq 25\%$

8.7.1 Corrective Actions:

- check calculations for errors
- check solid samples for homogeneity, if not homogeneous, flag the data in Tester's Comments
- if the sample is homogeneous, re-prepare and reanalyze the sample

8.8 Matrix Spike/Matrix Spike Duplicate Recoveries: if sufficient sample is available, spike two separate aliquots of a sample in each batch of 20 samples or less with an appropriate level (2-5 times the sample concentration if possible) of native dioxin/furans and each of the 2,3,7,8-substituted congeners. Calculate the recoveries as follows:

$$\text{Matrix Spike Recovery (\%)} = \frac{\text{spiked sample result} - \text{sample result}}{\text{amount spike added}} \times 100$$

Recoveries of matrix spiked internal standards must be between 40-135%

Native analyte recoveries must be 80-140%

RPD between duplicates should be $\leq 20\%$

8.8.1 Corrective Actions:

- check calculations for errors
- if recovery calculations aren't possible (due to high sample concs.) flag the data in the Sample report remarks section in Maxxlims
- if the blank spike is acceptable then flag the data as a possible Matrix interference

- check solid samples for homogeneity, if not homogeneous, flag the data
- if the sample is homogeneous, re-prepare and reanalyze the sample
- if both the blank spike and the matrix spikes exceed their respective limits re-prepare and reanalyze the sample the sample if sufficient sample is available
- if sufficient sample is not available flag the data in Maxxlms.

8.9 Standard Reference Materials: NBS 1614 is analyzed with each initial calibration as a check on the accuracy of the calibration. The calculated value is plotted against the true value for the solution.

Each analyte must be within $\pm 20\%$ of the true value

If not achieved, further investigation of standard ref. material and prepared calibration standard reliability is required.

8.10 Control Charts: Refer to COR WI-00055 Corporate Control Charting procedure for generating control charts via MaxLIMS and real time (i.e., plotted manually, each time the QC sample and/or standard is analyzed). Plot the blank spike recovery of 2,3,7,8-T4CDD and 2,3,4,7,8-P5CDF for both waters and soils on separate control charts. Update the chart immediately after the analysis of the QC point used or in the morning after an overnight run, prior to reporting of data. Monitor the chart for the development of trends on the chart. Take actions, if necessary, as defined in the SOP for Control Charting. If an "Out of Control" point is found, terminate the analysis and resolve the problem. Note the resolution directly on the chart or code the point to a reference in the analyst's workbook.

8.10.1 Possible Causes:

- deterioration of standard or reagents
- standard, QC sample or reagent preparation error
- standard contamination or evaporation
- improper sample introduction
- poor analyst technique or insufficient training
- deviation from SOP procedure
- imprecise measuring devices, i.e. pipettors, syringes

8.10.2 Corrective Actions: if "out of control points" are encountered

- check the other run QC, if acceptable report the data
- if not acceptable, reanalyze the QC samples and if acceptable, report the data
- if not acceptable, find and resolve the cause, re-extract and reanalyze the samples
- if insufficient sample exists report the data, flagged as "out of statistical control"
- if hold times will be exceeded upon re-extraction and reanalysis, flag the data
- if no reason can be found, report the data as "out of statistical control"

Note the resolution on the Control Chart or reference it to the Analyst's Workbook.

8.11 Additional QC: in addition to the QC samples listed above, blind replicates, audit and performance evaluation samples may be submitted. These samples may have specific instructions that must be followed, however, analysis is to proceed as for any other sample. Any USACE project has an Analytical Data Review Checklist, documented in the QA Manual, completed and submitted with the final data report.

9.0 DATA ANALYSIS:

9.1 Calculations: the internal standard method is used to quantify PCDD's/PCDF's. It relies upon consistent linearity of MS response over time and over the calibration range represented by the standard solutions defined in Table 3. This internal standard method is easily integrated into an automated routine for data quantification. Internal standard quantification is based on the use of Relative Response Factors (RRF). For native standards, the RRF is the ratio of analyte response factor to the response factor of the corresponding labeled surrogate (internal standard). These RRFs remain unchanged over the range of concentration for which MS response is linear. Using these RRFs, along with native and surrogate responses from the sample run, recovery-corrected concentrations of PCDD's/PCDF's are calculated directly. Internal standard recoveries are calculated separately and reported. They reflect the overall data quality.

Relative response factors for the native standard (RRFn) and for the Internal standard (RRFs) are calculated using the following equations:

$$RRFn = \frac{Ac * Csc}{Asc * Cc} \quad \text{and} \quad RRFs = \frac{Asc * Crs}{Ars * Csc}$$

Where:

RRFn = relative response factor, Native Standard to Internal Standard

RRFs = relative response factor, Internal Standard to Recovery Standard

Ac = quantification ion (single or both ions) peak area for Native Standard

Asc = quantification ion (single or both ions) peak area for the appropriate Internal Standard

Ars = quantification ion (single or both ions) peak area for 1,2,3,4-T4CDD13C12
 or 1,2,3,7,8,9-H6CDD13C12

Cc = concentration of the Native Standard (pg/uL)

Csc = concentration of the appropriate Internal Standard (pg/ uL)

Crs = concentration of 1,2,3,4-T4CDD13C12 or 1,2,3,7,8,9- H6CDD13C12 (pg/ uL)

Using the RRFs, sample PCDD's/PCDF concentrations (C) and internal std. recoveries (%R) are calculated as follows:

$$C(X) = \frac{\sum_{k=1}^n Ak \cdot Qss}{Ass \cdot RRFn} /Ws \text{ or } Vs \quad \text{and} \quad \%R(X) = \frac{Ass * Qrs * 100}{Ars * Qss * RRFs}$$

Where:

- C(X) = recovery-corrected quantity of analyte X (pg/g for solids, pg/L in liquids)
 Ak = quantification ion (single or both ions) peak area for the “kth” homologous isomer of analyte X (n=1 for isomer-specific analysis)
 Qss = amount of internal standard X added to the sample (pg)
 Ass = quantification ion (single or both ions) peak area for internal standard X in extract
 %R(X) = percent recovery of internal standard X
 Qrs = amount of 1,2,3,4-T4CDD13C12 (recovery std for T4 and P5-CDD/CDF) or 1,2,3,7,8,9-H6CDD13C12 (recovery std for H6, H7-CDD/CDF and O8CDD/DF) in sample extract (pg)
 Ars = quantification ion (single or both ions) peak area for 1,2,3,4-T4CDD13C12 or 1,2,3,7,8,9-H6CDD13C12 in sample extract
 Ws = weight of dry sample in grams
 Vs = volume of sample in L

For homologues represented by more than one isomer in the calibration standards, the “homologue-average” RRF is used to quantify all target analytes that are not 2,3,7,8-substituted congeners.

9.1.1 Toxic Equivalence Determination: Polychlorinated dibenzo-para-dioxins (PCDD’s) and Polychlorinated dibenzofurans (PCDF’s) are known to exist as widespread environmental contaminants and to be toxic in nature. The 2,3,7,8-substituted congeners have been assigned Toxicity Factors by NATO (NATO-CCMS, 1988), with 2,3,7,8-TCDD, the most toxic, given a value of 1. International Toxicity Equivalency Factors (ITEFs) are shown below.

Toxic Equivalence (TEQ) is determined by multiplying the concentration of each detected 2,3,7,8-substituted congener by its respective TEF. Individual and Total TEQ are determined as follows using I-TEFs from the table shown below.

$$\text{Individual TEQ} = (\text{congener conc. found}) * (\text{congener specific TEF})$$

$$\text{Total TEQ} = \text{Sum of Individual TEQs}$$

International Toxicity Equivalency Factors (I-TEF)

Congener of Concern	I-TEF
2,3,7,8-TCDD	1
1,2,3,7,8-P5CDD	0.5
1,2,3,4,7,8-H6CDD	0.1
1,2,3,6,7,8-H6CDD	0.1
1,2,3,7,8,9-H6CDD	0.1
1,2,3,4,6,7,8-H7CDD	0.01
OCDD	0.001
2,3,7,8-TCDF	0.1
2,3,4,7,8-P5CDF	0.5
1,2,3,7,8-P5CDF	0.05
1,2,3,4,7,8-H6CDF	0.1
1,2,3,6,7,8-H6CDF	0.1

2,3,4,6,7,8-H6CDF	0.1
1,2,3,7,8,9-H6CDF	0.1
1,2,3,4,6,7,8-H7CDF	0.01
1,2,3,4,7,8,9-H7CDF	0.01
OCDF	0.001

For the 2,3,7,8-substituted congeners that are non-detectable, the following TEQ calculation methods can be used:

- 2,3,7,8-substituted congener TEF x DL
- 2,3,7,8-substituted congener TEF x ½ DL
- 2,3,7,8-substituted congener TEF x 0 DL

Proper selection of the calculation method for TEQ determination of non-detectable PCDD's and PCDF's are based on a client specific requirements.

9.2 Data Transfer: data is processed using a custom application macro developed internally. A spreadsheet is generated which incorporates weights, dilution factors, splits, internal standard amounts added, recovery standard amounts added, toxic equivalence and estimated detection limits. The result file, once completed by authorized personnel is electronically transferred to MaxxLIMS using the super-interface upload macro.

9.3 Data Validation: Refer to BRL WI-00011 Review and Validation of Analytical Data and corresponding Data Review Checklist (BRL FCD-00002) to perform a primary and a secondary analytical data review and validation prior to issuance of the Certificate of Analysis. If the data and report are acceptable the Certificate of Analysis is signed by the Project Manager and sent to the client.

9.4 Data Storage: sample data is transferred to a separate computer system and backup monthly or as required.

10.0 DOCUMENTATION:

10.1 Tracking Sheet: before samples are prepared, a GC-MS sample tracking /work sheet is completed. This sheet includes details of the Job number, lab sample number, client sample ID, QC samples analyzed in the batch, spiking solutions used and their concentrations, preparation date and lot #, dates of analysis and cleanup, analyst's initials. A copy of the tracking /work sheet is maintained with analytical data

10.2 Instrument Logbook:

- Troubleshooting records with full descriptions of the actions taken to resolve the problem. This is required for all instances in which there is an acceptance criteria that is not achieved. Alternatively these may also be recorded on a separate tracking sheet designed for the analysis.
- Record of Instrument Service by the Supplier with the associated paperwork

10.3 Method Deviation Records: instances may arise in which the standard operating procedure may not be applicable to the nature of the sample and may require modifications to the normal methodology. These deviations must be discussed with the Supervisor or Operation Manager prior to application. Approval must be obtained as per COR WI-00040 and documented using QSI module for Policy Deviation Form. These deviations must also be described in the comment section of MaxxLIMS.

10.3.1 Sample Deviation Records: these deviations must be recorded in MaxxLIMS Comments.

10.4 Maintenance Tracking: analysts maintain logbooks/tracking sheets to include the following minimum information

- record of Instrument Service by the Supplier with the associated paperwork
- records of all maintenance performed indicating the date performed and by who

10.5 Standard and Reagent Preparation Tracking: record all preparations of standards and reagents in the Standard Preparation and the Reagent Preparation Logbooks. All records must contain at a minimum the following information

- Supplier Identification and Lot Number
- Date of Preparation and Expiry
- Concentration, and name of Analyst who prepared the standard

10.6 Certificates of Analysis for Standards and Reagents: all preparations of standards is recorded in the Standard Preparation Logbook. These records will contain at a minimum the following information.

- Supplier information and Lot Number
- Date received
- Date of Preparation and Expiry
- Concentration, and name of Analyst who prepared the standard

10.7 Storage of Records:

10.7.1 Paper Records: raw and calculated data, including calibrations and QC results are stored chronologically in file folders in the laboratory. These files are archived on-site for a period of one year and then transferred to an off-site storage for 5 years, unless otherwise instructed.

10.7.2 Electronic Media: data entered into LIMS is backed up daily

11.0 WASTE MANAGEMENT:

All efforts are taken to prevent or reduce to a minimum the effect of waste disposal on the environment. All solvents are collected for shipment to a recycling facility. All recyclable plastic, glass and paper products are shipped to an appropriate recycling facility. The disposal of waste materials and samples are to carried out in accordance with protocols outlined in the SOP for the Preparation, Storage and Disposal of Reagents and Standards and the SOP for the Receipt, Handling and Disposal of Hazardous Wastes. All waste disposal will comply with the Ontario Ministry of the Environment and Energy's Sewer Guidelines and Regulation 558.

Specific Disposal Issues: contaminated sample extracts are collected and sent for disposal to an approved hazardous waste subcontractor. Excess contaminated samples are either returned to the client or submitted for disposal as noted.

12.0 APPENDIX:

Table 1: Exact Masses of the Ions Monitored by Hi-Res Mass Spectrometry

Table 2: Theoretical Ion Abundance Ratios and their Control Limits

Table 3: EPA 8290 Calibration Standards

Table 4: Summary of WHO 1998 and WHO 2005 TEF values

Figure 1: Acceptable Chromatographic Separation for 2,3,7,8-T4CDD and 2,3,7,8,-T4CDF

TABLE 1:

EXACT MASSES OF THE IONS MONITORED BY HI-RES MASS SPECTROMETRY

Descriptor No:	Accurate Mass	Ion Type	Analyte
1 T ₄ CDF/T ₄ CDD/H ₆ CDPE	303.9016	M	T ₄ CDF
	305.8987	M+2	T ₄ CDF
	315.9419	M	T ₄ CDF- ¹³ C ₁₂
	317.9389	M+2	T ₄ CDF- ¹³ C ₁₂
	319.8965	M	T ₄ CDD
	321.8936	M+2	T ₄ CDD
	327.8847	M	T ₄ CDD- ³⁷ Cl
	331.9368	M	T ₄ CDD- ¹³ C ₁₂
	333.9339	M+2	T ₄ CDD- ¹³ C ₁₂
	375.8364	M+2	H ₆ CDPE
	292.9825	LOCK MASS	PFK
	2 P ₅ CDF/P ₅ CDD/H ₇ CDPE	339.8597	M+2
341.8568		M+4	P ₅ CDF
351.9000		M+2	P ₅ CDF- ¹³ C ₁₂
353.8970		M+4	P ₅ CDF- ¹³ C ₁₂
355.8546		M+2	P ₅ CDD
357.8517		M+4	P ₅ CDD
367.8949		M+2	P ₅ CDD- ¹³ C ₁₂
369.8919		M+4	P ₅ CDD- ¹³ C ₁₂
409.7974		M+2	H ₇ CDPE
354.9792		LOCK MASS	PFK
3 H ₆ CDF/H ₆ CDD/O ₈ CDPE	373.8207	M+2	H ₆ CDF
	375.8178	M+4	H ₆ CDF
	383.8639	M	H ₆ CDF- ¹³ C ₁₂
	385.8610	M+2	H ₆ CDF- ¹³ C ₁₂
	389.8156	M+2	H ₆ CDD
	391.8127	M+4	H ₆ CDD
	401.8559	M+2	H ₆ CDD- ¹³ C ₁₂
	403.8530	M+4	H ₆ CDD- ¹³ C ₁₂
	445.7555	M+4	O ₈ CDPE
	392.9760	LOCK MASS	PFK
	4 H ₇ CDF/H ₇ CDD/NCDPE	407.7818	M+2
409.7788		M+4	H ₇ CDF
417.8253		M	H ₇ CDF- ¹³ C ₁₂
419.8220		M+2	H ₇ CDF- ¹³ C ₁₂
423.7766		M+2	H ₇ CDD
425.7737		M+4	H ₇ CDD
435.8169		M+2	H ₇ CDD- ¹³ C ₁₂
437.8140		M+4	H ₇ CDD- ¹³ C ₁₂
479.7165		M+4	NCDPE
430.9728		LOCK MASS	PFK
5 O ₈ CDF/O ₈ CDD/DCDPE		441.7428	M+2
	443.7398	M+4	O ₈ CDF
	457.7377	M+2	O ₈ CDD
	459.7348	M+4	O ₈ CDD
	469.7780	M+2	O ₈ CDD- ¹³ C ₁₂
	471.7750	M+4	O ₈ CDD- ¹³ C ₁₂
	513.6775	M+4	DCDPE
	442.9728	LOCK MASS	PFK

H = 1.007825
 C = 12.000000
¹³C₁₂ = 13.003355
 F = 18.9964
 O = 15.994915
³⁵Cl = 34.968853
³⁷Cl = 36.965903

TABLE 2:

THEORETICAL ION ABUNDANCE RATIOS AND THEIR CONTROL LIMITS

Number of Cl 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	M/M+2	0.51	0.43	0.59	for H ₆ CDF- ¹³ C ₁₂ only
7	M/M+2	0.44	0.37	0.51	for H ₇ CDF- ¹³ C ₁₂ only
7	M+2/M+4	1.04	0.88	1.20	
8	M+2/M+4	0.89	0.76	1.02	

TABLE 3: EPA 8290 Calibration Standards

Component	Stock Conc. (ng/μl)	CS5		CS4		CS3		CS2		CS1	
		Conc. (pg/μl)	Vol. Req'd. (μl)	Conc. (pg/μl)	Vol. Req'd. (μl)						
Native Analytes											
2,3,7,8-TCDD	50	200	40	50	10	10	10	2.5	25 μl of native Intermediate	1	10 μl of native Intermediate
2,3,7,8-TCDF	50	200	40	50	10	10	10	2.5	25 μl of native Intermediate	1	10 μl of native Intermediate
P5-H7CDD/CDF	25	500	200	125	50	25	25	6.25	25 μl of native Intermediate	2.5	10 μl of native Intermediate
1,2,3,4,6,7,8,9-O8CDF	50	1000	200	250	50	50	50	12.5	25 μl of native Intermediate	5	10 μl of native Intermediate
1,2,3,4,6,7,8,9-O8CDD	50	1000	200	250	50	50	50	12.5	25 μl of native Intermediate	5	10 μl of native Intermediate
Internal Standards											
2,3,7,8-T4CDD ¹³ C ₁₂	50	50	10	50	10	50	50	50	10	50	10
2,3,7,8-T4CDF ¹³ C ₁₂	50	50	10	50	10	50	50	50	10	50	10
1,2,3,7,8-P5CDD ¹³ C ₁₂	50	50	10	50	10	50	50	50	10	50	10
1,2,3,7,8-P5CDF ¹³ C ₁₂	50	50	10	50	10	50	50	50	10	50	10
1,2,3,6,7,8-H6CDD ¹³ C ₁₂	50	125	25	125	25	125	125	125	25	125	25
1,2,3,6,7,8-H6CDF ¹³ C ₁₂	50	125	25	125	25	125	125	125	25	125	25
1,2,3,4,6,7,8-H7CDD ¹³ C ₁₂	50	125	25	125	25	125	125	125	25	125	25
1,2,3,4,6,7,8-H7CDF ¹³ C ₁₂	50	125	25	125	25	125	125	125	25	125	25
1,2,3,4,6,7,8,9-O8CDD ¹³ C ₁₂	50	250	50	250	50	250	250	250	50	250	50
Recovery Standards											
1,2,3,4-T4CDD ¹³ C ₁₂	50	50	10	50	10	50	50	50	10	50	10
1,2,3,7,8,9-H6CDD ¹³ C ₁₂	50	125	25	125	25	125	125	125	25	125	25

Final Volume of all standards is 10 ml.

TABLE 4: Summary of WHO 1998 and WHO 2005 TEF values.

Compound	WHO 1998 TEF	WHO 2005 TEF
<i>chlorinated dibenzo-p-dioxins</i>		
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	1	1
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.0001	0.0003
<i>chlorinated dibenzofurans</i>		
2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-PeCDF	0.05	0.03
2,3,4,7,8-PeCDF	0.5	0.3
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,6,7,8,9-HpCDF	0.01	0.01
OCDF	0.0001	0.0003
<i>non-ortho substituted PCBs</i>		
3,3',4,4'-tetraCB (PCB 77)	0.0001	0.0001
3,4,4',5-tetraCB (PCB 81)	0.0001	0.0003
3,3',4,4',5-pentaCB (PCB 126)	0.1	0.1
3,3',4,4',5,5'-hexaCB (PCB 169)	0.01	0.03
<i>mono-ortho substituted PCBs</i>		
2,3,3',4,4'-pentaCB (PCB 105)	0.0001	0.00003
2,3,4,4',5-pentaCB (PCB 114)	0.0005	0.00003
2,3',4,4',5-pentaCB (PCB 118)	0.0001	0.00003
2',3,4,4',5-pentaCB (PCB 123)	0.0001	0.00003
2,3,3',4,4',5-hexaCB (PCB 156)	0.0005	0.00003
2,3,3',4,4',5'-hexaCB (PCB 157)	0.0005	0.00003
2,3',4,4',5,5'-hexaCB (PCB 167)	0.00001	0.00003
2,3,3',4,4',5,5'-heptaCB (PCB 189)	0.0001	0.00003

*Bold values indicate a change in TEF value.

Ultra Trace Air Toxics SOP BRL SOP-00407 /
11

Campobello

Dioxin and Furan Extraction



Maxxam Analytics International Corporation
6740 Campobello Road
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905-817-5700

Document Identity	
Document Categorization	
Campobello Departments	Environmental HRMS

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- 📄 Ultra Trace Air Toxics FCD BRL FCD-00087 : Water Tracking Sheet
- 📄 Ultra Trace Air Toxics FCD BRL FCD-00102 : HR Soil/Tissue/Food Tracking sheet

Reason for Change

<p>Date of Change August 30, 2007</p> <p>Section Changed 2, 7.4, 10.4, 10.5</p> <p>Change Made Section 2, added clarification note on matrices Section 7.4, changed sample drying time from minimum of 4 hr to 12hr; added oven temp. range to be 105 to 115 C Sections 10.4 and 10.5 revised the steps to reflect current practice Minor corrections of typographical errors throughout the document</p>	Version 2
<p>Date of Change July 14, 2009</p> <p>Section Changed Header, 1.0, 4.0.1, 4.2, 7.3.1, 8.1-8.4, 10.1.2,</p> <p>Change Made Header updated Maxxam's current name 1.0, updated lab's current location 4.0.1, updated reference method 8290 to current revision 4.2, replaced SOP list with reference to Associated Documents 7.3.1, changed batch size from 14 to 20 samples 8.1-8.4, removed statements on Canadian protocol for QC frequencies (method blank, blank matrix spikes, matrix duplicates, MS/MSD, since they may vary. Additional or different frequency of QCs will be addressed on a project specific basis. 10.1.2, updated procedure to reflect current practice</p>	Version 3
<p>Date of Change August 26, 2013</p> <p>Section Changed 4.1.1, 7.3, 7.6, Table 1</p> <p>Change Made Section 4.1.1 and 4.1.2 Added use of tumbler as deviation from Ref. Method Section 7.3 Added option of extended method of shaking by using tumbler for water samples and using conical funnel with Na2SO4 for filter the extract. Reorganised steps to reflect current flow of each step of sample extraction. Section 7.6 Added to refer the separate BRL SOP-00402 and BRL SOP-00424 that describe sample preparation to avoid duplication. Table 1 removed DFCDN-TI, added DF-TI, DF-FD,DF-O</p> <p>Optional Field A Associated documents have been reviewed, and where required the CPro links were updated to reflect most current procedures in use by the HRMS laboratory</p>	Version 4
<p>Date of Change August 26, 2013</p> <p>Section Changed Header, 3.0, 8.3, 10.5.1, 10.5.2</p> <p>Change Made Header, Removed "DRAFT - for review purpose only", (this was inadvertently left after revision 4 was complete) 3.0, Changed to state for HRMS testing and added relevant reference method,EPA 1613B; removed reference to obsolete procedure BRL SOP-00214 8.3, Corrected from " Matrix" to "Sample" 10.5.1, Removed last sentence to eliminate redundancy 10.5.2, Removed last bullet to reflect current practice All highlighted changes from rev 4 are carried into rev 5, due to immediate SOP correction</p> <p>Optional Field A Associated documents have been reviewed, and where required the CPro links were updated to reflect most current procedures in use by the HRMS laboratory</p>	Version 5
<p>Date of Change September 30, 2013</p> <p>Section Changed 7.4 step 7</p> <p>Change Made Added information for extracting sample and keeping an archive</p> <p>Optional Field A removed section about moisture as this is done by the processing lab</p> <p>Optional Field B Added information about Method Spike</p>	Version 6
<p>Date of Change March 11, 2014</p> <p>Section Changed 7.5 added</p> <p>Change Made Section added for Fly Ash samples</p> <p>Optional Field A Note: associated documents have been reviewed, and no changes to them are required.</p>	Version 7
<p>Date of Change January 13, 2015</p> <p>Section Changed 7.3</p> <p>Change Made updated to reflect current practice; added details for food prep</p> <p>Optional Field A Associated Documents - no changes required</p>	Version 8
<p>Date of Change February 19, 2015</p> <p>Section Changed 4.4, 5.0, 7.0, 7.3, 7.4, 7.5, 7.6, 8.5, 10.1, 11.0</p> <p>Change Made 4.4 - added test codes for tissue and food 5.0 - added sampling requirements for Oil 7.0 - added requirement for starting validation checklist 7.3 - added extraction details 7.4 - added extraction details for solids 7.5 - added prep details for oil 7.6 - added prep details for food matrix 8.5 - added supplemental spike duplicate 10.1 - added documentation requirement for syringe ID</p>	Version 9

DIOXIN AND FURAN EXTRACTION

1.0 LOCATION:

This procedure is performed in the HRMS Preparation Laboratory.

2.0 PURPOSE:

This method is used for the extraction of liquids and solids for the analysis of polychlorinated dibenzo-*p*-dioxins, (PCDD's), and polychlorinated dibenzofurans, (PCDF's). It is to be used for analysis by low and high resolution mass spectrometry.

This method has been validated for all matrices stated in the document.

NOTE: For the purpose of this procedure's clarity on matrices, use the following reference

Water Matrix - ground water, drinking waters, surface waters, wastewaters, etc.

Food Matrix – includes, but is not limited to, biota, dairy, meat, eggs, processed food, fish and seafood

Soil Matrix - solids, chemical materials, sludge, sediments and other solid wastes

2.1 **Principle of the Method:** PCDD's and PCDF's are extracted from solid samples with toluene and from aqueous samples with dichloromethane (DCM).

2.2 **Nature of Samples:** samples can be from many different sources including incinerator ashes, soils, sediments, effluents and food products. Investigate for any information about the past history involving the samples or the presence of potentially interfering substances at elevated levels, (i.e. PCB). This information will allow the preparation technician to take a smaller aliquot of sample so that internal standards are not diluted out during analysis.

2.3 **Safety**

2.3.1 **General Considerations:** each reagent, analyte and sample should be treated as a potential health hazard and exposure should be reduced to the lowest possible level. On the basis of the available toxicological and physical properties of the PCDD's and PCDF's, these compounds should only be handled by highly trained personnel thoroughly familiar with the handling and cautionary procedures, and who understand the associated risks. All work related to the analysis of PCDD's and PCDF's should be carried out within a specially designed laboratory. Safety glasses and protective lab clothing should be worn at all times. Refer to the appropriate MSDS for further information.

2.3.2 **PCDD's and PCDF's:** the 2,3,7,8-tetrachlorodibenzo-p-dioxin isomer has been found to be acnegenic, carcinogenic and teratogenic in laboratory animal studies. It is soluble in water to ~200 ppt and in organic solvents to 0.14 %. It is a solid at room temperature and has a relatively low vapour pressure. The physical properties of the 135 other tetra to octa chlorinated PCDD's/PCDF's have not been well established. It is presumed that the physical properties of these congeners are generally similar to those of the 2,3,7,8-TCDD isomer.

Laboratory ware, safety clothing, and other items contaminated with PCDD/PCDF in the course of analyses must be carefully secured and subjected to proper disposal. In the unlikely event that analytical staff experience skin contact with PCDD/PCDF or samples containing these, the contaminated area should be immediately and thoroughly scrubbed using mild soap and water. Personnel involved in any such accident should seek medical advice.

3.0 **SCOPE**

This procedure is applicable to both solid, liquid and food matrices that are extracted for PCDD's and PCDF's by High Resolution Mass Spectrometry. It is based on EPA SW846 Method 8290A and EPA 1613B. However, client or regulatory requirements may dictate that a specific method be followed. The method can also be adapted to include additional matrices after appropriate validation procedures are done

For precision, bias and detection limit information, refer to the CPro method validation module of relevant procedures for analysis: BRL SOP-00406, PCDD's/DF's in Liquid and Solid Samples (EPA 8290A) and BRL SOP-00410, Dioxins/Furans in Water, Soil, Food and Biota by HRGC HRMS (EPA 1613).

3.1 **Chemical Abstracts No.**

<u>Analyte</u>	<u>Symbol</u>	<u>CAS No.</u>
2,3,7,8-Tetrachlorodibenzo-p-dioxin	TCDD	1746-01-6
1,2,3,7,8-Pentachlorodibenzo-p-dioxin	PeCDD	40321-76-4
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	HxCDD	39227-28-6
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	HxCDD	57653-85-7
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	HxCDD	19408-74-3
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	HpCDD	35822-46-9
1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin	OCDD	3268-87-9
2,3,7,8-Tetrachlorodibenzofuran	TCDF	51207-31-9
1,2,3,7,8-Pentachlorodibenzofuran	PeCDF	57117-41-6
2,3,4,7,8-Pentachlorodibenzofuran	PeCDF	57117-31-4

1,2,3,4,7,8-Hexachlorodibenzofuran	HxCDF	70648-26-9
1,2,3,6,7,8-Hexachlorodibenzofuran	HxCDF	57117-44-9
1,2,3,7,8,9-Hexachlorodibenzofuran	HxCDF	72918-21-9
2,3,4,6,7,8-Hexachlorodibenzofuran	HxCDF	60851-34-5
1,2,3,4,6,7,8-Heptachlorodibenzofuran	HpCDF	67562-39-4
1,2,3,4,7,8,9-Heptachlorodibenzofuran	HpCDF	55673-89-7
1,2,3,4,6,7,8,9-Octachlorodibenzofuran	OCDF	39001-02-0
Total Tetrachlorodibenzo-p-dioxin	TCDD	41903-57-5
Total Pentachlorodibenzo-p-dioxin	PeCDD	36088-22-9
Total Hexachlorodibenzo-p-dioxin	HxCDD	34465-46-8
Total Heptachlorodibenzo-p-dioxin	HpCDD	37871-00-4
Total Tetrachlorodibenzofuran	TCDF	55722-27-5
Total Pentachlorodibenzofuran	PeCDF	30402-15-4
Total Hexachlorodibenzofuran	HxCDF	55684-94-1
Total Heptachlorodibenzofuran	HpCDF	38998-75-3

3.2 **Interferences:** solvents, adsorbents, reagents, glassware and other sample processing hardware may yield artifacts or elevated baselines that may cause misinterpretation of the data. Proper cleaning of glassware is extremely important. Note that glassware may not only contaminate the samples, but may also remove the analytes of interest by adsorption on the glass surface. Method blanks must be analyzed in order to demonstrate that all laboratory materials are free from interferents under the conditions of the analysis. The use of high purity reagents and solvents helps to minimize interference problems.

The sensitivity of this method is dependent upon the level of interferences within a given matrix. Interferents co-extracted from the sample material will vary considerably with the matrix and the diversity of the site being sampled. PCDD's and PCDF's are often associated with other chlorinated organics, which may potentially interfere with the analysis. These include polychlorinated biphenyls, polychlorinated methoxybiphenyls, polychlorinated hydroxy diphenylethers, polychlorinated benzylphenyl ethers, polychlorinated diphenyl ethers, polychlorinated naphthalenes, polychlorinated xanthenes, polynuclear aromatics, and pesticides.

3.3 Definitions

See COR WI-00012 Corporate Definitions

4.0 REFERENCES

4.0.1 US EPA SW-846 8290A, Revision 1, February 2007

4.0.2 Environment Canada PCDD/PCDF in Pulp and Paper Mill Effluents (River Road Method),
EPS 1/RM/19, February 1992

4.0.3 US EPA Method 1613, Tetra through Octa-chlorinated Dioxins and Furans by Isotope
Dilution, Rev. B, Oct. '94

4.1 **Modifications and/or Improvements from Referenced Methods:**

4.1.1 **SW846 Method 8290A:**

- In addition to regular glassware washing, Maxxam cleans Hi Res Soxhlet apparatus with a further 16-18 hour Soxhlet extraction using toluene.
- Reference uses Snyder columns to concentrate extracts from aqueous samples, Maxxam uses rotary evaporators
- Maxxam air dries solid samples prior to extraction
- Maxxam uses either manual or tumbling at ~60-70rpm for shaking prior to separation by separatory funnel

4.1.2 **EPA Method 1613:**

- Maxxam air dries solid samples prior to extraction
- Maxxam uses either manual or tumbling at ~60-70rpm for shaking prior to separation by separatory funnel

4.1.3 **Environment Canada River Road Method:**

- None

4.2 Other Relevant SOPs – refer to Associated Documents of CompliantPro Section for links provided. Note that the pre-processing of food samples is done at workstation B0, following procedure CAM SOP-00704.

4.3 **Extraction Test Codes:**

Test codes may be created as needed

4.4 **Analytical Test Codes:** Other test codes may be created as needed.

Hi-Res Waters:

Analysis:

DFCDNPP-W

PCDD/PCDF by Environment Canada River Road protocol, EPS 1/RM/19

DFCDN-W

PCDD/PCDF's by modified EPA Method 8290 protocol

DFATG24-W

PCDD/PCDF by OMOEE MISA protocol

DF1613-W	PCDD/PCDF by EPA Method 1613 protocol
DF8290-W	PCDD/PCDF by EPA Method 8290 protocol
DFHRMS-LC	PCDD/PCDF in leachates by modified EPA 8290 protocol
DFT4CDD-W	2,3,7,8-TCDD by EPA Method 1613 protocol

Hi-Res Soils:

Analysis:

DFCDN-S	PCDD/PCDF by modified EPA Method 8290 protocol
DF1613-S	PCDD/PCDF by EPA Method 1613 protocol
DF8290-S	PCDD/PCDF by EPA Method 8290 protocol

Hi-Res Tissues/ Food/ Oils: Analysis:

DF-TI	PCDD/DF in tissue by EPA Method 1613 protocol
DF-FD	PCDD/PCDF by modified EPA Method 8290 protocol
DF-O	PCDD/PCDF by modified EPA Method 8290 protocol
DF-PT	PCDD/DF in plant tissue by EPA Method 1613 protocol

Hi-Res Swabs:

Analysis:

DF8290-SB	PCDD/DF in Swabs by EPA Method 8290 protocol
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Lo-Res Waters:

Analysis:

DF8280-W	PCDD/PCDF by EPA Method 8280 Protocol
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Lo-Res Soils:

Analysis:

DF8280-S	PCDD/PCDF by EPA Method 8280 Protocol
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4.5 Regulations/Agencies Supported

- Canadian Environmental Protection Act, River Road Protocol for Pulp and Paper Mill Effluent
- this method also applies to a variety of regulatory agencies and methods i.e. US EPA RCRA

5.0 SAMPLE HANDLING AND PRESERVATION

Biota or food samples are shipped either refrigerated or frozen and upon receipt they are frozen until extraction. All other samples should be stored at 2-6 °C during shipment. Samples should be stored at 2-6°C until the point of extraction. During transit, the samples should be packed in rigid-body coolers in an upright position. Due to the fragile nature of the containers, the samples should be well wrapped with protective packaging during shipment from the field site to the laboratory. Samples that exceed the hold time will be flagged on the Certificate of Analysis. Different hold times may be imposed by other regulating agencies or as determined by client specific projects. Project specific and regulatory requirements for preservation method and reporting criteria, (required detection limit, dry or wet weight basis), must be examined and made clear prior to sample analysis.

<u>Matrix</u>	<u>Container</u>	<u>Min. Vol.</u>	<u>Time to Extract</u>	<u>Time to Analysis</u>
Waters	4x1 L amber glass	800 mL	30 days	45 days
Soils/Sludge	100 mL amber glass	2x5 gram	30 days	45 days
Pulp	100 mL amber glass	2x15 gram	30 days	45 days
Biological	100 mL amber glass	2x20 gram	30 days	45 days
Oil	100 mL amber glass	5 mL	30 days	45 days

6.0 APPARATUS AND MATERIALS

6.1 Apparatus (includes Labware and Equipment): 1L and 2 L glass separatory funnels; 500 mL flat bottomed flasks; Soxhlet apparatus; 90 mm Buchner funnels; 1L vacuum flasks; graduated cylinders; disposable Pasteur pipettes; microsyringes; Allihn filters; glass wool: 8 micron; 40 mL borosilicate glass vials with closures, pre-rinsed with DCM (VWR Catalogue No. 66012-066); 1L amber glass bottles with teflon lined caps; 250 mL wide mouth jars with teflon-lined caps; 1 mL Reacti-vials, (Kimble 60700-1) or 5mL centrifuge tubes, pre-rinsed with DCM; Whatman 1.0 µm Acrodisc syringe filters; Buchi/Brinkman RF-121 Rotary evaporator, GPC System: Autovap As-2000 Sample Processing System, Autoprep 1000 Chromatograph, Autovap 1000-evaporation module. Other suitable suppliers may be used as appropriate. Equivalent labware and equipment may be purchased from other suppliers as available

Note: all glassware used for Hi-Res samples is kept separate from Lo-Res glassware. This includes flasks, Soxhlets, Allihn filters and microsyringes.

6.1.1 Glassware: clean glassware as in BRL WI-00006 General Glassware Washing.

6.2 Reagents: information regarding the concentration, source, lot number, preparation date, expiry date and analyst responsible is written on the label of the bottle used to store the solutions. This information is also recorded in the reagent preparation logbooks. Equivalent reagents may be

purchased from other suitable suppliers as available. Other volumes of a reagent solution may be prepared as necessary by modifying the amount of stock used appropriate to the final volume required.

6.2.1 **Nitrogen:** UHP from Praxair or equivalent

6.2.2 **RODI:** Reverse Osmosis Deionized Water, (RODI), >16M Ω purity, produced in house

6.2.3 **Solvents:** dichloromethane (DCM), toluene, hexane, cyclohexane, ethyl acetate, iso-octane are purchased from Fisher, Distilled in Glass quality, or equivalent. Toluene is purchased from Caledon, Distilled in Glass quality or equivalent. Store in its original container at ambient temperature for up to one (1) year.

6.2.4 **Anhydrous Sodium Sulfate:** granulated, reagent grade from Fisher or equivalent. Store in its original container at ambient temperature for up to 1 year. Prior to use, the Na₂SO₄ is rinsed/soxhlated with the same solvent used in for the extraction procedure.

6.2.5 **Sulfuric Acid (concentrated), H₂SO₄:** (Reagent grade), Fisher or other suitable supplier. Store in its original container at ambient temperature for up to one (1) year.

6.2.6 **Hydrochloric Acid (concentrated), HCl:** (Reagent grade), Fisher or other suitable supplier. Store in its original container at ambient temperature for up to one (1) year.

6.3 **Standards:** information regarding the concentration, source, lot number, preparation date, expiry date and analyst responsible is written on the label of the bottle used to store the solutions and in the Standard and Reagent Logbook. Equivalent standards may be purchased from other suitable suppliers as available. Other volumes of a standard may be prepared by modifying the amount of stock used appropriate to the final volume required.

6.3.1 **Internal Standard and Matrix Spike Preparation:** information regarding the labeled compounds and their concentration is specific to the type of analysis required. Details of Internal and Surrogate Standards and Blank and Matrix Spike preparation are found in the analytical SOP that is being followed for analysis. Also Method Blank preparation and frequency. For the purposes of extraction, Table 1 at the end of this SOP lists the amount and type of spike required for analytical test codes. Amounts and types may change based on the sample matrix or client requirements. All standards preparations, Lot No's., supplier information, and pertinent dates are documented by the analyst in the Standard Preparation Log Book located in the instrumentation laboratory.

SPIKES MUST BE WITNESSED BY A SECOND STAFF MEMBER FAMILIAR WITH THE PROCEDURE

Both the person spiking the solution and the witness must sign off the tracking sheet.

7.0 ANALYTICAL PROCEDURE

7.0.1 Sample ID Check:

Step 1 check that the MAXXAM laboratory label and the original container label have identical Client Ids

Step 2 Print a LIMS worksheet containing all sample IDs and appropriate QC for the batch. Start the Ultra Trace Worksheet validation checklist – BRL FCD-00002

In most cases, the following procedures for sample extractions and clean ups are followed. However, clients will occasionally submit or require a specific method to be followed. Aqueous samples with solids > 1.0% require filtration and separate analysis of the solids.

7.1 **Glassware:** clean glassware as in BRL WI-00006 General Glassware Washing. Ensure the appropriate glassware is used for the type of analysis to be done. (Lo-Res vs Hi-Res)

7.2 **Method Spike:** prepare a method spike with each batch of samples extracted. Spike a clean Reacti-vial or 5mL centrifuge tube with the same volume of internal standards and spikes that are used for the extraction. Store reacti-vial/5mL centrifuge tube in the fridge according to the test code and matrix. Reacti-vial/5mL centrifuge tube will be delivered to the instrument lab upon completion of the extracted samples.

7.3 Preparation of Liquid Samples (Water, Liquid Drinks etc.):

Note: for drinking water samples logged in for DFT4CDD-W – cleanup is optional.

Extraction of samples can be processed by either procedures outlined in 7.3.1 or 7.3.2.

7.3.1 **Extended liquid-liquid Extraction:** prior to any liquid extractions, use empty 1L amber bottles (rinse with DCM about 5 mL two times for QC, add RODI water to each bottle ~900mL. For all samples, make volume according to the bottle size about ~800 mL to ~900 mL each **(volume may vary according to the size of the sample bottle)**).

Samples Not Requiring Filtration (<1% Solids) Using the Tumbler:

Step 1 Confirm by inspecting the samples that they have no visible suspended materials do not require filtration.

Step 2 Using a calibrated bottle for comparison, mark the position of the ~900mL on the sample bottle and discard the excess sample into water waste, this is to allow enough headspace for tumbler

Step 3 Label the prepared QC (900mL of RODI water as method blank and blank spike. Note: prepare one of each for every batch of 20 samples, or less, depending on the client's requirements

Step 4 Add the internal standard as described in Sections 7.3.2.1

Step 5 Spike the blank and matrix spikes as described in Sections 7.3.2.3

- Step 6* Add 100mL of DCM to the sample bottle and shake vigorously for ~30 sec. Relieve the pressure and check for leak from cap if any leak, change the cap.
- Step 7* Put all samples in the Tumbler @ ~ 60 – 70 RPM for an hour. Record the start time for the extraction on the tracking sheet and fill in the tumbler tracking form. Also record the unique glassware numbers for each sample on the worksheet.
- Step 8* Prepare all glassware for the set during the time of tumbling
- Step 9* Rinse separatory funnels 3x with ~100-150 mL DCM, shaking for ~2 minutes each time
- Step 10* Prepare Allihn filters/ filters by placing them on the flasks and filling the filter ~1/3 to 1/2 full with anhydrous Na₂SO₄ or 10-20 grams of Na₂SO₄ for the funnel respectively. Rinse the 500 mL flask and filter combination 3 times with ~100-150 mL of DCM, shaking for ~2 minutes each time.
- Step 11* Label flasks and separatory funnels with sample number
- Step 12* After ~one hour tumbling transfer the samples and QC from the amber bottles into the labeled separatory funnels, taking care not to spill during transfer.
- Step 13* Allow the layers to stand for ~5-10 minutes to achieve separation
- Step 14* If necessary break up any emulsions as per Section 7.3.3
- Step 15* Drain the lower DCM of each sample and QC from the separatory funnel through their respective pre-rinsed and labeled Allihn filter/conical funnel flask combination.
- Step 16* Transfer samples and QC back into their bottles. For the second extraction, add 50 mL of DCM to the sample and QC bottles and shake vigorously for ~30 secs. Relieve the pressure and tumble for ~half an hour. Once complete, collect the DCM layer again as described in step 15.
- Step 17* Transfer samples and QC back into their bottles and extract the aqueous phase one more time as described in step 16 with ~50mL of DCM and ~half hour tumbling.
- Step 18* Once complete, collect the DCM layer again as described in step 15. Add an additional ~50mL of DCM to the Allihn filter or funnel of each sample and QC to rinse the Na₂SO₄. Note: A bulb can be used on the filter to ensure collection of the remaining DCM.
- Step 19* Add ~3-5 mL of iso-octane and rotary evaporate the extract to ~2 mL. Note: transfer samples directly from the flask to the first clean up column if no splits are required
- Step 20* Measure the sample volume by pouring the remaining sample after extraction into a 1000mL graduated cylinder. Record the volume on the tracking sheet and record QC volume of 900mL.
- Step 21* Proceed to Section 7.8

7.3.2 Samples Not Requiring Filtration (<1% Solids) using Manual Shaking: Prior to any liquid extractions, cleaned glassware must be thoroughly rinsed as follows:

- Step 1* Separatory funnels are rinsed 3 times with ~100-150 mL of DCM, shaking for ~2 minutes each time and releasing the pressure as required.
- Step 2* Prepare Allihn filters/ conical funnel by placing them on the flasks and filling the filter ~1/3 to 1/2 full with anhydrous Na₂SO₄ or ~10-20 grams of Na₂SO₄ for the funnel respectively. Rinse the 500mL flask and filter combination 3 times with ~100-

150 mL of DCM, shaking for 2 minutes each time.

Step 3 Label flasks and separatory funnels with sample number.

For each sample perform the following:

- Step 1* Mark the position of the meniscus on the bottle to allow the initial volume determination. (Note: for River Road protocol weigh the bottles)
- Step 2* Label cleaned flasks and separatory funnels with sample number.
- Step 3* Fill the method blank and blank spike separatory funnel with ~1L of RODI water for the QC. Note: prepare one of each for every batch of 20 samples, or less, depending on the client's requirements
- Step 4* Pour the samples into their marked 2L separatory funnel.
- Step 5* Add the internal standard as described in Sections 7.3.2.1.
- Step 6* Spike the blank and matrix spikes as described in Sections 7.3.2.3 and record start time on tracking sheet, as well as the unique glassware numbers on the worksheet for each sample.
- Step 7* Add ~150 mL of DCM to each sample bottle and shake vigorously for ~30 sec and add this DCM to each respective sample separatory funnel.
- Step 8* For the first extraction of the aqueous phase, shake the separatory funnel vigorously for ~ 4-5 minutes, with occasional venting.
- Step 9* Allow the layers to stand for ~5-10 minutes to achieve separation.
- Step 10* If necessary break up any emulsions as per Section 7.3.3.
- Step 11* Drain the lower DCM of each sample and QC from the separatory funnel through their respective pre-rinsed and labeled Allihn filter/conical funnel flask combination.
- Step 12* Extract the aqueous phase a second time with ~100 mL of DCM added to the separatory funnel, shaking vigorously for ~3 minutes and occasionally venting.
- Step 13* Drain the lower DCM of each sample and QC from the separatory funnel through their respective pre rinsed and labeled Allihn filter/conical funnel flask combination.
- Step 14* Extract the aqueous phase a third time with ~100 mL of DCM added to the separatory funnel, shaking vigorously for at least 1 minute and occasionally venting.
- Step 15* Drain the lower DCM of each sample and QC from the separatory funnel through their respective pre rinsed and labeled Allihn filter/conical funnel flask combination.
- Step 16* Add an additional ~50mL of DCM to the Allihn filter or funnel of each sample and QC to rinse the Na₂SO₄. Note: A bulb can be used on the filter to ensure collection of the remaining DCM.
- Step 17* Add ~3-5 mL of iso-octane and rotary evaporate the extract to ~2 mL. Note: transfer samples directly from the flask to the first clean up column if no splits are required
- Step 18* Measure the sample volume by pouring the remaining sample after extraction into a 1000 mL graduated cylinder. Record the volume on the tracking sheet and record QC volume of 1000mL.
- Step 19* Proceed to Section 7.8

7.3.2.1 Internal Standard Spiking Water Samples:

SPIKES MUST BE WITNESSED BY A SECOND STAFF MEMBER FAMILIAR WITH THE PROCEDURE
Both the person spiking the solution and the witness must sign off the tracking sheet

- Step 1* use the syringe dedicated for spiking the Internal Standard [record the spiking solution ID and syringe ID on the tracking sheet]
- Step 2* prior to spiking, rinse the syringe several times with acetone
- Step 3* a dilution of the appropriate internal standard is prepared, on a daily basis and noted on the tracking sheet by transferring using the dedicated syringe, the volume as follows into a 25 mL volumetric flask:

Method:	Volume Int. Std.	Final volume With Acetone
EPA 23 & EPA 1613B	500 µL	25 mL
EPA 8290A	250 µL	25 mL
River Road EPS 1/RM/19	250 µL	25 mL

Note: depending on sample batch size, a different final volume of Daily Working Internal Standard, may be prepared by modifying the amount of relevant internal standard used appropriate to the final volume required.

- Step 4* rinse the dedicated internal syringe thoroughly with acetone after use
- Step 5* using a vortex mixer, thoroughly mix this solution prior to use
- Step 6* using a syringe, transfer 1.0 mL of this Daily Working Internal Standard, to the method blank, the blank spike, samples, duplicates or matrix spikes
- Step 7* Spike the prepared method spike with the volume of internal standards (not the daily working standard) that is used for the extraction of that method. Rinse the dedicated internal syringe thoroughly with acetone after use

7.3.2.2 Internal Standard Spiking Soil Samples:

- Step 1* use the syringe dedicated for spiking the Internal Standard [record the spiking solution ID and syringe ID on the tracking sheet]
- Step 2* prior to spiking, rinse the syringe several times with acetone
- Step 3* use this syringe to add the appropriate amount of the relevant Internal Standard as per Appendix Table 1, to the method blank, the blank spike, samples, duplicates and matrix spikes
- Step 4* rinse the syringe thoroughly with acetone after use

Note: do not use syringes intended for matrix spikes when spiking internal standards.

SPIKES MUST BE WITNESSED BY A SECOND STAFF MEMBER FAMILIAR WITH THE PROCEDURE
Both the person spiking the solution and the witness must sign off the tracking sheet

7.3.2.3 Blank and Sample Matrix Spikes:

- Step 1* use the syringe dedicated for matrix spiking [record the spiking solution ID and syringe ID on the tracking sheet]
- Step 2* rinse the syringe several times with acetone
- Step 3* spike the blank spike and matrix spike samples with the native spike mixture, (see Appendix Table 1, for volumes used)
- Step 4* Spike the prepared method spike with the volume of native standard that is used for the extraction of that method. Rinse the dedicated internal syringe thoroughly with acetone after use.

Note: do not use syringes intended for internal standards when spiking matrix spikes.

**SPIKES MUST BE WITNESSED BY A SECOND STAFF MEMBER FAMILIAR WITH THE PROCEDURE
Both the person spiking the solution and the witness must sign off the tracking sheet**

7.3.3 Samples Requiring Filtration (Solids >1%): filter these samples prior to extraction

- Step 1* samples that have visible suspended solids require filtration
- Step 2* For samples that require manual shake, mark the position of the meniscus on the bottle to allow the initial volume determination.

7.3.3.1 Extraction of Water Portion of Sample:

- Step 1* rinse a pre-washed 1 L vacuum flask 3x with DCM
- Step 2* rinse a 90 mm Buchner funnel 3x with DCM
- Step 3* pre-weigh an 11 cm Gelman glass fiber filter and record the weight on tracking sheet
- Step 4* Carefully pour the sample into the funnel with the vacuum applied. Use additional filters, which have been weighed, if there is a large amount of solid material.
- Step 5* rinse the bottle with minimal RODI, ensure particulates are transferred, if required
- Step 6* keep sample bottle for extraction
- Step 7* continue suction until the flow stops completely
- Step 8* Carefully transfer the filter(s) used to a Petri dish or pre-rinsed aluminum foil, allowing drying for a few hours or overnight at room temperature if necessary. All filters used will be combined and extracted in one Soxhlet body. Record final weight of dried filter on tracking sheet prior to Soxhlet extraction.
- Step 9* If performing manual extraction, transfer the filtered liquid contents of the flask to the clean labeled separatory funnel. Rinse the flask and the funnel with DCM and add to the separatory funnel and proceed to 7.3.2 Step 2.
- Step 10* If performing tumbler extraction, transfer the filtered liquid contents of the flask to the sample bottle and mark the position of ~900mL on sample bottles. Discard excess sample into water waste so as to allow enough headspace for tumbler extraction. Rinse the flask and the funnel with ~50 mL DCM and set aside to add to the sample bottle as first extraction. Proceed to 7.3.1 Step 3.

7.3.3.2 Extraction of the Solids Portion of the Water Sample:

- Step 1* Prepare a Soxhlet apparatus with the filter according to Section 7.4, steps 1-3 and label glassware.
- Step 2* Weigh dried filter(s) and record weight on the tracking sheet.
- Step 3* Add ~250-300 mL toluene to the flask and add all filters used for the sample to the same Soxhlet body. Cover with ~1.5 cm of anhydrous Na₂SO₄ and proceed as in Section 7.4, step 11. Note: the filters are not spiked with any standards.
- Step 4* Once solid portion has extracted for 16 hours, rotary evaporate the extract to ~2 mL and combine with rotovaped extract of the water portion. Concentrate combined extracts to ~2 mL prior to cleanup.

7.3.4 **Emulsions:** emulsions covering >1/3 of the organic layer must be broken up. The following techniques may help to break up the emulsified layer

Option 1:

- Step 1* use a glass rod to break up the emulsion or
- Step 2* Drain the organic layer into multiple DCM rinsed centrifuge tubes, if required and centrifuge the sample for ~5 minutes at 3000 rpm.
- Step 3* if the emulsion still exists add ~2 drops of conc. H₂SO₄ and shake gently, (use caution!), then re-centrifuge the layer
- Step 4* Using a pipette, transfer the separated DCM layer to the samples respective Allihn filter or funnel. Carefully pour the centrifuge tube(s) contents back to the appropriate separatory funnel. If performing tumbler extraction, drain the funnel back into the sample bottle once the centrifuge material has been added back.
- Step 5* If performing a tumbler extraction, rinse the tubes with a total of ~50 mL of DCM and add to the sample bottle to continue extraction. If performing a manual extraction, rinse the tubes with a total of ~100 mL of DCM and continue extraction.
- Step 6* Repeat if necessary before completing the third extraction.

Option 2:

- Step 1* Drain the organic layer into 250 mL wide mouth clear glass jar, well rinsed with DCM and add an additional ~10 mL of DCM.
- Step 2* Shake for ~1 min to achieve separation. If necessary, add additional DCM to separate the organic layer.
- Step 3* Using a pipette, transfer the separated DCM layer to the samples respective Allihn filter or funnel. Carefully pour the jars' contents back to the appropriate separatory funnel. If performing tumbler extraction, drain the funnel back into the sample bottle once the centrifuge material has been added back.
- Step 4* If performing a tumbler extraction, rinse the jar with a total of ~50 mL of DCM and add to the sample bottle to continue extraction. If performing a manual extraction, rinse the jar with a total of ~100 mL of DCM and continue extraction.
- Step 5* Repeat if necessary before completing the third extraction.

7.4 Preparation of Solid Samples (Soil, Sediment, Meat, Processed food, Cheese, Egg, Ash, etc.):

- Step 1* Prepare all glassware that has been soxhlated with glass wool and anhydrous Na₂SO₄ in the Soxhlet body as follows:
- Step 2* Remove the solvent in the flask from overnight soxhlation, discard to waste and add ~150 mL toluene to the Soxhlet body to rinse the Na₂SO₄ and glass wool. Allow the toluene to cycle through to the flask and shake thoroughly for ~2 min.
- Step 3* Repeat this cleaning 2 more times with an additional ~150 mL for each cleaning, shaking for ~2 min each time.
- Step 4* label the flasks and Soxhlet apparatus
- Step 5* add enough, ~250-300 mL, toluene to the flask so that the sample extraction will cycle and not go dry
- Step 6* Accurately weigh 2-10 g of each sample and ~10g of Ottawa Sand for the Blank and Blank Spike – this will be a single spike. (Note: weight may be dictated by nature of the sample, amount of sample provided by the client or the client having specific MDL requirements that need to be met). Alternately ~20g of each sample and Ottawa Sand for the Blank and Blank Spike is accurately weighed and double spiked. Note: once the extraction is complete (minimum of 16 hour soxhlation) the double spiked extract is accurately split and one portion is used for cleanup while the other is kept as an archive

Note: for food type samples use an appropriate matrix similar to the type of sample being analyzed for Blank and Blank Spike and record this info on the worksheet/tracking sheet.

- Step 7* Record weights on the work sheet including QC weight and record as well as unique glassware numbers for each sample. Also record the lot numbers for Na₂SO₄, glass wool and QC material
- Step 8* carefully add each sample to a Soxhlet and cover with ~1.5cm of anhydrous Na₂SO₄
- Step 9* spike the sample with the internal standard, see Section 7.3.2.2
- Step 10* spike the blank spike and matrix spikes, see Section 7.3.2.3
- Step 11* rinse the inside of the Soxhlet with ~ 10mL toluene
- Step 12* place the Soxhlet apparatus on a burner and wrap the bodies with aluminum foil
- Step 13* turn on the condenser water supply, set the burners on “high” and extract for 16-18 hrs. Record start time on tracking sheet.
- Step 14* After 16-18 hr soxhlation, record the time burners are shut off on the tracking sheet. Cool and remove from the burners.
- Step 15* Quantitatively transfer the toluene left in the Soxhlet condenser area to the 500 mL flask.
- Step 16* rinse the Soxhlet apparatus several times with ~ 10mL toluene and cycle in the flask
- Step 17* rotary evaporate the extract to ~1 mL and add 1mL of iso-octane
- Step 18* proceed to Section 7.8

7.5 Preparation of Oil Samples

- Step 1* Check that the Maxxam laboratory label and the original container label have identical Client Ids

- Step 2* Initial the preparation/extraction sheet in the appropriate box verifying this check has been completed
- Step 3* Accurately weigh 0.1 to 0.2 grams of sample oil and 0.1 to 0.2g of corn oil for QC into a 40mL pre-cleaned vial and spike with 20 μ L of the internal standard mixture containing isotopically labeled standards. Record the weight of samples as well as the QC on the worksheet. Also include the lot of the QC used
- Step 4* Dissolve the sample in ~10mL of DCM
- Step 5* Shake the sample vigorously until all the sample is dissolved
- Step 6* Record the start time of the extraction on the worksheet

Sample Cleanup: Proceed to BRL SOP-00405 "Clean UP of Sample extracts for PCDD and PCDF Analysis" and start with section 7.A.1.2.1 "Sulphuric Acid Extraction"

7.6 Preparation of Fly Ash, Food Samples

Caution: Because of the tendency of fly ash to "fly", all handling steps should be performed in a hood in order to minimize contamination.

- Step 1* Place funnel with an 11 cm Gelman glass fiber filter onto a 250mL wide mouth glass jar that has been rinsed 3x with DCM and labelled.
- Step 2* Fly Ash - Tare the jar and funnel and accurately weigh about 4g of fly ash to 2 decimal places onto the glass fiber filter. For the Blank and Blank Spike weigh out ~4 g of Ottawa Sand. Note: ~4g sample size will be double spiked and the extract is then accurately split and one portion is used for cleanup while the other is kept as an archive).
Food – Make sure each sample is homogenized prior to sub sampling Samples with particle sizes greater than 5mm are subjected to grinding, homogenization or blending. The method of reducing the particle size to less than 5mm is matrix dependent. In general, hard particles can be reduced by grinding them with a mortar and pestle. Softer particles can be reduced in size by using a meat grinder.
Tare the jar and funnel and accurately weigh ~5g onto the glass fiber filter.
- Step 3* Record weights on the work sheet including QC weight. Also record the lot numbers for Na₂SO₄, glass wool and QC material
- Step 4* Add ~20mL of 2 M HCL to the filter, taking care to cover the entire sample, and allow it to sit for ~1 hr.
- Step 5* After 1hr rinse the filter with ~200mL of RODI water and once the water has completed dripping, set the sample in the filter to air dry overnight.
- Step 6* The RODI rinse water that is collected in the jar can then be extracted. Add ~20mL DCM to the samples and QC and shake for ~2mins. Transfer the DCM layer to a rinsed and labelled 40 mL glass vial.
- Step 7* Repeat the extraction 2 more times with ~20 mL of DCM, shaking for ~2 min each time. Transfer the DCM layer to the 40 mL vial and concentrate on the NE-Vap to ~2mL. This water extract is later combined to the filter

toluene extract after it has completed the 16 hr. soxhlet extraction and is rotary evaporated to ~2 mL.

- Step 8* Once the filter and sample are dry place the sample and filter paper into a Soxhlet and flask glassware that has been prepared as described in 7.4 Step 1-5.
- Step 9* Carefully add each sample and QC filter to the Soxhlet and cover with ~1.5cm of anhydrous Na₂SO₄.
- Step 10* Spike the sample with the internal standard, see Section 7.3.2.2.
- Step 11* Spike the blank spike and matrix spikes, see Section 7.3.2.3.
- Step 12* Rinse the inside of the Soxhlet with ~ 10mL toluene.
- Step 13* Place the Soxhlet apparatus on a burner and wrap the bodies with aluminum foil.
- Step 14* Turn on the condenser water supply, set the burners on “high” and extract for 16-18 hrs. Record start time on tracking sheet.
- Step 15* After 16-18 hr soxhlation, record the time burners are shut off on the tracking sheet. Cool and remove from the burners.
- Step 16* Quantitatively cycle the toluene left in the Soxhlet condenser area to the 500 mL flask.
- Step 17* Rinse the Soxhlet apparatus with ~ 10mL toluene and cycle in the flask.
- Step 18* Rotary evaporate the extract to ~1 mL and add 1 mL iso-octane. This will be combined with the water portion extract.
- Step 19* All ash sample extracts require a sulfuric acid extraction before proceeding with the cleanup as described in 7.8 – information on this and the cleanup procedure is found in BRL SOP-00405.

7.7 Preparation of Pine Needles:

- See BRL SOP-00424 for prep of Pine Needles

7.8 **GPC Procedure:** See BRL SOP-00003, Clean Up of Extracts Using Gel Permeation Chromatography for GPC calibration and procedure.

7.9 **Cleanup and Fractionation Procedure:** see BRL SOP-00405 "SOP for the Clean Up of Sample Extracts For PCDD and PCDF Analysis.

8.0 QUALITY CONTROL:

8.1 **Method Spike:** a method spike is prepared with each batch of samples. The method spike consists of all the spiking solutions added to the blank spike.

8.2 **Method Blanks:** Prepare a method blank for each batch of 20 samples using blank matrix. For water samples use RODI water, for solid samples use Na₂SO₄ mixed with a like matrix. Frequency can vary to less than 20 samples if required by regulations or written contractual protocols.

8.3 **Blank Matrix Spikes, (Reference Sample/LCS):** A minimum of one blank spike is extracted for every 20 samples unless regulations or contracts require or allow a different frequency. An aliquot, equal to the method blank aliquot is spiked with the matrix spike solution.

8.4 **Sample Duplicate:** A minimum of one sample duplicate is extracted for every 20 samples unless regulations or contracts require or allow a different frequency. The sample duplicate is a randomly selected sample which was received with sufficient amount to allow for 2 analyses. This is not required if an MS/MSD is prepared.

Note: Some protocols may require matrix spike and matrix spike duplicates within a batch to monitor precision. If this is being done duplicate analysis is not required. If there are positive results, duplicate analysis may be substituted for matrix spike duplicates

8.5 **Sample Matrix Spike/Sample Matrix Spike Duplicates (MS/MSD):** The frequency for the sample matrix spikes is at a minimum of every 20 samples or as stated in contractual requirements. The sample matrix spike and spike duplicate are prepared using a randomly selected sample which was received with sufficient amount to allow for 2 additional analyses.

Note: If insufficient sample is submitted by the client to perform a duplicate Matrix Spike sample, a Duplicate Blank Matrix Spike will be performed. This will be noted on the worksheet.

8.6 **Additional Quality Control:** in addition to the samples mentioned above, SRMs, blind replicates, audit and performance evaluation samples may be submitted or required by the relevant analysis SOP. These samples may have specific instructions that must be followed; however, analysis is to proceed as for any other sample.

9.0 DATA CALCULATIONS:

9.1 **Data Storage:** the original tracking/work sheets are stored in binders in the extraction lab. A photocopy accompanies the extracts to the instrument.

10.0 DOCUMENTATION

10.1 **Preparation/Extraction Tracking /Work Sheets:** A tracking /work sheet is completed for each batch of samples. It contains Job /sample specific information i.e.; Job number, extraction date, clean up date, sample number, client name, client sample id, syringe ID, sample weight/volume, number of splits, amount and type of spike added, witness signoff, solvent lots, reagent lots or preparation dates and any additional information pertaining to the extraction or cleanup. A

photocopy accompanies the completed samples to the instrument and the original is kept in a binder in the HRMS Prep Lab.

10.1.1 Sample Deviation Records: Deviations must be recorded in the MaxLIMS report remarks area which is linked to the Job number / worksheet number. These entries appear on the Certificate of Analysis. Examples are as follows:

- analyzed past hold time
- sample is not homogeneous

10.1.2 Method Deviation Records: instances may arise in which the standard operating procedure may not be applicable to the nature of the sample and may require modifications to the normal methodology. These deviations must be discussed with the Supervisor or Operations Manager prior to application. Refer to COR WI-00040, Corporate Procedure for Policy Deviation to determine if deviation is deemed appropriate; record the procedure in the CPro Policy Deviation Form and submit to the Supervisor or Operations Manager for approval. Deviation must be approved prior to its implementation. These deviations must also be described in the MaxLIMS Job report remarks section. This information is retrieved by the project manager and is included in the final report sent to the client.

10.2 Maintenance Tracking: analysts maintain separate logbooks or specific tracking sheets in which they include the following minimum information

- record of Instrument Service by the Supplier with the associated paperwork
- records of all maintenance performed indicating the date performed and by who

10.3 Standard and Reagent Preparation Tracking: record all preparations of standards and reagents in the Standard Preparation and the Reagent Preparation Logbooks. All records must contain at a minimum the following information

- Supplier Identification and Lot Number
- Date of Preparation and Expiry
- Concentration and name of Analyst who prepared the standard

10.4 Certificates of Analysis for Standards and Reagents: certificate of analyses are kept for all solutions utilized in this SOP. These records will contain at a minimum the following information.

- supplier information and Lot Number
- date received

10.5 Storage of Records:

10.5.1 Paper Records:

- raw and calculated data, including calibrations and QC results are stored chronologically in folders in the laboratory as space permits. These files are archived to the warehouse for long term storage (i.e., 5-year retention time).

10.5.2 Electronic Media:

- data entered into LIMS is backed up daily by IT

11.0 WASTE MANAGEMENT:

All efforts are taken to prevent or reduce to a minimum the effect of waste disposal on the environment. All solvents are collected for shipment to a recycling facility. All recyclable plastic, glass and paper products are shipped to an appropriate recycling facility. The disposal of waste materials and samples are to be carried out in accordance with protocols outlined in the SOP for the Preparation, Storage and Disposal of Reagents and Standards and the SOP for the Receipt, Handling and Disposal of Hazardous Wastes. All waste disposals will comply with the Ontario Ministry of the Environment Sewer Guidelines and Regulation 558.

11.1 Specific Disposal Issues: contaminated sample extracts are collected and sent for disposal to an approved hazardous waste subcontractor. Excess contaminated samples are either returned to the client or submitted for disposal as noted.

11.2 Safety & Disposal

General Safety requirements for this SOP are provided in the critical task analysis (CTA). In addition to the CTA, additional guidance on Maxxam's Environment, Health and Safety (EHS) program are found in various Safe Work Procedures, Safety Policies, and the Safety Guide (See MEHS WI-00013).

- 11.2.1** The use of personal protective equipment (PPE), including safety glasses and lab coats are mandatory in all Maxxam labs. It is the responsibility of the analyst to read and understand the CTA associated with this SOP and ensure that any additional identified hazard controls are used (e.g. nitrile gloves, splash goggles, fume hoods, respirators, etc.).
- 11.2.2** Material safety data sheets for all chemical reagents are available to personnel using this method. Training on the interpretation of MSDS sheets is provided during WHMIS training upon hire. Staff performing this method shall review the associated MSDS sheets for chemicals used in this procedure and ensure they understand the associated hazards and safety controls required to work safely with each chemical.
- 11.2.3** General information for chemical waste and sample disposal is described in the Health and Safety work instructions. Disposal of all samples, extracts and reagents must be done in accordance with local, provincial and federal laws and regulations. Chemical wastes and sample disposal protocols are described in CAM WI-00018 and CAM SOP-00105.
- 11.2.4** The reagent used in this method contains mercury. All waste must be disposed of as hazardous waste and may not be discarded in the sink.

12.0 APPENDIX

- Table 1: Internal Standard and Matrix Spike Amounts for Liquid and Solid Samples

**TABLE 1:
INTERNAL STANDARD AND MATRIX SPIKE AMOUNTS
FOR LIQUID AND SOLID SAMPLES**

Testcode	Internal Standard	Matrix (Native) Spike	Cleanup Alternate Standard
Waters			
DFCDNPP-W	As per 7.3.1.1, River Road Internal Standard	20 µl River Road Matrix Spike	
DFCDN-W DFHRMS-LC	As per 7.3.1.1, EPA 23 Internal Standard	5 µl EPA 23 Matrix Spike	
DFATG24-W	As per 7.3.1.1, EPA 23 Internal Standard	5 µl EPA 23 Matrix Spike	
DF1613-W DFDW-W DFT4CDD-W	As per 7.3.1.1, EPA 1613 Method Spike	5 µl EPA 'PAR' Spike Solution	5 µL Alt. Std. (Clean-up)
DF8290-W -	As per 7.3.1.1, Region 4 / 8290 Internal Standard	20 µl Region 4 /8290 Matrix Spike	
DF8280-W	50 µl Lo-Res PCDD/F Spike Solution	10 µl EPA 23 Matrix Spike	
Solids			
DFCDN-S DF-FD DF-O	20 µl EPA 23 Internal Standard	5 µl EPA 23 Matrix Spike	
DF1613-S DF-TI	20 µl EPA 1613 Method Spike	5 µl EPA 'PAR' Spike Solution	5 µL Alt. Std. (Clean-up)
DF8290-S	25 µl Region 4 / 8290 Internal S Standard	50 µl Region 4 / 8290 Matrix Spike	
DF8280-S	50 µl Lo-Res PCDD/F Spike Solution	10 µl EPA 23 Matrix Spike	

Ultra Trace Air Toxics SOP BRL SOP-00408 /
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Ultra Trace Air Toxics

PCB CONGENERS ANALYSES BY HRGC/HRMS (Based on EPA 1668A and 1668B)



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Document Identity

Document Categorization

Ultra Trace Air Toxics Departments Environmental
Hidden HRMS

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Release and Audit Schedule

Release Schedule When Approved
 Allow Administrator to Release Document Early

Expiration Schedule When Superseded or Obsolete

Audit Schedule 12 Month(s)

Special Handling on Release

Update Completed Trainee Records

Insert Text

- BRL SOP-00408 R14
- Attachment 1
- Attachment 2
- 2005 WHO Update on TEFs for Dioxins, Furans and PCB Congeners

Associated Documents

Document Control Documents

- Burlington FCD BRL FCD-00002 : Data Review Checklist
- Burlington FCD BRL FCD-00003 : Organic Control Chart Out of Control Checklist
- Burlington FCD BRL FCD-00052 : MDL Template for Multi-Analyte Tests
- Burlington WI BRL WI-00011 : Review and Validation of Analytical Data
- Burlington SOP BRL SOP-00003 : GPC Cleanup
- Burlington SOP BRL SOP-00409 : HRMS PCB Congener extraction and cleanup of liquid, soil and air samples
- Corporate WI Publish to All COR WI-00010 : Corporate Procedure for Nonconformances
- Corporate WI Publish to All COR WI-00011 : Corporate Procedure for Corrective and Preventative Actions
- Corporate WI Publish to All COR WI-00012 : Definitions
- Corporate WI Publish to All COR WI-00018 : Determination of Estimation of Analytical Uncertainty of Measurement
- Corporate WI Publish to All COR WI-00040 : Corporate Procedure for Policy Deviation Forms
- Corporate WI Publish to All COR WI-00044 : Manual Integration of Chromatographic Peaks

-  Corporate WI Publish to All COR WI-00049 : Continuing Calibration Verification (CCV) Acceptance Criteria
-  Campobello WI CAM WI-00095 : Environmental Method Validation (NELAC + DOD requirements)
-  Corporate WI Publish to All COR WI-00050 : Environmental Chemistry Method Validation
-  Corporate WI Publish to All COR WI-00055 : Corporate Procedure for Control Charting
-  Campobello WI CAM WI-00121 : Maxxam Lab QM Supplement for TNI-NELAC 2009 QSM and DoD QSM Version 5.0
-  Campobello SOP CAM SOP-00704 : Sample Preparation - Food
-  Campobello WI CAM WI-00018 : Waste Disposal
-  Campobello SOP CAM SOP-00105 : Archiving, Retrieval and Disposal of Samples

Reason for Change

<p>Date of Change October 11, 2007</p> <p>Section Changed 3.0, 8.10, 9.3, 12.0</p> <p>Change Made 2.0-clarified matrices 3.5-removed the list of definitions 3.6- added reference to MU procedrue 8.9-clarified control chart practice 9.3-clarified data validation practice 12.0 added 2005 WHO updae on TEFs for Dioxins and Dioxin-like Compounds</p>	Version 2
<p>Date of Change April 17, 2008</p> <p>Section Changed throughout the document</p> <p>Change Made This revision involved error corrections of units from "milli" to "micro" and corrections to symbol "less than or equal to" that inadvertently took place when embedding rev 2 into the QSI SOP template. Section "Other Relevant SOPs" was removed from the text since they are listed in "Associated Documents".</p>	Version 3
<p>Date of Change October 19, 2009</p> <p>Section Changed header, title in attached document, 4.0, 4.1, 4.2, 6.5, 7.2.5.1, 7.2.6, 8.2.1, 8.3-8.6; 9.1, 9.6,</p> <p>Change Made header; removed "Inc." from Maxxam's name title; added EPA 1668B 4.0-4.1 added reference to EPA 1668B 4.2; updated list of test codes 6.5; added option of EPA 1668B, updated 6.5.4.1 to reflect current practice. 7.2.5.1; revised to reflect current practice 7.2.6.1; added "typical" 8.2.1; removed "should be" and replaced with "and" 8.3-8.6; added reference to Table6 A and B 9.1 & 9.6; added reference to EPA 1668B 12.0; incorporated Tables 1-9 since it is an attached document</p>	Version 4
<p>Date of Change December 7, 2009</p> <p>Section Changed 3.6, 4.1.5, 6.3, 6.5.2.1, 6.5.6.1, 6.5.7, 6.5.8, 7.2.5.3, 7.2.6.2, 9.2.2, 10.8</p> <p>Change Made Minor corrections throughout the SOP 3.6, added "internal standard" 4.1.5, 6.3, 6.5.6.1, 6.5.7, 6.5.8, added "and/or 1668B" 6.5.2.1, replaced "are used as surrogates for calculation of" with "to calculate" 7.2.5.3, corrected from Cis to Cs 7.2.6.2, replace "pre-run continuing calibration check" with "initial calibration standard" 9.2.2, replaced RR with RF 10.8, updated to reflect current practice on storage of records</p>	Version 5
<p>Date of Change June 1, 2010</p> <p>Section Changed 3.2, 3.3, 8.4, 10.2, 10.8.1</p> <p>Change Made 3.2+3.3 redefined correlation between MDL and detection limit, as well as Maxxam's RDL and LOQ, added performance of quarterly LOD and LOQ 8.4 added DoD requirements for method blank criteria & corrective actions re: DoD related projects 10.2 updated to reflect current practice re: use of COR WI-00040, Corporate Procedure for Policy Deviation Forms 10.8.1. updated storage of records offsite to reflect current practice</p>	Version 6
<p>Date of Change December 7, 2010</p> <p>Section Changed title, 3.2</p> <p>Change Made Title; added EPA 1668A + B 3.2; updated reference to CAM WI-00095</p>	Version 7
<p>Date of Change January 6, 2012</p> <p>Section Changed 6.5, 7.2.5, 7.2.6.2, 8.9, 10.3.1, 12.0, Table 4</p> <p>Change Made 6.5 removed second paragraph regarding marking solvent level of vials. Change years of storage for intermediate and working standards from 3 years to 2 years. 7.2.2 change reference for Table 4 to Table 5 for theoretical ratios. 7.2.5 re-word and reference section for resolution.</p>	Version 8

	7.2.6.2 added in brackets that mspike is used as an aid only. 8.9 Control charting- changed to COR WI-00055 added 2 more PCB congeners for trending. 10.3.1. Added reference to CAM FCD-00328. Section 12.0 corrected spelling 'retention' Table 4 updated acquisition experiment to current settings and placed as an attachment	
Date of Change	January 16, 2015	Version 9
Section Changed	2.0, 6.0, 6.1, 6.2, 6.4.2.1,6.4.3.1,6.4.4.1,6.4.5.1,6.4.6.1,6.4.7,6.6,6.6.1,7.2.2, 7.2.5.3,7.2.6.1,7.2.6.2,8.1.3,8.2,8.8.1	
Change Made	2.0,7.2.2,8.8.1 changed resolving power to "10,000 for the center m/z and ≥ 8,000 for the low and high m/z's" 6.0 removed "6.1 sample extract containers", removed "6.2 Miscellaneous Equipment" and re-numbered entire section. 6.3 modified"6.3 Gas Chromatograph/Mass Spectrometer/Data System" into "6.1 Instrumentation". Modified column using description 6.2 added "6.2 Apparatus" and "6.2.1 Glassware Quality Control" section 6.4.2.1,6.4.3.1,6.4.4.1,6.4.5.1, added "The volume of stock standards used may vary ...located in the Instrument laboratory." 6.4.6.1 added 209mixture final concentration. 6.4.7 added additional low level working standard cs0.5 concentration and preparation. 6.6 removed previous section 6.6,6.6.1, added section 6.5 Initial Calibration Verification Standard (ICV) 7.2.5.3 corrected concentration reference from "table 2" to "section 6.4.6.1" 7.2.6.1 added "solvent" before"209mix", replaced "CS3_PCB Reference Std" with "Initial Calibration Verification Standard (ICV):" to consistent with the name in 6.5 7.2.6.2 added "Internal QC samples (resin proofs, trap proofs, solvent proofs, IDOC, verification of new standard solutions) may be analyzed outside the required 12 hours" 8.1.3 added 2nd Source standard criteria. 8.2 added a note for CS3 Post-run calibration check remediation.	
Optional Field A	Associated documents have been reviewed and where required, the CPro links were updated to reflect most current procedures in the laboratory.	
Date of Change	February 11, 2015	Version 10
Section Changed	Title,2.0,2.1,2.2,3.2,9.2.3	
Change Made	Title Changed title form"DETERMINATION OF CHLORINATED BIPHENYL HOMOLOGUES AND INDIVIDUAL CONGENERS IN LIQUID SOLID AND AIR SAMPLES BY HI-RES MASS SPECTRPMETRY (Based on EPA Methods 1668A and 1668B)" into "DETERMINATION OF CHLORINATED BIPHENYL CONGENERS IN LIQUID, SOLID, AIR, and TISSUE BY HRGC/HRMS (Based on EPA 1668A and 1668B) 2.0,2.1,2.2,3.2,9.2.3 added "tissue" as matrix to related section.	
Optional Field A	Associated Documents - reviewed and updated to current revisions. No other changes required	
Date of Change	February 23, 2015	Version 11
Section Changed	2,5.1, 9.2.3	
Change Made	revised 2 to include food/tissue; added statement regarding validation 5.1 and 9.2.3-revised to include food/tissue. 4.2- added reference to sample pre-processing procedure.	
Date of Change	February 24, 2015	Version 12
Section Changed	BRL SOP-00408, 11.0	
Change Made	BRL SOP-00408 - corrected version number on pages 11.0 - added CAM WI-00018 and CAM SOP-00105	
Optional Field A	Associated Documents - reviewed and updated to current revisions. No other changes required	
Date of Change	February 25, 2015	Version 13
Section Changed	6.1.1, 12.0	
Change Made	6.1.1 - added reference to Attachment 2 12.0 - added Attachment 2	
Date of Change	February 25, 2015	Version 14
Section Changed	BRL SOP-00408 R13	
Change Made	Page numbering corrupted in the word document - revised to correct; no changes made to content of document	
Optional Field A	Associated Documents - reviewed; no changes required	

Approval Status Table			
Approver	Source	Role for Approvers	Parallel-Everybody Segment
Approver	Action	Date	Comment
Betsy Cliffe	Approve	February 25, 2015 3:53 PM GMT-5	
Salima Haniff	Approve	February 25, 2015 3:49 PM GMT-5	

PCB CONGENERS ANALYSES BY HRGC/HRMS (Based on EPA Methods 1668A and 1668B)

1.0 LOCATION:

This procedure is performed in the HRMS Prep Laboratory and the HRMS Instrumentation Laboratory.

2.0 PURPOSE:

This method is used to measure the concentration of chlorinated biphenyl congeners in water, soil, air and food samples. The technique can measure total homologues, (mono to decachlorobiphenyl), and can readily be used for the determination of individual congeners. Specifically, the toxic non-ortho and mono-ortho substituted congeners are determined using this technique, however, the method can be applied to the analysis of all 209 congeners.

This method has been validated for all matrices stated in the document.

NOTE: For the purpose of this procedure's clarity on matrices, use the following reference

Water Matrix: ground water, drinking waters, surface waters, wastewaters, etc.

Soil Matrix: solids, chemical materials, sludges, sediments and other solid wastes

Air Matrix: air filters, impringers, swabs, and other air traps

Food Matrices: fish, meat, oil, dairy, eggs, processed food and plant tissue, etc.

2.1 Principal of the Method: chlorinated biphenyls are widely found substances in the environment and consist of 209 congeners varying in level of biphenyl chlorination from mono through deca. Some of the congeners have no ortho chlorine substitution or a single ortho chlorine substitution and have been found to exhibit greater toxicity. These compounds are often targeted in the analytical scheme.

Chlorinated biphenyls are removed from samples using solvent extraction. Once the sample extract has been concentrated, it goes through a series of cleanup procedures to remove potential chemical interferences.

Following cleanup, the extract is analyzed by high-resolution gas chromatography/high-resolution mass spectrometry, (HRGC/HRMS), using an SPB-Octyl column and the MS operated at resolving power of $\geq 10,000$ for the center m/z and $\geq 8,000$ for the low and high m/z 's. . Analysis proceeds once the elution windows for all of the isomers in each congener group have been established. All 209 congeners are analyzed, however, only the requested congeners are reported. If total homologues are requested, then the sum of the congeners from each homologue group is reported.

2.2 Nature of the Samples: samples can be from many different sources including groundwater or surface water, industrial effluents, incinerator ashes, ambient air, stack gas emissions, soils, and food. The laboratory should be made aware of any past history involving the samples or the presence of potentially interfering substances at elevated levels, (e.g. aliphatic hydrocarbons). This allows prep

technicians to take a smaller aliquot of sample so that internal standards are not diluted out during analysis.

2.3 Safety Considerations: the toxicity or carcinogenicity of each compound or reagent used in this method has not been established precisely. Each compound should be treated as a potential health hazard and exposure should be reduced to the lowest possible level. On the basis of the available toxicological and physical properties of the chlorinated biphenyls, these compounds should only be handled by highly trained staff thoroughly familiar with handling and cautionary procedures, and who understand the associated risks. All work related to the analysis of chlorinated biphenyls should be carried out within a specially designed laboratory.

In general, use the same precautions taken for the analysis of PCDD/DF. This includes purchasing dilute standards where possible as opposed to the purchase of neat standards.

3.0 SCOPE:

This method is applicable to the determination of chlorinated biphenyl congeners and total homologues, (via quantitation of all 209 congeners), in water, solid and air samples by HRGC/HRMS. The full list of all 209 PCB congeners is found in the Appendix. The most requested congeners are the following World Health Organization, (WHO) list:

WHO Congener List	IUPAC Number
3,3',4,4'-Tetrachlorobiphenyl	77
3,4,4',5-Tetrachlorobiphenyl	81
2,3,3',4,4'-Pentachlorobiphenyl	105
2,3,4,4',5-Pentachlorobiphenyl	114
2,3',4,4',5-Pentachlorobiphenyl	118
2',3,4,4',5-Pentachlorobiphenyl	123
3,3',4,4',5-Pentachlorobiphenyl	126
2,3,3',4,4',5-Hexachlorobiphenyl	156
2,3,3',4,4',5'-Hexachlorobiphenyl	157
2,3',4,4',5,5'-Hexachlorobiphenyl	167
3,3',4,4',5,5'-Hexachlorobiphenyl	169
2,2',3,3',4,4',5-Heptachlorobiphenyl	170
2,2',3,4,4',5,5'-Heptachlorobiphenyl	180
2,3,3',4,4',5,5'-Heptachlorobiphenyl	189

3.1 Linear Range: the method is calibrated from 1.0–2000 ng/mL, as shown in Table 2 of the Appendix.

3.2 Detection Limit: Detection Limit is also referred to as Method Detection Limits (MDL): an MDL is the minimum concentration of a substance that can be measured and reported with 99% confidence

that the analyte concentration is greater than zero. MDLs are determined by the procedure outlined in CAM WI-00095, Environmental Chemistry Method Development, Revision and Validation.

Target MDLs are verified annually by spiking similar matrices replicates at the CS2-CS3 levels. These samples are carried through the full extraction and cleanup procedure. MDLs are determined by multiplying the standard deviation of the results by the Student's t-Value for the number of replicates used. If Target Limits are not achieved, the exercise is repeated spiking at a lower level. An MDL study is used to determine if the target limits outlined in test methods have been achieved. These are maintained on file in the CompliantPro MDL Module as well as at the instrument. To meet DoD- ELAP requirements, these limits are then used to determine spiking levels for the Limit of Detection (LOD) verification. Each matrix is spiked two to three times the target limit (derived above) for a single analyte test or one to four times the detection limit for a multi-analyte test.

NOTE: As per CAM WI-00121, section D.1.2.1, Maxxam HRMS Lab schedules quarterly LOD verifications for each respective matrix to meet DoD-ELAP requirements, where applicable.

Estimated Detection Limit (EDL): EDLs are sample specific and are calculated on a case specific basis for all analytes. It is possible to determine chlorinated biphenyl congeners in the range of 40 ppq for water, and 5 ppt for solids. These values increase if total homologues including mono-trichlorobiphenyl are requested, as the final volume may not be adjusted as low because of losses due to volatility. If a signal produced is not at least 2.5 times the average background level at the expected retention time for specific isomers, the area response for the noise is calculated as follows:

$$2.5 \times \text{peak intensity of background noise} \times \frac{\text{area of internal standard}}{\text{height of internal standard}}$$

This is done for either the quantitation ion or the confirmation ion. Using theoretical ratios for the specific degree of chlorination an area for the second ion is generated. These areas are then totaled and applied to the same calculation scheme as for "positive" hits (see Section 9). EMPCs (Estimated Maximum Possible Concentrations) are calculated whenever peaks are detected that meet all criteria except for ratios. The area in this case is recalculated (factored up or down) to meet the classical ratio and the result is flagged as an EMPC (NDR, not detected because of ratios, for Canadian Method)

NOTE: Maxxam HRMS lab schedules quarterly LOD verifications. They are analyzed with the next batch of samples for respective matrix.

3.3 Reporting Detection Limit (RDL): Reporting Detection Limit is also referred to as Limit of Quantitation (LOQ), equivalent to the Low Level Standard.

NOTE: As per CAM WI-00121, section D.1.2.1, Maxxam HRMS lab schedules quarterly LOQ verifications for each respective matrix to meet DoD-ELAP requirements, where applicable.

3.4 Interferences: the sensitivity of this method is dependent upon the level of interferences within a given matrix. Solvents, reagents, glassware and other sample processing hardware may yield artifacts

or elevated baselines that may cause misinterpretation of the data. Proper cleaning of glassware is extremely important. Improper cleaning of glassware may not only contaminate the samples, but may also remove the analytes of interest by adsorption on the glass surface. Method blanks must be analyzed in order to demonstrate that all laboratory materials are free from interference under the conditions of the analysis. The use of high purity reagents and solvents helps to minimize interference problems.

A variety of interferences can be found including chlorinated hydrocarbons and aliphatic hydrocarbons. Although the aliphatics do not exhibit masses that are used in quantitation of the higher chlorinated biphenyls, the presence of excessive levels can impact the chromatography and suppress ionization. Compounds causing interferences may often be present at concentration levels several orders of magnitude higher than the chlorinated biphenyls present.

Cleanup procedures are used to reduce or eliminate these interferences to the maximum extent practicable in order to ensure reliable quantitation at trace levels. Despite rigorous cleanup procedures, the possibility of matrix interference may still exist. If detection limits are seriously elevated by the excessive background, the sample extract may have to be cleaned up using alternative techniques or reported at elevated detection levels.

3.5 Definitions:

Corporate Definitions are found in COR WI-00012

3.6 Measurement Uncertainty: defines an interval about a sample result that would be expected to contain a large fraction of the distribution of values that would occur through repeated analysis of similar samples using the same methodology. Uncertainty is expressed as the standard deviation of the mean of a set of data (Blank Spikes/Laboratory Control Samples). Laboratory blunders or human errors are not incorporated into the calculations. Refer to COR WI-00018, Determination of Estimation of Analytical Uncertainty of Measurement.

The reported Expanded Uncertainty of an analyte is specific to the laboratory method used and incorporates laboratory procedures; physical measurements, (volume, temperature and mass), environmental variation, reagent and standard purity, sample preparation procedures (if applicable), personnel and instrumental parameters.

The most significant factors affecting the uncertainty of a measurement arise from the field-sampling program. They involve field site sample homogeneity; sampling technique; cleanliness of sampling equipment/containers; cross contamination of samples; environmental conditions; subsampling techniques; preservation techniques; sample storage; time to submit to laboratory. These variations are not incorporated into MAXXAM's uncertainty calculations.

MAXXAM uses a coverage factor "k" (multiplier of the combined standard uncertainty) to obtain an Expanded Uncertainty. MAXXAM reports to a confidence level of 95% (k=2).

MAXXAM does not correct sample data for bias or recoveries (except surrogate / internal standard recoveries in isotope dilution methods). The final decision on the acceptability and application of the reported data is the responsibility of the client.

PCB 77 in Waters Uncertainty is $\pm 20.0\%$ (95% Confidence Interval or $k = 2$)

PCB 180 in Waters Uncertainty is $\pm 20.0\%$ (95% Confidence Interval or $k = 2$)

PCB 77 in Solids Uncertainty is $\pm 20.6\%$ (95% Confidence Interval or $k = 2$)

PCB 180 in Solids Uncertainty is $\pm 23.4\%$ (95% Confidence Interval or $k = 2$)

PCB 77 in Air Uncertainty is $\pm 19.0\%$ (95% Confidence Interval or $k = 2$)

PCB 180 in Air Uncertainty is $\pm 20.2\%$ (95% Confidence Interval or $k = 2$)

4.0 REFERENCES:

4.0.1 Reference Methods:

- EPA Method 1668, Rev. A, Office of Water, EPA-821-R-00-002, Dec. 1999, "Chlorinated Biphenyl Congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS" (with corrections and changes through August 20, 2003).
- EPA Methods 1668, Rev. B, Office of Water, EPA-821-R-08-020, Nov. 2008, "Chlorinated Biphenyl Congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS".

How to add Rev.C

4.0.2 Additional Information Sources:

- World Health Organization, United Nations, Geneva, Switzerland
- New York State Dept. of Environmental Conservation, Draft Analytical Service Protocol, Method HRMS-1

4.1 Modifications and/or Improvements from EPA 1668A and EPA 1668B: Maxxam follows EPA 1668A and/or EPA 1668B as documented with the following exceptions.

4.1.1 Absolute Retention Time: Maxxam does not adhere to the 15-second absolute retention time criteria, (EPA Method 1668 A and 1668 B, section 15.4.1.1). The SPB-octyl column is prone to rapid phase degradation and loss of retention time. As a result, an otherwise valid calibration (and associated analytical data) would sometimes have to be rejected. As long as the SPB-octyl column, (or any other column in which retention times are inherently changing), is being recommended for the analysis, this type of absolute retention time criteria should not apply.

4.1.2 GC Temperature Programming and Relative Retention Times: Maxxam does not adhere to the decachlorobiphenyl retention time requirement of >55 minutes as given in Sections 6.9.1.1.1 and 10.1.2.2 of EPA Method 1668A and EPA1668B. This time criterion is based on Method 1668A's and 1668B's recommended GC temperature program, which is not acceptable for optimum method performance. Maxxam's GC program has been optimized based on peak shape and peak separation

for injection temperature and ramp rate. These differences include a higher injection temperature, a higher temperature between the two temperature ramps and a slower ramp rate for each of the two ramps. Better GC performance, (peak shape/separation), is achieved while still maintaining DeCB elution within < 50 minutes.

As a result of the changes to the temperature program, the relative retention time criteria in EPA 1668A and EPA 1668B, Table 2, and sections 10.1.2.3 and 15.4.1.2 are also no longer appropriate.

4.1.3 Signal to Noise Ratio (10:1) for Dichlorobiphenyls in CS1: Maxxam does not adhere to the S/N ratio of 10:1 for dichlorobiphenyls in CS1 as listed in Section 10.3.3 of EPA Method 1668A and 1668B. The PFK used for mass drift correction interferes at the mass of the confirmation ion reducing sensitivity significantly. The S/N criterion is achievable for other standard levels and other homologue groups. It is noteworthy that dichlorobiphenyls are of less concern with respect to toxicity, and as such, the resulting slightly raised detection limits should be of minor concern. Our minimum criteria for the S/N ratio of di CB's in the CS1 standard is 2.5:1.

4.1.4 Addition of 180L and 170L to Labeled LOC Mix and 180 and 170 Natives to Isotope Dilution Calibration: compare Table 7 of this SOP, and Table 2 of EPA 1668A and 1668B for a summary of changes in the assignment of retention time and quantitation references to some hepta CBs as a result of the addition of these internal standards. EPA 1668A and 1668B allow this as an option (see EPA 1668A and 1668B section 7.9.1). The use of these internals gives better quantitation of certain heptachlorobiphenyls. In particular, the quantitation of PCB's 180 and 170 can thus be calculated by isotope dilution, and have been added to the 5-point calibration since they are also on the WHO list of toxic congeners.

4.1.5 Minimum Detection Limits, Minimum Reporting Limits, and Reporting Units: see Sections 3.2 and 9.6 of this SOP for detailed discussions on how this procedure differs from EPA 1668A and 1668B.

4.1.6 Concentrations of Native and Labeled Compounds in Stock and Spiking Solutions and Final Extracts: see Table 1 of this SOP and Table 3 of EPA 1668A and 1668B for a comparison of how this procedure differs from EPA 1668A and 1668B. Although Maxxam uses different spiking solution levels, the final concentration in extract is as per EPA 1668A and 1668B. Note also that the spiking solutions are made up in nonane instead of acetone. Nonane is much less volatile and thus the solution is less prone to become concentrated over time.

4.1.7 Selection of Injection Internal (Recovery) Standard Used for Quantitation of Some Internal Standards: in some cases, matrix or inlet contamination leads to suppression of a recovery standard, causing erroneously high recoveries of some internal standards. This is especially problematic in cases where no recovery standard is present in the same acquisition function or homologue group of an internal standard, and so EPA 1668A and EPA 1668B default to using a recovery standard which is more prone to suppression from a later function. Improved quantitation can be realized by selecting an earlier recovery standard, such as PCB 9L instead of PCB 52L for quantitation of PCB 37L, and PCB 138L instead of PCB 194L for quantitation of PCB 188L.

4.1.8 Ions Used for Analysis of Decachlorobiphenyl: it was found that PFK interference makes use of the M+2 ion (495.7) difficult. We use the M+4 and M+6 ions for analysis of Deca CB (497.7/499.7 for native, and 509.7/511.7 for labeled). The theoretical ion ratio has been estimated as 1.20.

4.1.9 Number of Acquisition Functions: EPA 1668A and/or and EPA 1668B method use 6 acquisition functions, whereas Maxxam use 7.

4.1.10 PCB Field Spike Solution: Since this method will also be used for air sampling methods, a labeled PCB solution is added to sampling apparatus as a Field Spike. This solution contains PCB's 31L, 95L, and 153L.

4.2 Analytical Testcodes: the following test codes are used for analyzing chlorinated biphenyl congeners Additional test codes are created as required.

Test Codes	Use
PCBCONH-IP	PCB Congeners in Air samples
PCBCONH-TR	PCB Congeners in Train samples
PCBCONHR-S	PCB Congeners in Soils
PCBCONHR-W	PCB Congeners in Waters
PCBCONHR-T	PCB Congeners in Tissues
PCBHRMS-S	WHO List PCB's in Solids
PCBHRMS-F	WHO List PCB's in Air samples
PCBHRMS-W	WHO List PCB's in Waters
PCBHRMS-TI	WHO List PCB's in Tissues
PCBCONH-PT	PCB Congeners in Plant Tissue
PCBCONH-SB	PCB Congeners in Swabs

Note that for food matrices, sample pre-processing occurs at lab bench B0, following procedure CAM SOP-00704.

5.0 SAMPLE HANDLING AND PRESERVATION:

Due to the fragile nature of the containers, the samples should be well wrapped with protective packaging during shipment from the field site to the laboratory. All samples should be maintained at 2-6 °C during shipment and until analysis. Samples that exceed the hold time will be flagged on the Certificate of Analysis. Different hold times may be imposed by other regulating agencies or as determined by client specific projects. Project specific and regulatory requirements for preservation method and reporting criteria, (required detection limit, dry or wet weight basis), must be examined and made clear prior to sample analysis. Chlorinated biphenyls congeners are stable for at least a year when properly stored by refrigeration, (water, soil, air), or freezing, (tissue/food).

5.1 Sample Hold Times: in general, chlorinated biphenyls are stable for at least 1 year when stored as indicated, i.e. refrigeration for water, soil and air and freezing for tissues/food.

Matrix	Container	Min. Vol.
Waters	1 L amber glass	800 mL
Soils	100 mL amber glass	20 g
Oils	vial or jar	1 mL

Food/ tissues	glass jar	20 g
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For waters, sludges and similar materials containing $\leq 5\%$ solids, use suitably cleaned amber glass bottles, 1 L minimum, with screw cap, pre-cleaned to EPA specifications.

For soils, sediments, sludges, paper pulps, filter cake, compost, and similar materials that contain $>5\%$ solids use wide mouth, amber glass, 200 mL minimum, pre-cleaned to EPA specifications. Caps must be Teflon lined.

5.2 Extract Hold Times: extracts are stored in clear glass vials at room temperature for up to 1 year prior to analysis

6.0 APPARATUS AND MATERIALS:

6.1 Instrumentation: High Resolution GCs coupled to High Resolution Mass Spectrometers

6.1.1 Gas Chromatographs: HP 6890 or equivalent with splitless injection port for capillary column, temperature program with isothermal hold. The GC shall be equipped with either of the following columns. The first column is preferred because it can separate more individual congeners.

- Column #1: 30 m x 0.25 mm ID; 0.25 μm film SPB-Octyl, (Supelco 24218-U, or equivalent)
- Column #2: 30 m x 0.25 mm ID; 0.25 μm film DB-5, (J&W or HP-5). If required as per client request, this column may be used to separate, for example, PCBs 156 and 157, which would otherwise co-elute on column #1.
- Refer to Attachment 2 for client specific separation of PCB congeners
- DB-5, 60 m x 0.25 mm ID; 0.25 μm film thickness (or equivalent). This column is used to perform an additional analysis on a second GC column phase to confirm the presence of levels of PCB 169 when required.

6.1.2 Mass Spectrometers: Micromass, Autospec or Autospec Ultima, capable of 28-70 eV electron impact ionization, and repetitively selectively monitoring 12 exact m/z 's minimum at high resolution, $\geq 10,000$, during a period less than 1.5 seconds. The mass spectrometer, (MS), shall be interfaced to the GC such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beams. It will have a data system capable of collecting, recording, and storing MS data.

6.2 Apparatus: autosampler vials; assorted gas-tight micro syringes; assorted screw-cap amber vials with teflon-lined caps

6.2.1 Glassware Quality Control: all extraction glassware is engraved with a specific serial number. Glassware used for processing samples is tracked using this number. All glassware is subjected to a proven, rigorous cleaning procedure after which it is acceptable for reuse. Method blank analyses confirm the acceptability of this procedure.

- Soxhlet apparatus that were exposed to samples resulting in highly-coloured extracts are soaked

in a soap solution (Extran) overnight

- after soaking they are rinsed thoroughly with successive rinses of RODI water and acetone
- all Soxhlets are then cycled with toluene overnight
- Rotovap glassware is rinsed thoroughly with appropriate solvents after each use

6.3 Reagents: refer to BRL SOP-00409 for the reagents used in sample extraction

6.3.1 Compressed Gases: Ultra High Purity Nitrogen and Helium

6.4 Standards: information regarding the concentration, source, lot number, preparation date, expiry date and analyst responsible is written on the label of the bottle used to store the solutions and in the Standard and Reagent Log Book located in the instrument lab. Equivalent standards may be purchased from other suitable suppliers as available. Other volumes of a standard may be prepared by modifying the amount of stock used appropriate to the final volume required.

Standards can be purchased at varying concentrations, as individual congeners, or as mixes therefore preparations may vary though the final concentrations are as outlined in the Tables 1-6 in the Appendix.

6.4.1 Stock Standards: chlorinated biphenyl stock standards are purchased in solution from a suitable supplier, i.e. Wellington Labs, Accustandard or CIL. They are stored as per manufacturer's directions. Once prepared, working and intermediate standards are transferred to amber glass vials with Teflon-lined caps and stored at 2-6 °C for up to 2 yrs.

6.4.2 Stock Internal Standard Solution (50 ug/mL): the stock solution, Method 1668A and/or 1668B Toxics/LOC/Window Defining Solution Standard, is purchased from Accustandard at a concentration of 50 ug/mL of each of the components listed in Appendix Table 1. Storage and expiry are as per manufacturer's instructions.

6.4.2.1 Internal Standard Spiking Solution (0.4 ug/mL): using an appropriate gas-tight syringe, add 200 uL of the Stock Internal Standard Solution to a 25 mL volumetric flask. Dilute to volume with nonane. Transfer to an appropriate-sized amber glass vial with a Teflon-lined cap. This spiking standard is stored in a refrigerator at 2 to 6 °C for up to 2 years. The internal standards are used to calculate native PCB levels by isotope dilution. See BRL SOP-00409, Section 7.1 for spiking amounts used.

6.4.3 Stock Individual Cleanup Standard (50 ug/mL): 28L, 111L and 178L standards are purchased from Wellington. They are stored following the manufacturer's directions.

6.5.3.1 Mixed Stock Cleanup Standard (0.4 ug/mL each): using an appropriate gas-tight syringe, add 200 uL of each of 28L, 111L and 178L Stock Individual Cleanup Standards to a 25 mL volumetric flask. Dilute to volume with nonane. Transfer to an appropriate size amber glass vial with a Teflon-lined lid. Store at 2-6 °C for up to 2 years. This cleanup standard is added to all extracts prior to cleanup to measure the efficiency of the cleanup process. See BRL SOP-00409 Section 7.1 for spiking amounts used.

6.4.4 Mixed Stock Recovery Standard (5 ug/mL): Method 1668A and/or 1668B Injection Internal Standard Solution is purchased and contains the labeled chlorinated biphenyls: 9L, 52L, 101L, 138L and 194L. Store as per manufacturer's directions.

6.4.4.1 Working Recovery Standard (1 ng/uL): using an appropriate gas-tight syringe, add 1 mL of the mixed stock recovery standard to a 5 mL volumetric flask. Dilute to volume with nonane. Transfer to an appropriate size amber glass vial with a Teflon lid. This mixed stock standard is stored in a refrigerator at 2-6 °C for up to 2 years. 10 uL of the recovery standard is added to the 100 uL extract prior to analysis.

6.4.5 Stock Individual Field Spike Standards (50 ug/mL): 31L, 95L and 153L standards are purchased from Wellington. They are stored following the manufacturer's directions.

6.4.5.1 Field Spike Standard Spiking Solution (0.4 ug/mL each): using an appropriate gas-tight syringe, add 200 uL of each of 31L, 95L and 153L Stock Individual Cleanup Standards to a 25 mL volumetric flask. Dilute to volume with nonane. Transfer to an appropriate size amber glass vial with a Teflon-lined lid. Store at 2-6 °C for up to 2 years. This Field Spike solution is added to air sampling apparatus before sampling. 5 uL added to the apparatus prior to sampling gives a final extract concentration of 100 pg/uL.

6.4.6 Stock Method 1668A and/or 1668B - Combined Congener Standard: the solutions are mixes purchased as a set from Accustandard at varying concentrations and are stored following the manufacturer's directions.

6.4.6.1 Working Method 1668A and/or 1668B - Combined Congener Standard (209mixture): all 209 congeners are prepared in a separate mixture at a final concentration of 25 ng/mL for mono to tetra congeners; 50 ng/mL for penta to hepta congeners; and 75 ng/mL for octa to deca congeners, all in a solution of nonane. The concentration of all labeled standards in this solution is 100 ng/mL. The volumes below are added using gas-tight syringes, to a 5 mL volumetric flask, and diluted to final volume with nonane. The mixed standard is stored in an amber glass vial, with a Teflon-lined cap, at 2-6 °C for up to 2 years.

Mixes	Stock Conc. (ng/uL)	Volume (uL)	Final Conc. (ng/ml)
M1668A-1-0.01X	2.5/5.0/7.5	50	25/50/75
M1668A-2-0.01X	2.5/5.0/7.5	50	25/50/75
M1668A-3-0.01X	2.5/5.0	50	25/50
M1668A-4-0.01X	2.5/5.0	50	25/50
M1668A-5-0.01X	2.5/5.0/7.5	50	25/50/75
Internal Std. Spiking Solution	0.4	1250	100
Clean Up Standard Solution	0.4	1250	100
Field Spike Spiking Solution	0.4	1250	100
Injection Internal Standards	5	100	100
Nonane	-	900	-

6.4.7 Calibration Standards (CS1 to CS5): are used to establish linearity and relative response factors for those compounds in the initial calibration solutions. These RRFs are used to quantify the calibration verification and the OPR sample. These solutions permit the relative response, (labeled to native), and response factor to be measured as a function of concentration. Use the CS3 standard for calibration verification, (VER). Combine the solutions as described below to produce the 5 calibration solutions. Appendix Table 2 shows the components of each solution.

Add the specified volume of each standard to the Calibration Standards. Make up to the final volumes with nonane. These solutions are stored in a refrigerator at 2-6 °C for up to 2 years.

Solution	Conc. (ug/mL)	CS1	CS2	CS3	CS4	CS5
		Volume added (uL)				
1668A and/or 1668B Combined Congener Std	20	-	-	25	100	500
M1668A and/or 1668B PCB Matrix Spike Solution	0.1	50	250	-	-	-
Internal Standard Spiking Solution	0.4	1250	1250	2500	1250	1250
Clean up Standard Spiking Solution	0.4	1250	1250	2500	1250	1250
Field Spike Standard Spiking Solution	0.4	1250	1250	2500	1250	1250
Injection Internal Standards	5	100	100	200	100	100
Final Volume (mL)		5	5	10	5	5

An additional working standard, CS0.5 (0.5 ug/mL), may be used as per client request

Solution	Conc. (ug/mL)	CS0.5 Volume added (uL)
1668A and/or 1668B Combined Congener Std	20	-
M1668A and/or 1668B PCB Matrix Spike Solution	0.1	25
Internal Standard Spiking Solution	0.4	1250
Clean up Standard Spiking Solution	0.4	1250
Field Spike Standard Spiking Solution	0.4	1250
Injection Internal Standards	5	100

Final Volume (mL)

5

6.4.8 Stock Precision and Recovery (PAR) Standard (Matrix Spiking Stock Solution 20 ug/mL): the stock solution Method 1668A and/or 1668B -Combined Congener Std. is purchased containing the compounds as outlined in Appendix Table 1, at a concentration of 20 ug/mL of each component. Store the stock solution as per manufacturer's directions.

6.4.8.1 Working Precision and Recovery (PAR) Standard (Matrix Spiking Solution 0.1 ug/mL): using an appropriate gas-tight syringe, add 125 uL of the stock PAR standard to a 25 mL volumetric flask. Dilute to volume with nonane. Transfer to an appropriate size amber glass vial with a Teflon lid. This mixed stock standard is stored in a refrigerator at 2-6 °C for up to 2 years. The solution is used to determine the Ongoing Performance and Recovery, (OPR), and to prepare matrix spikes. See BRL SOP-00409 section. 7.1 for spike amounts used.

6.5 Initial Calibration Verification Standard (ICV): purchased as an injection ready standard (if available) from a second source supplier equivalent in concentration to CS3.

7.0 ANALYTICAL PROCEDURE:

Clients may occasionally require a specific method to be followed. Contact the Project Manager for specific instructions.

7.1 Procedures for Sample Preparation: refer to BRL SOP-00409

7.2 Analysis:

7.2.1 GC Operating Conditions: optimize the GC to meet the minimum retention times for the internal standards.

Column:	30 M SPB- Octyl
Injector temperature:	250 °C
Interface temperature:	270 °C
Initial temperature:	100 °C
Initial time:	1 min
Temperature program:	100 to 200 °C at 10 °C/min, 200 to 273 °C at 2.0 °C/min and hold for a total of 47.5 min

The GC conditions may be optimized for compound separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, blanks, IPR and OPR aliquots, and samples.

It may become desirable or necessary to perform an additional analysis on a second GC column phase to confirm the presence and levels of PCB 169 (see Section 9.1.6 and Appendix Table 4). If this analysis is performed, the following are the GC conditions:

Column:	DB-5, 60 m x 0.25 mm ID, 0.25 mm film thickness (or equivalent)
Injector temperature:	290 °C
Interface temperature:	290 °C
Initial temperature:	50 °C
Initial time:	3 min
Temperature program:	50 to 320 °C at 12 °C/min, and hold for 5.5 min

7.2.2 Mass Spectrometer Operation:

- Mass spectrometer, (MS), resolution: obtain a selected ion current profile, (SICP), of each analyte in Table 1 at the two exact m/z 's specified in Table 4 and at a minimum resolving power of 8000 ($\geq 10,000$ for the center m/z and $\geq 8,000$ for the low and high m/z 's) by injecting an authentic standard of the CBs either singularly or as part of a mixture in which there is no interference between closely eluted components.
- Analysis time for CBs may exceed 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, (i.e. 5 ppm in mass), can have serious adverse effects on instrument performance. Therefore, a mass-drift correction is mandatory and a lock-mass m/z from PFK is used for drift correction. The lock-mass m/z is dependent on the exact m/z 's monitored within each descriptor, as shown in Table 5. The level of PFK metered into the HRMS during analyses should be adjusted so that the amplitude of the most intense selected lock-mass m/z signal, (regardless of the descriptor number), does not exceed 10% of the full-scale deflection for a given set of detector parameters. 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 necessitating increased frequency of source cleaning.

- Using a PFK molecular leak, tune the instrument to meet the minimum required resolving power of 10,000, (10% valley), at m/z 304.9824 or any other reference signal close to m/z 331, (from PeCB). For each descriptor, (Table 4), monitor and record the resolution and exact m/z 's of 3 to 5 reference peaks covering the mass range of the descriptor. The resolution must be $\geq 10,000$ for the center m/z and must be $\geq 8,000$ for the low and high m/z 's. The deviation between the exact and theoretical m/z 's, (Table 5), for each exact m/z monitored must be <5 ppm.
- Ion abundance ratios, minimum levels, signal-to-noise ratios, and absolute retention times: choose an injection volume of either 1 or 2 μ L, consistent with the capability of the HRGC/HRMS instrument. Inject a 1 or 2 μ L aliquot of the CS1 calibration solution, (Table 2).
- Measure the SICP areas for each analyte, and compute the ion abundance ratios at the exact m/z 's specified in Table 4. Compare the computed ratio to the theoretical ratio given in Table 5.

- The exact m/z to be monitored in each descriptor are shown in Table 4. Each group or descriptor shall be monitored in succession as a function of GC retention time to ensure that all of the toxic congeners are detected. Additional m/z's may be monitored in each descriptor. The m/z's may be divided among more than the descriptors listed in Table 4; provided that the laboratory is able to monitor the m/z's of all the congeners that may elute from the GC in a given retention-time window.
- Operate the mass spectrometer in a mass-drift correction mode, using PFK to provide lock m/z's. The lock mass for each group of m/z's is shown in Table 4. Monitor each lock mass. It shall not vary by more than $\pm 20\%$ throughout its respective retention time window. Variations of the lock mass by $>20\%$ indicate the presence of co-eluting interferences that may significantly reduce the sensitivity of the mass spectrometer. Re-injection of another aliquot of the sample extract will not likely resolve the problem, unless it is a carryover problem from a previous sample. Additional cleanup of the extract may be required to remove the interferences.
- Except for DiPCB natives, the peaks representing the congeners and labeled compounds in the CS1 calibration standard must have signal-to-noise ratios, (S/N), $> 10:1$. Otherwise, the mass spectrometer shall be adjusted and this test repeated until this criterion is met.

7.2.3 Chromatographic Criteria:

- Absolute retention time of congener 169 shall exceed 20 minutes on the SPB-Octyl column. Otherwise, the GC temperature program shall be adjusted and this test repeated until the above-stated minimum retention time criteria are met. There is no retention time minimum for congener 209.
- Retention-time windows: analyze the window defining mixtures using the optimized temperature program. Table 3 gives the elution order, (first/last), of the window-defining compounds.
- The column must uniquely resolve congeners 34 from 23 and 187 from 182, and congeners 156 and 157 must co-elute within 2 seconds at the peak maximum. Unique resolution means a valley height $\leq 40\%$ of the shorter of the two peaks that result when the combined 209 congener solution is analyzed.

7.2.4 Defining Retention Time Windows: analyze the 209 Standard Mix to define the window. All congeners within a homologue group must elute within the descriptors set up to acquire the masses of these congeners.

7.2.5 Calibration:

- Calibration by isotope dilution: Isotope dilution calibration is used only for the native chlorinated biphenyls for which labeled compounds are added to samples prior to extraction. The reference compound for each native compound is shown in Table 7. In general, true isotope dilution is applied to the toxic congeners as each of the labeled standards has been added as an internal standard. All congeners for which there is a labeled internal standard added are calculated against the corresponding labeled internal standard.
- A calibration curve encompassing the concentration range is prepared for each compound to be determined. The relative response (RR) of each compound to its appropriate quantitation reference compound vs. concentration in each standard solution is computed according to the procedures described below. Five calibration points are employed for the compounds

identified in Table 2. All other congeners are calculated from a single injection of the full 209 congener mix (see “Calibration By Internal Standard” below).

The relative response of each native CB relative to its labeled analog is determined using the area responses of both the primary and secondary exact m/z's specified in Table 4, for each calibration standard, as follows:

RR =	$\frac{(A1_n + A2_n) C_1}{(A1_l + A2_l) C_n}$
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Where:

$A1_n$ and $A2_n$ = The areas of the primary and secondary m/z's for the target congener.

$A1_l$ and $A2_l$ = The areas of the primary and secondary m/z's for the labeled compound.

C_1 = The concentration of the labeled compound in the calibration standard, (Table 2).

C_n = The concentration of the native compound in the calibration standard, (Table 2).

To calibrate the analytical system for native standards by isotope dilution, inject a volume of calibration standards CS1 through CS5 consistent with volumes injected for all samples and other QC injections. Compute the relative response (RR), at each concentration.

7.2.5.1 Linearity: if the relative response for any native compound is constant (<20% coefficient of variation) over the calibration range, an averaged relative response may be used for that compound. Otherwise, the complete calibration curve for that compound must be used over the five-point calibration range.

7.2.5.2 Calibration by Internal Standard: the internal standard method is applied to determination of the native congeners for which a labeled compound is not available. These congener calibrations are calculated against the average internal standards from that homologue group. Compute and store the response factor (RF) for all native CBs except the Native Toxics/LOC CBs. Use the average (mean) response of the labeled compounds at each level of chlorination (LOC) as the quantitation reference. For the combinations of congeners that co-elute, compute a combined RF for the co-eluted group. For example, for congener 122, the areas at the two exact m/z's for 104L, 105L, 114L, 123L, 118L and 126L are summed and the total area is divided by 6, (because there are 6 congeners in the quantitation reference).

7.2.5.3 Response Factors: Internal standard calibration requires the determination of response factors (RF), defined as

RF =	$\frac{(A1_s + A2_s) C_{is}}{(A1_{is} + A2_{is}) C_s}$
------	--

Where:

$A1_s$ and $A2_s$ = areas of the primary and secondary m/z's for the target congener

$A1_{is}$ and $A2_{is}$ = average areas of the primary and secondary m/z's for the internal standards in that homologue group

C_{is} = concentration of the internal standard, (6.4.6.1)

C_s = concentration of the compound in 209mixture standard, (6.4.6.1)

- To calibrate for labeled compounds by the internal standardization method, inject 1.0-2.0 uL of the 209 Mix calibration std. Compute the response factor, (RF), of each compound to be calculated in this way.
- Combined calibration: by using calibration solutions containing the native congeners and the internal standards, as well as injection of a standard with all 209 congeners, a single set of analyses can be used to calibrate for the isotope dilution and internal standard methods. This calibration is verified each shift, by analyzing the calibration verification standard, (VER, Table 2). Recalibrate if any of the calibration verification criteria are exceeded. See Table 6.

7.2.5 Run Sequence: at the beginning and the end of a run sequence, a hardcopy of the Resolution check is printed out. The operator manually verifies resolution of Section 7.2.2. has been achieved for each multi group experiment; see the descriptor groups in see Table 4.

7.2.6.1 Typical Initial Calibration: (process takes ~10 hours to perform)

- Solvent (optional)
- CS1_PCB
- CS2_PCB
- CS3_PCB
- CS4_PCB
- CS5_PCB
- Solvent
- 209 Mix_PCB
- Initial Calibration Verification Standard (ICV): (second source check)
- Solvent (optional)

7.2.6.2 Typical Sample Analysis Sequence: process takes ~14 hours to perform.

- CS3_PCB (Pre-run Continuing Calibration Check or VER injection)
- 209 Mix_PCB
- Solvent (optional)
- OPR (ongoing precision and recovery or blank spike)
- Solvent
- Method blank
- Sample 1
- Sample 2
- Sample 3
- Sample 4
- Sample 5
- Sample 6
- Sample 7
- Solvent (optional)
- CS3_PCB (Post-run Calibration Check)
- MSpike (Spike solution reference standard, only used as an aid to determine the source of potential problems)

- Solvent (optional)

Note: If desired, “solvent” injections may be fortified with internal and recovery standards so that carry-over can be quantified. The last sample run before the Post-run Calibration Check must be completed within 12 hours after injection of the Pre-run Calibration Check. Internal QC samples (resin proofs, trap proofs, solvent proofs, IDOC, verification of new standard solutions) may be analyzed outside the required 12 hours

7.2.7 Routine Maintenance: record all results of maintenance performed in the Maintenance Logbook

7.2.7.1 Daily Maintenance: perform the following if a 3:1 signal to noise ratio cannot be met on the confirming ions for any one compound at the method detection limit or if peak tailing is observed

- change the injector insert and septum
- cut off 15-18 inches of the column

7.2.7.2 Monthly Maintenance:

- check and clean the ion source if required

7.2.7.3 Annual Maintenance:

- check all pump oils, (rough and diffusion pumps), for integrity
- perform system bake out, (may be required more frequently)
- check chillers for leaks or excessive wear of pumps

8.0 QUALITY CONTROL:

8.1 Initial Calibration: instrument calibration is performed initially and then as required. A 5-point calibration is performed for toxic congeners. Acceptance criteria:

8.1.1 CS1 Standard: S/N ratios for all congeners must be 10:1 (2.5:1 for diCBs). All congeners, native and labeled, must have ion ratios within the control limits (See Table 5).

8.1.2 Five Point Calibration: Using the calculations defined earlier, %RSD of RRFs must be $\leq 20\%$ in order to use average RRF for quantitation.

8.1.3 2nd Source standard should be $\leq 50\%$ for both native and labeled congeners analytes.

8.1.4. Corrective Actions: if the above criterion is not met

- Calibration must be repeated following remedial action.

8.2 Continuing Calibration: a pre-run continuing calibration or VER is performed at the beginning of every 12 hour run using a CS3 standard. Acceptance criteria are outlined below.

8.2.1 Percent Difference in RRF: must be $\leq 30\%$ for all native congeners and $\leq 50\%$ for all internal standard compounds. See Table 6 for acceptance criteria of cleanup standards.

8.2.2 Abundance Ratios: must be within $\pm 15\%$ of theoretical for all compounds.

8.2.3 Signal-To-Noise Ratio: must be at least 10:1 for all compounds.

8.2.5 Post-Run Calibration Check: the CS3 standard is run at the end of each 12-hour sequence to provide further confidence in the data. If this check does not meet the above criteria, remedial action must be taken before any further analyses are performed

NOTE: if the sample analysis sequence was unable to be completed due to instrument failure or carryover due to high sample, immediately run a CS3 Post-run calibration check to validate the sample data. If this fails to meet criteria, all samples **must** be re-injected.

8.2.4 Corrective Actions: remedial action is required. This may include GC inlet maintenance, preparation of a fresh calibration standard, or re-tuning. If remedial steps do not correct the problem, re-establishment of a 5-point calibration is required.

8.3 Internal Standard Recoveries:

Recoveries must be within the limits outlines in EPA method 1668A/B Table 6.

8.3.1 Corrective Actions: failure to meet these criteria may result in re-analysis with further cleanup if sample amounts permit, or data flagging with a technical explanation.

- if internal standard recovery is less than the acceptance criteria for the method blank or OPR, the entire extraction batch must be re-extracted (or the archive portion processed and re-analyzed).
- if the internal standard recovery is less than the acceptance criteria for a sample, that sample must be re-extracted (or the archive portion processed and re-analyzed).
- if the internal standard recovery is greater than the acceptance criteria, it is likely due to interference in the extract causing lock mass/recovery standard suppression. In this case, a dilution should be run as per EPA 1668A and/or 1668B, Section 18.5.1. and the post run calibration verified.
- if the dilution's internal standard recoveries are still high and the post calibration fails, a new calibration is performed and the extract is reanalyzed.
- however if it passes, results are flagged and reported.

8.4 Method Blank Analysis: analyze 1 per sample extraction batch, with batch sizes ≤ 20 samples

Method blanks should be $< \text{CS1 Calibration Standard concentration}$.

Method blanks **MUST** be $<$ the published EMLs in EPA 1668A and/or 1668B, Table 2.

NOTE: for DoD-ELAP samples, the method blank will be considered to be contaminated if:

- The concentration of any target analyte in the blank exceeds 1/2 the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater);
- The concentration of any common laboratory contaminant in the blank exceeds the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater); or
- The blank result otherwise affects the samples results as per the test method requirements or the project-specific objectives

Note: The appropriate EMLs are published in EPA 1668A and/or 1668B, Table 2. It should be noted that the last column of that table (pg/uL in extract) must be divided by 5 when comparing our method blanks using that column (ie for air samples) since we use 100 uL of extract rather than 20 uL.

8.4.1 Corrective Actions:

- investigate possible source of contamination by checking at a minimum: instrument Spike Standard Solutions, Recovery Standards, proofing of glassware, proofing of solvent and absorbents used in clean-up
- if the CS1 criteria above are not met, the extraction process should be investigated for sources of contamination. Data can still be accepted provided that the other criteria are met.
- if the EML criteria are not met, the extraction process must stop until the source of contamination is found. All of the samples in the extraction batch affected must be re-prepared and reanalyzed
- if sufficient sample is not available then any positive sample data must be flagged as possibly contaminated to the level found in the Method Blank.

Note: a written explanation of the problem and potential data quality impact must be supplied.

8.5 Laboratory Duplicates: analyze on a randomly selected sample at a frequency of 1 in 20 or 1 per sample batch if projects require. If a MS and MSD are performed on a given sample, this analysis need not be conducted.

$$\text{RPD (\%)} = \frac{(1^{\text{st}} \text{ sample result} - \text{duplicate result}) \times 100}{(1^{\text{st}} \text{ sample result} + \text{duplicate result})/2}$$

RPD must be \leq 30%

8.5.1 Corrective Actions:

- check calculations for errors
- check solid samples for homogeneity; if not homogeneous, flag the data in Tester's Comments
- if the sample is homogeneous, re-prepare and reanalyze the sample

8.6 Matrix Spike/Matrix Spike Duplicate Recoveries: two separate sub-aliquots of a randomly selected sample in each batch of 20 or less is spiked with an appropriate level, (depending upon expected sample concentration expectations), of congeners. Spike at a level 2-5X higher than the sample if possible. If a regulatory limit is involved, spike at the regulatory limit. If there is insufficient sample, this step may be omitted.

$$\text{Spike Recovery (\%)} = \frac{\text{Spiked Sample Result} - \text{Sample Result} \times 100}{\text{Amount Spike Added}}$$

For EPA 1668A: Recoveries must be 50-150 %

For EPA 1668B: Recoveries must be within the limits outlined in Table 6.

%RPD between matrix spike and matrix spike duplicate must be $\leq 30\%$

8.6.1 Corrective Actions: if the above criteria are exceeded

- check calculations for errors
- flag the data or reanalyze if contractual issues require
- if the blank spike is acceptable then flag the data as a possible Matrix interference
- check solid samples for homogeneity, if not homogeneous, flag the data in Tester's Comments

8.7 Ongoing Precision and Recovery: analyze the extract of the ongoing precision and recovery, (OPR), aliquot prior to analysis of samples from the same batch. Compute the concentration of each native congener by isotope dilution for those compounds that have labeled analogs. Compute the concentration of the native congeners that have no labeled analog. Compute the concentration for each labeled compound by the internal standard method.

For EPA 1668A:

Concentrations of native materials must be within 50-150%.

Internal standard recoveries must meet the defined criteria in Table 6A

For EPA 1668B:

Native and Internal standard recoveries must be within the limits outlined in Table 6B

8.8 Chromatographic Criteria: the chromatographic criteria outlined in Section 7.2.3 must be met prior to beginning analysis. In addition, these criteria must be met on an ongoing basis and can be determined from retention times of internal standards throughout runs. Daily changes of retention time are most often required and window changes are made on the basis of results of the 209 congener mix run in the last batch.

8.8.1 Mass Resolution: mass resolution must meet the following criteria

The resolution must be $\geq 10,000$ for the center m/z and must be $\geq 8,000$ for the low and high m/z 's.

8.9 Control Charts: Refer to COR WI-00055 Control Charting procedure for generating control charts via MaxLIMS and real time (i.e., plotted manually, each time the QC sample and/or standard is analyzed). Plot the blank spike data for PCB 77, PCB 180, PCB 126 and PCB 169 on separate control charts as per matrix. Update the chart immediately after the analysis of the QC point used or in the

morning after an overnight run, prior to reporting of data. Monitor the chart for the development of trends on the chart. Take actions, if necessary, as defined in the SOP for Control Charting. If an "Out of Control" point is found but meets method criteria, the root cause is investigated, documented and solved. Note the resolution directly on the chart or code the point to a reference in the analyst's workbook.

8.9.1 Possible Causes:

- deterioration of standard or reagents
- standard, QC sample or reagent preparation error
- standard contamination or evaporation
- improper sample introduction
- poor analyst technique or insufficient training
- deviation from SOP procedure
- imprecise measuring devices, i.e. pipettors, syringes

8.9.2 Corrective Actions: if "out of control points" are encountered

- check the other run QC, if acceptable report the data
- if not acceptable, reanalyze the QC samples and if acceptable, report the data
- if not acceptable, find and resolve the cause, re-extract and reanalyze the samples
- if insufficient sample exists report the data, flagged as "out of statistical control"
- if hold times will be exceeded upon re-extraction and reanalysis, flag the data
- if no reason can be found, report the data as "out of statistical control", i.e. flag the data

8.10 Additional QC Requirements: the exact QC requirements for any given project should be discussed with the project manager to ensure that project contractual requirements are met. For example, certain regions of EPA require MDL verification studies, triplicate analysis and other special QC requirements not identified in this SOP.

9.0 DATA ANALYSIS:

9.1 Identification Criteria: the following criteria must be met for positive identification of an analyte

9.1.1 Peak Responses, (monitored ions):

MUST BE > 2.5 times the background noise level

9.1.2 Peak Area Ratios, (2 monitored molecular ions for each congener):

MUST BE within $\pm 15\%$ of theoretical, or $\pm 15\%$ of the ratio in the last CS3 injection (refer to EPA 1668A and/or 1668B, Section 16.3).

9.1.3 Congener Analysis: the peak must be within the chromatographic window established for elution of that particular homologue group. For specific congeners, peaks must co-elute with their isotopically labeled internal standard within $+3/-1$ seconds. For congeners without labeled internal standards, peak must be within ± 4 seconds of expected retention time, unless retention time shift is clearly

indicated by other compounds in the same chromatographic window, or retention times in the mixed congener standard.

9.1.4 Peak Maximums, (for the two monitored ions of each congener):

MUST maximize within ± 2 seconds of each other.

9.1.5 Estimated Maximum Possible Concentration (EMPC): for peaks meeting all other criteria except for ratios, EMPCs are calculated. In this case, the area is recalculated (factored up or down) to meet the classical ratio and the result is reported as < EMPC and flagged as NDR (Not Detected due to Ratio).

9.1.6 Interference From Higher Levels of Chlorination (LOC): in some cases, fragment ions from congeners at higher levels of chlorination may interfere with quantitation of co-eluting congeners at lower levels of chlorination. (See EPA 1668A and/or 1668B, Sections 16.5 and 18.1). In the worst case, false positives could result (sometimes even for congeners in the WHO list of toxic PCBs).

It is left to the experienced analyst to determine the presence or absence of a congener where these types of interferences are possible. If it is believed that a congener at a lower LOC is being significantly enhanced by fragments from a large co-eluting peak at higher LOC, the result for the lower LOC PCB may be reported as an EMPC.

In the case where fragments at higher levels of chlorination affect the identification or quantitation of PCB 169 such that the EMPC is higher than the EML published in EPA 1668A, the result should be confirmed by analysis of the sample on the 60 m DB-5 column (see Section 7.2.1 and Appendix Table 4 for analysis conditions).

9.1.7 Analyst Discretion: According to EPA 1668A and/or 1668B, Section 16.5, an experienced analyst must determine the presence or absence of the congener in cases where not all of the positive identification criteria have been met. In some cases (for example where the ion ratio of an added labeled compound does not meet the criteria due to excessive dilution or some matrix or anomalous effect) the result may be taken to be positive as per this disclaimer. In other cases where data impact is greater, for example a WHO list toxic congener at significant levels where one or more positive id criteria fail, further work must be done (i.e. dilution and/or re-injection of extract).

9.2 Data Calculations:

9.2.1 Isotope Dilution Quantitation: by adding a known amount of a labeled compound to every sample prior to extraction, correction for recovery of the congener can be made because the native compound and its labeled analog behave similarly during extraction, concentration, and gas chromatography. Relative response, (RR), values, as defined in Section 7.2.5, are used in conjunction with Selected Ion Current Profile, (SICP), or chromatographically determined peak areas from an injected extract to determine concentrations directly, using the following equation:

$$C_{\text{ex}} \text{ (ng/mL)} = \frac{(A_{1_n} + A_{2_n}) C_1}{(A_{1_1} + A_{2_1}) \text{ RR}}$$

where:

C_{ex} = the concentration of the congener in the extract

$A1_n$ and $A2_n$ = The areas of the primary and secondary m/z's for the congener

$A1_l$ and $A2_l$ = The areas of the primary and secondary m/z's for the labeled compound.

C_l = The concentration of the labeled compound in the extract, (Table 1)

RR = relative response value, See formula in Section 7.2.5

9.2.2 Internal Standard Quantitation and Labeled Compound Recovery: compute the concentrations of labeled analogs, (including the cleanup standard), in the extract using the response factors determined from the initial calibration data and the following equation:

$$C_{ex} \text{ (ng/mL)} = \frac{(A1_s + A2_s) C_{is}}{(A1_{is} + A2_{is}) RF}$$

where:

C_{ex} = the concentration of the congener in the extract

$A1_s$ and $A2_s$ = areas of the primary and secondary m/z's for the congener

$A1_{is}$ and $A2_{is}$ = areas of the primary and secondary m/z's for the internal standard.

C_{is} = concentration of the internal standard, (Table 1).

RF = response factor, see formula in Section 7.2.5.3

Using the concentration in the extract determined above, compute the percent recovery of the labeled compounds, (including the cleanup standard), using the following equation:

$$\text{Recovery (\%)} = \frac{\text{Concentration found (ug/mL)} * 100}{\text{Concentration spiked (ug/mL)}}$$

The appropriate recovery standard for each labeled internal standard is identified in Table 2.

9.2.3 Solid/ Food/Tissue Samples Calculation: the concentration of a native congener in the solid phase of the sample is computed as follows (see Method 1668A, Section 11.2.2.3)

$$\text{Concentration in solid (ng/kg)} = \frac{(C_{EX} \times V_{EX})}{W_S}$$

where:

C_{EX} = concentration of the compound in the extract in ng/mL

V_{EX} = extract volume in mL

W_S = sample weight, (dry weight), in kg

9.2.4 Aqueous Sample Calculation: the concentration of a native congener in the aqueous phase of the sample is computed using the concentration of the compound in the extract and the volume of water extracted as follows:

$$\text{Concentration in aqueous phase, (ng/L)} = \frac{(C_{EX} \times V_{EX})}{W_S}$$

where:

C_{EX} = concentration of the compound in the extract in ng/mL

V_{EX} = extract volume in mL

W_S = sample volume in liters

9.2.5 Dilutions: if the SIPC area or height at either quantitation m/z for any compound exceeds the calibration range of the system, the sample may be diluted appropriately to bring the value into calibration range. If this involves significant dilution such that internal standard recoveries can no longer be determined, then a smaller sample aliquot must be extracted. Results for congeners in samples that have been diluted are reported at the least dilute level at which the areas at the quantitation m/z's are within the calibration range.

9.2.6 Total Homologue Calculation: the total concentration of all congeners in a given homologue series, (i.e., total TCB, total PeCB, total HxCB, etc.), may be reported by summing the concentrations of all congeners identified in that level of chlorination, including both the toxic and other congeners. In this case, the sum of all congeners from a specific homologue group are summed from the individual calculations and reported.

9.3 Data Transfer: An excel worksheet is created for each analytical run using a macro generated in house. This worksheet summarizes all the peak areas for the analytes detected, the retention times of the quantitation and confirmation ions along with their ratios as well as the calculated concentrations. A qualified individual checks each sample data file for missed peaks and proper integration and also calculates an MDL for the mass spectra channel. Dilutions and dry weights, if necessary, are also incorporated into the calculated concentrations.

All final data, including all supporting QC data, i.e. method blank, blank spike and matrix spike are posted to LIMS using a custom upload macro and the Superinterface.

9.4 Data Validation: Refer to BRL WI-00011 Review and Validation of Analytical Data and corresponding Data Review Checklist (BRL FCD-00002) to perform a primary and a secondary analytical data review and validation prior to issuance of the Certificate of Analysis. If the data and report are acceptable the Certificate of Analysis is signed by the Project Manager and sent to the client.

9.5 Data Acquisition and Storage: MS data shall be collected, recorded, and stored.

9.5.1 Data Acquisition: the signal at each exact m/z shall be collected repetitively throughout the monitoring period and stored on a mass storage device.

9.5.2 Response Factors and Multi-Point Calibrations: the data system is used to record and maintain lists of response factors, (response ratios for isotope dilution), and multi-point calibration curves. Computations of relative standard deviation, (coefficient of variation), shall be used to test calibration linearity. Statistics on initial performance and ongoing performance are computed and maintained, either on the instrument computer or on a separate computer.

9.6 Reporting Levels and Units: As noted in Section 3.2 of this procedure, Maxxam reports results using a different approach than the manner prescribed by EPA 1668A and/or 1668B:

9.6.1 Maxxam Procedure:

- all results are reported that meet positive id criteria, down to the level of the estimated MDL for that congener and homologue group (See Section 3.2 for estimation of MDL)
- consequently, reported results may not only be lower than EPA 1668A and/or 1668B EMLs, but often lower than CS1 level too
- results are reported in this way with the assumed understanding that levels below EPA 1668A and/or 1668B EMLs may not be environmentally significant, and may contain a normal but unknown element of laboratory interference
- we report aqueous sample results as ng/L, solids as ng/g, and air as total ng (all results to 3 decimal places)

10.0 DOCUMENTATION:

10.1 Tracking Sheet: before samples are prepared, a GC-MS sample tracking /work sheet is completed. This sheet includes details of the Job number, lab sample number, client sample ID, QC samples analyzed in the batch, spiking solutions used and their concentrations, preparation date and lot #, dates of analysis and cleanup, analyst's initials. A copy of the tracking /work sheet is maintained with analytical data.

10.2 Instrument Logbook:

- Troubleshooting records with full descriptions of the actions taken to resolve the problem. This is required for all instances in which there is an acceptance criteria that is not achieved. Alternatively these may also be recorded on a separate tracking sheet designed for the analysis.
- Record of Instrument Service by the Supplier with the associated paperwork

10.3 Method Deviation Records: instances may arise in which the standard operating procedure may not be applicable to the nature of the sample and may require modifications to the normal methodology. These deviations must be discussed with the Supervisor or Operation Manager prior to application. Approval must be obtained as per COR WI-00040 and documented using CompliantPro module for Policy Deviation Form. These deviations must also be described in the comment section of MaxxLIMS.

10.3.1 Sample Deviation Records: these deviations must be recorded in MaxxLIMS Comments, a Bench Level Deviation /Non-conformance Form, CAM FCD-00328 can be used to document sample deviations.

10.4 Maintenance Tracking: analysts maintain logbooks/tracking sheets to include the following minimum information

- record of Instrument Service by the Supplier with the associated paperwork
- records of all maintenance performed indicating the date performed and by who

10.5 Standard and Reagent Preparation Tracking: record all preparations of standards and reagents in the Standard Preparation and the Reagent Preparation Logbooks. All records must contain at a minimum the following information

- Supplier Identification and Lot Number
- Date of Preparation and Expiry
- Concentration, and name of Analyst who prepared the standard

10.6 Certificates of Analysis for Standards and Reagents: certificate of analyses are kept for all inorganic salts and solutions utilized in this SOP. These records will contain at a minimum the following information.

- supplier information and Lot Number
- date received

10.7 Storage of Records:

10.7.1 Paper Records: raw and calculated data, including calibrations and QC results are stored chronologically in file folders in the laboratory. These files are archived on-site for a period of one year and then transferred to an off-site storage for 5 years, unless otherwise instructed.

10.7.2 Electronic Media: data entered into LIMS is backed up daily.

11.0 WASTE MANAGEMENT:

All efforts are taken to prevent or reduce to a minimum the effect of waste disposal on the environment. All solvents are collected for shipment to a recycling facility. All recyclable plastic, glass and paper products are shipped to an appropriate recycling facility. The disposal of waste materials and samples are to be carried out in accordance with protocols outlined in CAM SOP-00105 and CAM WI-00018. All waste disposals will comply with the Ontario Ministry of the Environment and Energy's Sewer Guidelines and Regulation 558.

11.1 Specific Disposal Issues:

11.1.1 High PCB Samples: samples exceeding the criteria below are labeled with a bright orange sticker, indicating "CAUTION DO NOT DISPOSE". The concentration of PCBs found must be written on the label. They are disposed of as per CAM WI-00018.

Total PCB in Oils >50 ppm

Total PCB in Soils >50 mg/kg

12.0 APPENDIX - Tables:

Table 1: Concentration of Stock/Spiking Solutions Containing Chlorinated Biphenyls and Labeled Compounds

Table 2: Concentration of Chlorinated Biphenyls in Calibration and Calibration Verification Solutions

Table 3: GC Retention Time Window Defining Solution Congener Analysis, Functions 1 to 7 and PCB 169

Table 4: Toxic Confirmation Analysis (1 Function), Example included as Attachment 1.

Table 5: Theoretical Ion Abundance Ratios and QC limits

Table 6: QC Acceptance Criteria for Chlorinated Biphenyls in VER, IPR, OPR and Samples

Table 7: Retention Times (RT), RT References and Quantitation References

Table 8: PCB Congeners

Table 9: PCB Homologues

Attachment 1: Mass Descriptors for Total Homologue (7 Function)

Attachment 2: PCB Separation Documentation

Table 1:

**Concentrations of Native and Labeled Chlorinated Biphenyls in
Stock Solutions, Spiking Solutions and Final Extracts**

CB CONGENER	IUPAC ¹	STOCK ($\mu\text{g/mL}$)	SPIKING ($\text{ng}/\mu\text{L}$)	EXTRACT (ng/mL)
NATIVE STANDARDS				
2-MoCB	1	20	0.1	50
4-MoCB	3	20	0.1	50
2,2'-DiCB	4	20	0.1	50
4,4'-DiCB	15	20	0.1	50
2,2',6'-TrCB	19	20	0.1	50
3,4,4'-TrCB	37	20	0.1	50
2,2',6,6'-TeCB	54	20	0.1	50
3,3',4,4'-TeCB	77	20	0.1	50
3,4,4',5-TeCB	81	20	0.1	50
2,2',4,6,6'-PeCB	104	20	0.1	50
2,3,3',4,4'-PeCB	105	20	0.1	50
2,3,4,4',5-PeCB	114	20	0.1	50
2,3',4,4',5-PeCB	118	20	0.1	50
2',3,4,4',5-PeCB	123	20	0.1	50
3,3',4,4',5-PeCB	126	20	0.1	50
2,2',4,4',6,6'-HxCB	155	20	0.1	50
2,3,3',4,4',5-HxCB	156	20	0.1	50
2,3,3',4,4',5-HxCB	157	20	0.1	50
2,3',4,4',5,5'-HxCB	167	20	0.1	50
3,3',4,4',5,5'-HxCB	169	20	0.1	50
2,2',3,3',4,4',5-HpCB	170	20	0.1	50
2,2',3,4,4',5,5'-HpCB	180	20	0.1	50
2,2',3,4',5,6,6'-HpCB	188	20	0.1	50
2,3,3',4,4',5,5'-HpCB	189	20	0.1	50
2,2',3,3',5,5',6,6'-OoCB	202	20	0.1	50
2,3,3',4,4',5,5',6-OoCB	205	20	0.1	50
2,2',3,3',4,4',5,5',6-NoCB	206	20	0.1	50
2,2',3,3',4',5,5',6,6'-NoCB	208	20	0.1	50
DeCB	209	20	0.1	50

Table 1: Continued
Concentrations of Native and Labeled Chlorinated Biphenyls in
Stock Solutions, Spiking Solutions and Final Extracts

CB CONGENER	IUPAC ¹	STOCK (µg/mL)	SPIKING (ng/µL)	EXTRACT (ng/mL)
INTERNAL STANDARDS				
13C12-2-MoCB	1L	50	0.4	100
13C12-4-MoCB	3L	50	0.4	100
13C12-2,2'-DiCB	4L	50	0.4	100
13C12-4,4'-DiCB	15L	50	0.4	100
13C12-2,2',6'-TrCB	19L	50	0.4	100
13C12-3,4,4'-TrCB	37L	50	0.4	100
13C12-2,2',6,6'-TeCB	54L	50	0.4	100
13C12-3,3',4,4'-TeCB	77L	50	0.4	100
13C12-3,4,4',5'-TeCB	81L	50	0.4	100
13C12-2,2',4,6,6'-PeCB	104L	50	0.4	100
13C12-2,3,3',4,4'-PeCB	105L	50	0.4	100
13C12-2,3,4,4',5'-PeCB	114L	50	0.4	100
13C12-2,3',4,4',5'-PeCB	118L	50	0.4	100
13C12-2',3,4,4',5'-PeCB	123L	50	0.4	100
13C12-3,3',4,4',5'-PeCB	126L	50	0.4	100
13C12-2,2',4,4',6,6'-HxCB	155L	50	0.4	100
13C12-2,3,3',4,4',5'-HxCB	156L	50	0.4	100
13C12-2,3,3',4,4',5',5'-HxCB	157L	50	0.4	100
13C12-2,3',4,4',5,5'-HxCB	167L	50	0.4	100
13C12-3,3',4,4',5,5'-HxCB	169L	50	0.4	100
13C12-2,2',3,3',4,4',5'-HpCB	170L	50	0.4	100
13C12-2,2',3,4,4',5,5'-HpCB	180L	50	0.4	100
13C12-2,2',3,4',5,6,6'-HpCB	188L	50	0.4	100
13C12-2,3,3',4,4',5,5'-HpCB	189L	50	0.4	100
13C12-2,2',3,3',5,5',6,6'-OxCB	202L	50	0.4	100
13C12-2,3,3',4,4',5,5',6-OxCB	205L	50	0.4	100
13C12-2,2',3,3',4,4',5,5',6-NoCB	206L	50	0.4	100
13C12-2,2',3,3',4',5,5',6,6'-NoCB	208L	50	0.4	100
13C12-DeCB	209L	50	0.4	100
CLEANUP STANDARDS				
13C12-2,4,4'-TrCB	28L	50	0.4	100
13C12-2,3,3',5,5'-PeCB	111L	50	0.4	100
13C12-2,2',3,3',5,5',6'-HpCB	178L	50	0.4	100
RECOVERY STANDARDS				

13C12-2,5-DiCB	9L	5.0	1.0	100
13C12-2,2',5,5'-TeCB	52L	5.0	1.0	100
13C12-2,2',4',5,5'-PeCB	101L	5.0	1.0	100
13C12-2,2',3',4,4',5'-HxCB	138L	5.0	1.0	100
13C12-2,2',3,3',4,4',5,5'-OcCB	194L	5.0	1.0	100

1. Suffix "L" indicates labeled compound

Table 2:
Concentration of CB Congeners in Calibration and Calibration Verification Standards

CB CONGENER	IUPAC1	CS-1 (ng/mL)	CS-2 (ng/mL)	CS-3 (VER) (ng/mL)	CS-4 (ng/mL)	CS-5 (ng/mL)
NATIVE STANDARDS						
2-MoCB	1	1.0	5.0	50	400	2000
4-MoCB	3	1.0	5.0	50	400	2000
2,2'-DiCB	4	1.0	5.0	50	400	2000
4,4'-DiCB	15	1.0	5.0	50	400	2000
2,2',6'-TrCB	19	1.0	5.0	50	400	2000
3,4,4'-TrCB	37	1.0	5.0	50	400	2000
2,2',6,6'-TeCB	54	1.0	5.0	50	400	2000
3,3',4,4'-TeCB	77	1.0	5.0	50	400	2000
3,4,4',5-TeCB	81	1.0	5.0	50	400	2000
2,2',4,6,6'-PeCB	104	1.0	5.0	50	400	2000
2,3,3',4,4'-PeCB	105	1.0	5.0	50	400	2000
2,3,4,4',5-PeCB	114	1.0	5.0	50	400	2000
2,3',4,4',5-PeCB	118	1.0	5.0	50	400	2000
2',3,4,4',5-PeCB	123	1.0	5.0	50	400	2000
3,3',4,4',5-PeCB	126	1.0	5.0	50	400	2000
2,2',4,4',6,6'-HxCB	155	1.0	5.0	50	400	2000
2,3,3',4,4',5-HxCB	156	1.0	5.0	50	400	2000
2,3,3',4,4',5-HxCB	157	1.0	5.0	50	400	2000
2,3',4,4',5,5'-HxCB	167	1.0	5.0	50	400	2000
3,3',4,4',5,5'-HxCB	169	1.0	5.0	50	400	2000
2,2',3,3',4,4',5-HpCB	170	1.0	5.0	50	400	2000
2,2',3,4,4',5,5'-HpCB	180	1.0	5.0	50	400	2000
2,2',3,4',5,6,6'-HpCB	188	1.0	5.0	50	400	2000
2,3,3',4,4',5,5'-HpCB	189	1.0	5.0	50	400	2000

2,2',3,3',5,5',6,6'-O ₂ CB	202	1.0	5.0	50	400	2000
2,3,3',4,4',5,5',6-O ₂ CB	205	1.0	5.0	50	400	2000
2,2',3,3',4,4',5,5',6-NoCB	206	1.0	5.0	50	400	2000
2,2',3,3',4',5,5',6,6'-NoCB	208	1.0	5.0	50	400	2000
DeCB	209	1.0	5.0	50	400	2000

Table 2: Continued
Concentration of CB Congeners in Calibration and Calibration Verification Standards

CB CONGENER	IUPAC1	CS-1 (ng/mL)	CS-2 (ng/mL)	CS-3 (VER) (ng/mL)	CS-4 (ng/mL)	CS-5 (ng/mL)
INTERNAL STANDARDS						
13C12-2-MoCB	1L	100	100	100	100	100
13C12-4-MoCB	3L	100	100	100	100	100
13C12-2,2'-DiCB	4L	100	100	100	100	100
13C12-4,4'-DiCB	15L	100	100	100	100	100
13C12-2,2',6'-TrCB	19L	100	100	100	100	100
13C12-3,4,4'-TrCB	37L	100	100	100	100	100
13C12-2,2',6,6'-TeCB	54L	100	100	100	100	100
13C12-3,3',4,4'-TeCB	77L	100	100	100	100	100
13C12-3,4,4',5-TeCB	81L	100	100	100	100	100
13C12-2,2',4,6,6'-PeCB	104L	100	100	100	100	100
13C12-2,3,3',4,4'-PeCB	105L	100	100	100	100	100
13C12-2,3,4,4',5-PeCB	114L	100	100	100	100	100
13C12-2,3',4,4',5-PeCB	118L	100	100	100	100	100
13C12-2',3,4,4',5-PeCB	123L	100	100	100	100	100
13C12-3,3',4,4',5-PeCB	126L	100	100	100	100	100
13C12-2,2',4,4',6,6'-HxCB	155L	100	100	100	100	100
13C12-2,3,3',4,4',5-HxCB	156L	100	100	100	100	100
13C12-2,3,3',4,4',5'-HxCB	157L	100	100	100	100	100
13C12-2,3',4,4',5,5'-HxCB	167L	100	100	100	100	100
13C12-3,3',4,4',5,5'-HxCB	169L	100	100	100	100	100
13C12-2,2',3,3',4,4',5-HpCB	170L	100	100	100	100	100
13C12-2,2',3,4,4',5,5'-HpCB	180L	100	100	100	100	100
13C12-2,2',3,4',5,6,6'-HpCB	188L	100	100	100	100	100
13C12-2,3,3',4,4',5,5'-HpCB	189L	100	100	100	100	100
13C12-2,2',3,3',5,5',6,6'-OcCB	202L	100	100	100	100	100
13C12-2,3,3',4,4',5,5',6-OcCB	205L	100	100	100	100	100
13C12-2,2',3,3',4,4',5,5',6-NoCB	206L	100	100	100	100	100
13C12-2,2',3,3',4',5,5',6,6'-NoCB	208L	100	100	100	100	100
13C12-DeCB	209L	100	100	100	100	100
CLEANUP STANDARDS						
13C12-2,4,4'-TrCB	28L	100	100	100	100	100
13C12-2,3,3',5,5'-PeCB	111L	100	100	100	100	100
13C12-2,2',3,3',5,5',6-HpCB	178L	100	100	100	100	100
FIELD SPIKE STANDARDS						

13C12-2,4',5-TrCB	31L	100	100	100	100	100
13C12-2,2',3,5',6-PeCB	95L	100	100	100	100	100
13C12-2,2',4,4',5,5'-HxCB	153L	100	100	100	100	100

RECOVERY STANDARDS

13C12-2,5-DiCB	9L	100	100	100	100	100
13C12-2,2',5,5'-TeCB	52L	100	100	100	100	100
13C12-2,2',4',5,5'-PeCB	101L	100	100	100	100	100
13C12-2,2',3',4,4',5'-HxCB	138L	100	100	100	100	100
13C12-2,2',3,3',4,4',5,5'-OcCB	194L	100	100	100	100	100

1. Suffix "L" indicates labeled compound

Table 3:**GC Retention Time Window Defining Solution**

Congener Group		First eluted³		Last eluted
MoCB	1	2-	3	4-
DiCB	4	2,6	15	4,4'
TrCB	19	2,2',6	37	3,4,4'
TeCB	54	2,2',6,6'	77	3,3',4,4'
PeCB	104	2,2',4,6,6'	126	3,3',4,4',5
HxCB	155	2,2',4,4',6,6'	169	3,3',4,4',5,5'
HpCB	188	2,2',3,4',5,6',6'	189	2,3,3',4,4',5,5'
OcCB	202	2,2',3,3',5,5',6,6'	205	2,3,3',4,4',5,5',6
NoCB	208	2,2',3,3',4,5,5',6,6'	206	2,2',3,3',4,4',5,5',6
DeCB	209	2,2',3,3',4,4',5,5',6,6'	209	2,2',3,3',4,4',5,5',6,6'

1. All compounds are at a concentration of 100 ng/mL in iso-octane

Table 4:**Mass Descriptors for PCB Congener Analysis**

See Attachment 1 (7 functions)

Mass Descriptors for PCB 169 Confirmation Analysis:**1668ACONF_ULTA (1 Function)****Function 1**

Type : SIR Voltage
 Calibration file used : B1040830B
 High mass : 497.7
 Low mass : 331.0
 Resolution : 10000
 Ionization mode : EI+
 Accelerating Voltage : 8000.0V
 Magnet 1 control : Current
 Start Time : 23:00
 End Time : 26:00
 Fast lock : On
 Number of channels : 10
 Cycle time (ms) : 1000

Channel	Mass	Ch Time (ms)	Delay (ms)
1 (Lock)	330.9792	80	20
2	330.9792	80	20
3	359.8415	80	20
4	361.8385	80	20
5	371.8817	80	20
6	373.8788	80	20
7	393.8025	80	20
8	427.7635	80	20
9	461.7246	80	20
10	497.6828	80	20

Primary Span Lock (Peaks) 2.00
 Secondary Span Lock (Peaks) 1.00
 Lock Level (mV) 5
 Step Lock (Peaks) 0.020
 Septum flow : Off

Table 5:

Theoretical Ion Abundance Ratios and QC limits

Number of chlorine atoms	m/z's forming ratio	Theoretical ratio	QC limit	
			Lower	Upper
1	M/(M+2)	3.13	2.66	3.6
2	M/(M+2)	1.56	1.33	1.79
3	M/(M+2)	1.04	0.88	1.20
4	M/(M+2)	0.77	0.65	0.89
5, unlabelled	(M+2)/(M+4)	1.55	1.32	1.78
5, ¹³ C-labelled	M/(M+2)	0.62	0.53	0.71
6	M/(M+2)	0.51	0.43	0.59
6	(M+2)/(M+4)	1.24	1.05	1.43
7	M/(M+2)	0.44	0.37	0.51
7	(M+2)/(M+4)	1.05	0.88	1.20
8	(M+2)/(M+4)	0.89	0.76	1.02
9	(M+2)/(M+4)	0.77	0.65	0.89
10	(M+4)/(M+6)	1.20	1.04	1.38

Table 6A – EPA 1668A:

QC Acceptance Criteria for Chlorinated Biphenyls in VER, IPR, OPR and Samples¹

CB CONGENER	IUPAC ²	Test Conc (ng/mL) ³	VER ⁴ (%)	IPR		OPR (%)	Compound Recovery (Matrix Spike) (%)
				RSD (%)	X(%)		
NATIVE STANDARDS							
2-MoCB	1	50	70-130	40	60-140	50-150	50-150
4-MoCB	3	50	70-130	40	60-140	50-150	50-150
2,2'-DiCB	4	50	70-130	40	60-140	50-150	50-150
4,4'-DiCB	15	50	70-130	40	60-140	50-150	50-150
2,2',6'-TrCB	19	50	70-130	40	60-140	50-150	50-150
3,4,4'-TrCB	37	50	70-130	40	60-140	50-150	50-150
2,2',6,6'-TeCB	54	50	70-130	40	60-140	50-150	50-150
3,3',4,4'-TeCB	77	50	70-130	40	60-140	50-150	50-150
3,4,4',5-TeCB	81	50	70-130	40	60-140	50-150	50-150
2,2',4,6,6'-PeCB	104	50	70-130	40	60-140	50-150	50-150
2,3,3',4,4'-PeCB	105	50	70-130	40	60-140	50-150	50-150
2,3,4,4',5-PeCB	114	50	70-130	40	60-140	50-150	50-150
2,3',4,4',5-PeCB	118	50	70-130	40	60-140	50-150	50-150
2',3,4,4',5-PeCB	123	50	70-130	40	60-140	50-150	50-150
3,3',4,4',5-PeCB	126	50	70-130	40	60-140	50-150	50-150
2,2',4,4',6,6'-HxCB	155	50	70-130	40	60-140	50-150	50-150
2,3,3',4,4',5-HxCB	156	50	70-130	40	60-140	50-150	50-150
2,3,3',4,4',5-HxCB	157	50	70-130	40	60-140	50-150	50-150
2,3',4,4',5,5'-HxCB	167	50	70-130	40	60-140	50-150	50-150
3,3',4,4',5,5'-HxCB	169	50	70-130	40	60-140	50-150	50-150
2,2',3,3',4,4',5-HpCB	170	50	70-130	40	60-140	50-150	50-150
2,2',3,4,4',5,5'-HpCB	180	50	70-130	40	60-140	50-150	50-150
2,2',3,4',5,6,6'-HpCB	188	50	70-130	40	60-140	50-150	50-150
2,3,3',4,4',5,5'-HpCB	189	50	70-130	40	60-140	50-150	50-150
2,2',3,3',5,5',6,6'- OcCB	202	50	70-130	40	60-140	50-150	50-150
2,3,3',4,4',5,5',6-OcCB	205	50	70-130	40	60-140	50-150	50-150
2,2',3,3',4,4',5,5',6- NoCB	206	50	70-130	40	60-140	50-150	50-150
2,2',3,3',4',5,5',6,6'- NoCB	208	50	70-130	40	60-140	50-150	50-150
DeCB	209	50	70-130	40	60-140	50-150	50-150

Table 6A – EPA 1668A: Continued

QC Acceptance Criteria for Chlorinated Biphenyls in VER, IPR, OPR and Samples¹

CB CONGENER	IUPAC ²	Test Conc (ng/mL) ₃	VER ⁴ (%)	IPR		OPR (%)	Compound Recovery (Sample) (%)
				RSD (%)	X(%)		
INTERNAL STANDARDS							
13C12-2-MoCB	1L	100	50-150	50	20-135	15-140	15-150
13C12-4-MoCB	3L	100	50-150	50	20-135	15-140	15-150
13C12-2,2'-DiCB	4L	100	50-150	50	35-135	30-140	25-150
13C12-4,4'-DiCB	15L	100	50-150	50	35-135	30-140	25-150
13C12-2,2',6'-TrCB	19L	100	50-150	50	35-135	30-140	25-150
13C12-3,4,4'-TrCB	37L	100	50-150	50	35-135	30-140	25-150
13C12-2,2',6,6'-TeCB	54L	100	50-150	50	35-135	30-140	25-150
13C12-3,3',4,4'-TeCB	77L	100	50-150	50	35-135	30-140	25-150
13C12-3,4,4',5'-TeCB	81L	100	50-150	50	35-135	30-140	25-150
13C12-2,2',4,6,6'-PeCB	104L	100	50-150	50	35-135	30-140	25-150
13C12-2,3,3',4,4'-PeCB	105L	100	50-150	50	35-135	30-140	25-150
13C12-2,3,4,4',5'-PeCB	114L	100	50-150	50	35-135	30-140	25-150
13C12-2,3',4,4',5'-PeCB	118L	100	50-150	50	35-135	30-140	25-150
13C12-2',3,4,4',5'-PeCB	123L	100	50-150	50	35-135	30-140	25-150
13C12-3,3',4,4',5'-PeCB	126L	100	50-150	50	35-135	30-140	25-150
13C12-2,2',4,4',6,6'-HxCB	155L	100	50-150	50	35-135	30-140	25-150
13C12-2,3,3',4,4',5'-HxCB	156L	100	50-150	50	35-135	30-140	25-150
13C12-2,3,3',4,4',5'-HxCB	157L	100	50-150	50	35-135	30-140	25-150
13C12-2,3',4,4',5,5'-HxCB	167L	100	50-150	50	35-135	30-140	25-150
13C12-3,3',4,4',5,5'-HxCB	169L	100	50-150	50	35-135	30-140	25-150
13C12-2,2',3,3',4,4',5'-HpCB	170L	100	50-150	50	35-135	30-140	25-150
13C12-2,2',3,4,4',5,5'-HpCB	180L	100	50-150	50	35-135	30-140	25-150
13C12-2,2',3,4',5,6,6'-HpCB	188L	100	50-150	50	35-135	30-140	25-150
13C12-2,3,3',4,4',5,5'-HpCB	189L	100	50-150	50	35-135	30-140	25-150
13C12-2,2',3,3',5,5',6,6'-OoCB	202L	100	50-150	50	35-135	30-140	25-150
13C12-2,3,3',4,4',5,5',6'-OoCB	205L	100	50-150	50	35-135	30-140	25-150
13C12-2,2',3,3',4,4',5,5',6'-NoCB	206L	100	50-150	50	35-135	30-140	25-150
13C12-2,2',3,3',4',5,5',6,6'-NoCB	208L	100	50-150	50	35-135	30-140	25-150
13C12-DeCB	209L	100	50-150	50	35-135	30-140	25-150

CLEANUP STANDARDS

13C12-2,4,4'-TrCB	28L	100	60-130	45	45-120	40-125	30-135
13C12-2,3,3',5,5'-PeCB	111L	100	60-130	45	45-120	40-125	30-135
13C12-2,2',3,3',5,5',6-HpCB	178L	100	60-130	45	45-120	40-125	30-135

1. QC acceptance criteria for IPR, OPR and samples based on a 20 μ L extract final volume.
2. Suffix "L" indicates labeled compound.
3. See Table 5.
4. Section 15.3.
5. CBs 156 and 157 are tested as the sum of the two congeners.

Table 6B-EPA 1668B
QC acceptance criteria for VER, IPR, OPR, and labeled compounds in samples 1,2

CB CONGENER	IUPAC ²	Test Conc (ng/mL) ³	VER ⁴ (%)	IPR		OPR (%)	Compound Recovery (Matrix Spike) (%)
				RSD (%)	X(%)		
NATIVE STANDARDS							
2-MoCB	1	50	70-130	25	84-119	71-132	NA
4-MoCB	3	50	70-130	22	83-112	72-123	NA
2,2'-DiCB	4	50	70-130	18	82-105	73-114	NA
4,4'-DiCB	15	50	70-130	17	85-107	76-116	NA
2,2',6'-TrCB	19	50	70-130	13	86-103	79-109	NA
3,4,4'-TrCB	37	50	70-130	26	77-109	64-122	NA
2,2',6,6'-TeCB	54	50	70-130	17	84-106	76-114	NA
3,3',4,4'-TeCB	77	50	70-130	20	81-106	71-116	NA
3,4,4',5-TeCB	81	50	70-130	20	81-106	70-116	NA
2,2',4,6,6'-PeCB	104	50	70-130	19	83-107	74-117	NA
2,3,3',4,4'-PeCB	105	50	70-130	19	83-107	73-117	NA
2,3,4,4',5-PeCB	114	50	70-130	18	83-105	74-113	NA
2,3',4,4',5-PeCB	118	50	70-130	13	88-105	81-112	NA
2',3,4,4',5-PeCB	123	50	70-130	16	82-102	74-109	NA
3,3',4,4',5-PeCB	126	50	70-130	17	82-104	74-113	NA
2,2',4,4',6,6'-HxCB	155	50	70-130	15	86-105	79-112	NA
2,3,3',4,4',5-HxCB	156	50	70-130	16	87-108	78-117	NA
2,3,3',4,4',5-HxCB	157	50	70-130	16	87-108	78-117	NA
2,3',4,4',5,5'-HxCB	167	50	70-130	13	85-101	79-107	NA
3,3',4,4',5,5'-HxCB	169	50	70-130	16	80-100	73-108	NA
2,2',3,4',5,6,6'-HpCB	188	50	70-130	14	88-106	81-113	NA
2,3,3',4,4',5,5'-HpCB	189	50	70-130	16	85-106	77-114	NA
2,2',3,3',5,5',6,6'- OcCB	202	50	70-130	17	82-104	74-112	NA
2,3,3',4,4',5,5',6-OcCB	205	50	70-130	15	87-107	79-115	NA
2,2',3,3',4,4',5,5',6- NoCB	206	50	70-130	17	85-106	76-115	NA
2,2',3,3',4',5,5',6,6'- NoCB	208	50	70-130	17	86-108	77-116	NA
DeCB	209	50	70-130	20	81-106	71-116	NA

Table 6B- EPA 1668B: continued.
QC acceptance criteria for VER, IPR, OPR, and labeled compounds in samples 1,

CB CONGENER	IUPAC ²	Test Conc (ng/mL) ₃	VER ⁴ (%)	IPR		OPR (%)	Compound Recovery (Sample) (%)
				RSD (%)	X(%)		
INTERNAL STANDARDS							
13C12-2-MoCB	1L	100	50-150	78	21-100	2-100	4-100
13C12-4-MoCB	3L	100	50-150	63	31-100	13-100	11-106
13C12-2,2'-DiCB	4L	100	50-150	56	35-100	18-100	14-107
13C12-4,4'-DiCB	15L	100	50-150	70	34-100	10-118	19-107
13C12-2,2',6'-TrCB	19L	100	50-150	68	32-100	10-106	1-108
13C12-3,4,4'-TrCB	37L	100	50-150	57	47-104	24-128	25-123
13C12-2,2',6,6'-TeCB	54L	100	50-150	62	37-100	16-111	13-105
13C12-3,3',4,4'-TeCB	77L	100	50-150	35	57-100	43-105	31-109
13C12-3,4,4',5'-TeCB	81L	100	50-150	33	57-100	44-102	14-127
13C12-2,2',4,6,6'-PeCB	104L	100	50-150	48	49-100	30-115	36-115
13C12-2,3,3',4,4'-PeCB	105L	100	50-150	31	66-101	52-116	50-111
13C12-2,3,4,4',5'-PeCB	114L	100	50-150	41	57-100	39-117	41-121
13C12-2,3',4,4',5'-PeCB	118L	100	50-150	33	65-102	51-117	49-111
13C12-2',3,4,4',5'-PeCB	123L	100	50-150	32	66-103	52-118	49-116
13C12-3,3',4,4',5'-PeCB	126L	100	50-150	29	67-100	54-113	50-106
13C12-2,2',4,4',6,6'-HxCB	155L	100	50-150	42	58-103	40-121	25-124
13C12-2,3,3',4,4',5'-HxCB	156L	100	50-150	35	61-100	46-115	40-120
13C12-2,3,3',4,4',5'-HxCB	157L	100	50-150	35	61-100	46-115	40-120
13C12-2,3',4,4',5,5'-HxCB	167L	100	50-150	24	74-103	63-115	45-118
13C12-3,3',4,4',5,5'-HxCB	169L	100	50-150	33	66-103	51-117	37-117
13C12-2,2',3,4',5,6,6'-HpCB	188L	100	50-150	47	53-102	33-121	23-125
13C12-2,3,3',4,4',5,5'-HpCB	189L	100	50-150	28	68-100	55-112	47-116
13C12-2,2',3,3',5,5',6,6'-OcCB	202L	100	50-150	50	59-113	33-136	31-134
13C12-2,3,3',4,4',5,5',6-OcCB	205L	100	50-150	21	70-100	61-103	46-115
13C12-2,2',3,3',4,4',5,5',6-NoCB	206L	100	50-150	29	64-100	51-107	38-122
13C12-2,2',3,3',4',5,5',6,6'-NoCB	208L	100	50-150	32	62-100	48-111	31-126
13C12-DeCB	209L	100	50-150	30	65-100	52-111	43-115

CLEANUP STANDARDS

13C12-2,4,4'-TrCB	28L	100	60-130	63	43-106	18-131	14-131
13C12-2,3,3',5,5'-PeCB	111L	100	60-130	23	75-102	64-113	57-112
13C12-2,2',3,3',5,5',6-HpCB	178L	100	60-130	30	78-117	62-133	57-125

- 1 QC acceptance criteria for IPR, OPR and samples based on a 20 µL extract final volume.
- 2 Suffix "L" indicates labeled compound.
- 3 See Table 5.
- 4 Section 15.3.
- 5 CBs 156 and 157 are tested as the sum of the two congeners.
- 6 For EPA 1668B, if PCB-170 and PCB-180 are included, Maxxam will use EPA 1668A QC acceptance criteria for VER, IPR, OPR and Samples.

**Table 7:
Retention Times (RT), RT References and Quantitation References**

CI # (1)	IUPAC # (2,3)	Retention Time Ref. (4)	Quantitation Reference (5)
Compounds using 9L (13C12-2,5-DiCB) as Labeled injection internal standard			
CB Congener			
Monochlorobiphenyls			
1	1	1L	1L
1	2	3L	1L/3L
1	3	3L	3L
Dichlorobiphenyls			
2	4	4L	4L
2	10	4L	4L/15L
2	9	4L	4L/15L
2	7	4L	4L/15L
2	6	4L	4L/15L
2	5	4L	4L/15L
2	8	4L	4L/15L
2	14	15L	4L/15L
2	11	15L	4L/15L
2	13	15L	4L/15L
2	12	15L	4L/15L
2	13/12	15L	4L/15L
2	15	15L	15L
Trichlorobiphenyls			
3	19	19L	19L
3	30	19L	19L/37L
3	18	19L	19L/37L
3	30/18	19L	19L/37L
3	17	19L	19L/37L
3	27	19L	19L/37L
3	24	19L	19L/37L
3	16	19L	19L/37L
3	32	19L	19L/37L
3	34	19L	19L/37L
3	23	19L	19L/37L
3	29	19L	19L/37L
3	26	19L	19L/37L
3	26/29	19L	19L/37L
3	25	37L	19L/37L
3	31	37L	19L/37L
3	28	37L	19L/37L
3	20	37L	19L/37L
3	28/20	37L	19L/37L
3	21	37L	19L/37L

Table 7: continued

Retention Times (RT), RT References and Quantitation References

CI # (1)	IUPAC # (2,3)	Retention Time Ref. (4)	Quantitation Reference (5)
3	33	37L	19L/37L
3	21/33	37L	19L/37L
3	22	37L	19L/37L
3	36	37L	19L/37L
3	39	37L	19L/37L
3	38	37L	19L/37L
3	35	37L	19L/37L
3	37	37L	37L

Labeled Compounds

1	1L	9L	9L
1	3L	9L	9L
2	4L	9L	9L
2	15L	9L	9L
3	19L	9L	9L
3	37L	52L	52L

Compounds using 52L (13C12-2,2',5,5'-TeCB) as Labeled injection internal standard

CB Congener

Tetrachlorobiphenyls

4	54	54L	54L
4	50	54L	54L/81L/77L
4	53	54L	54L/81L/77L
4	50/53	54L	54L/81L/77L
4	45	54L	54L/81L/77L
4	51	54L	54L/81L/77L
4	45/51	54L	54L/81L/77L
4	46	54L	54L/81L/77L
4	52	54L	54L/81L/77L
4	73	54L	54L/81L/77L
4	43	54L	54L/81L/77L
4	69	54L	54L/81L/77L
4	49	54L	54L/81L/77L
4	69/49	54L	54L/81L/77L
4	48	54L	54L/81L/77L
4	65	54L	54L/81L/77L
4	47	54L	54L/81L/77L
4	44	54L	54L/81L/77L
4	44/47/65	54L	54L/81L/77L
4	62	54L	54L/81L/77L
4	75	54L	54L/81L/77L
4	59	54L	54L/81L/77L
4	59/62/75	54L	54L/81L/77L

Table 7: continued

Retention Times (RT), RT References and Quantitation References

CI # (1)	IUPAC # (2,3)	Retention Time Ref. (4)	Quantitation Reference (5)
4	42	54L	54L/81L/77L
4	41	54L	54L/81L/77L
4	71	54L	54L/81L/77L
4	40	54L	54L/81L/77L
4	41/40/71	54L	54L/81L/77L
4	64	54L	54L/81L/77L
4	72	81L	54L/81L/77L
4	68	81L	54L/81L/77L
4	57	81L	54L/81L/77L
4	58	81L	54L/81L/77L
4	67	81L	54L/81L/77L
4	63	81L	54L/81L/77L
4	61	81L	54L/81L/77L
4	70	81L	54L/81L/77L
4	76	81L	54L/81L/77L
4	74	81L	54L/81L/77L
4	61/70/74/76	81L	54L/81L/77L
4	66	81L	54L/81L/77L
4	55	81L	54L/81L/77L
4	56	81L	54L/81L/77L
4	60	81L	54L/81L/77L
4	80	81L	54L/81L/77L
4	79	81L	54L/81L/77L
4	78	81L	54L/81L/77L
4	81	81L	81L
4	77	77L	77L

Labeled compounds

4	54L	52L	52L
4	81L	52L	52L
4	77L	52L	52L

Compounds using 101L (13C12-2,2',4,5,5'-PeCB) as Labeled injection internal standard

CB congener

Pentachlorobiphenyls

5	104	104L	104L
5	96	104L	104L/123L/118L/114L/105L
5	103	104L	104L/123L/118L/114L/105L
5	94	104L	104L/123L/118L/114L/105L
5	95	104L	104L/123L/118L/114L/105L
5	100	104L	104L/123L/118L/114L/105L
5	93	104L	104L/123L/118L/114L/105L
5	102	104L	104L/123L/118L/114L/105L

Table 7: continued

Retention Times (RT), RT References and Quantitation References

CI # (1)	IUPAC # (2,3)	Retention Time Ref. (4)	Quantitation Reference (5)
5	98	104L	104L/123L/118L/114L/105L
5	95/100/93/102/98	104L	104L/123L/118L/114L/105L
5	88	104L	104L/123L/118L/114L/105L
5	91	104L	104L/123L/118L/114L/105L
5	88/91	104L	104L/123L/118L/114L/105L
5	84	104L	104L/123L/118L/114L/105L
5	89	104L	104L/123L/118L/114L/105L
5	121	104L	104L/123L/118L/114L/105L
5	92	104L	104L/123L/118L/114L/105L
5	113	104L	104L/123L/118L/114L/105L
5	90	104L	104L/123L/118L/114L/105L
5	101	104L	104L/123L/118L/114L/105L
5	113/90/101	104L	104L/123L/118L/114L/105L
5	83	104L	104L/123L/118L/114L/105L
5	99	104L	104L/123L/118L/114L/105L
5	83/99	104L	104L/123L/118L/114L/105L
5	112	104L	104L/123L/118L/114L/105L
5	119	104L	104L/123L/118L/114L/105L
5	109	104L	104L/123L/118L/114L/105L
5	86	104L	104L/123L/118L/114L/105L
5	97	104L	104L/123L/118L/114L/105L
5	125	104L	104L/123L/118L/114L/105L
5	87	104L	104L/123L/118L/114L/105L
5	109/119/86/97/125/87	104L	104L/123L/118L/114L/105L
5	117	104L	104L/123L/118L/114L/105L
5	116	104L	104L/123L/118L/114L/105L
5	85	104L	104L/123L/118L/114L/105L
5	117/116/85	104L	104L/123L/118L/114L/105L
5	110	104L	104L/123L/118L/114L/105L
5	115	104L	104L/123L/118L/114L/105L
5	110/115	104L	104L/123L/118L/114L/105L
5	82	104L	104L/123L/118L/114L/105L
5	111	104L	104L/123L/118L/114L/105L
5	120	104L	104L/123L/118L/114L/105L
5	108	123L	104L/123L/118L/114L/105L
5	124	123L	104L/123L/118L/114L/105L
5	108/124	123L	104L/123L/118L/114L/105L
5	107	123L	104L/123L/118L/114L/105L
5	123	123L	123L
5	106	123L	104L/123L/118L/114L/105L
5	118	118L	118L

Table 7: continued

Retention Times (RT), RT References and Quantitation References

CI # (1)	IUPAC # (2,3)	Retention Time Ref. (4)	Quantitation Reference (5)
5	122	118L	104L/123L/114L/118L/105L
5	114	114L	114L
5	105	105L	105L
5	127	126L	104L/123L/114L/118L/105L
5	126	126L	126L

Labeled compounds

5	104L	101L	101L
5	123L	101L	101L
5	118L	101L	101L
5	114L	101L	101L
5	105L	101L	101L
5	126L	101L	101L

Compounds using 138L (13C12-2,2,'3,4,4',5'-HxCB) as Labeled injection standard

Hexachlorobiphenyls

6	155	155L	155L
6	152	155L	155L/167L/156L/157L/169L
6	150	155L	155L/167L/156L/157L/169L
6	136	155L	155L/167L/156L/157L/169L
6	145	155L	155L/167L/156L/157L/169L
6	148	155L	155L/167L/156L/157L/169L
6	151	155L	155L/167L/156L/157L/169L
6	135	155L	155L/167L/156L/157L/169L
6	154	155L	155L/167L/156L/157L/169L
6	151/135/154	155L	155L/167L/156L/157L/169L
6	144	155L	155L/167L/156L/157L/169L
6	147	155L	155L/167L/156L/157L/169L
6	149	155L	155L/167L/156L/157L/169L
6	147/149	155L	155L/167L/156L/157L/169L
6	134	155L	155L/167L/156L/157L/169L
6	143	155L	155L/167L/156L/157L/169L
6	134/143	155L	155L/167L/156L/157L/169L
6	139	155L	155L/167L/156L/157L/169L
6	140	155L	155L/167L/156L/157L/169L
6	139/140	155L	155L/167L/156L/157L/169L
6	131	155L	155L/167L/156L/157L/169L
6	142	155L	155L/167L/156L/157L/169L
6	132	155L	155L/167L/156L/157L/169L
6	133	155L	155L/167L/156L/157L/169L
6	165	167L	155L/167L/156L/157L/169L
6	146	167L	155L/167L/156L/157L/169L
6	161	167L	155L/167L/156L/157L/169L

Table 7: continued

Retention Times (RT), RT References and Quantitation References

CI # (1)	IUPAC # (2,3)	Retention Time Ref. (4)	Quantitation Reference (5)
6	153	167L	155L/167L/156L/157L/169L
6	168	167L	155L/167L/156L/157L/169L
6	153/168	167L	155L/167L/156L/157L/169L
6	141	167L	155L/167L/156L/157L/169L
6	130	167L	155L/167L/156L/157L/169L
6	137	167L	155L/167L/156L/157L/169L
6	164	167L	155L/167L/156L/157L/169L
6	138	167L	155L/167L/156L/157L/169L
6	163	167L	155L/167L/156L/157L/169L
6	129	167L	155L/167L/156L/157L/169L
6	160	167L	155L/167L/156L/157L/169L
6	138/163/129/160	167L	155L/167L/156L/157L/169L
6	158	167L	155L/167L/156L/157L/169L
6	166	167L	155L/167L/156L/157L/169L
6	128	167L	155L/167L/156L/157L/169L
6	128/166	167L	155L/167L/156L/157L/169L
6	159	167L	155L/167L/156L/157L/169L
6	162	167L	155L/167L/156L/157L/169L
6	167	167L	167L
6	156	156L/157L	156L/157L
6	157	156L/157L	156L/157L
6	156/157	156L/157L	156L/157L
6	169	169L	169L

Labeled compounds

6	155L	138L	138L
6	167L	138L	138L
6	156L	138L	138L
6	157L	138L	138L
6	156L/157L	138L	138L
6	169L	138L	138L

Compounds using 194L (13C12-2,2'3,3',4,4',5,5'-O₂CB) as Labeled injection internal standard

CB Congener

Heptachlorobiphenyls

7	188	188L	188L
7	179	188L	188L/180L/170L/189L
7	184	188L	188L/180L/170L/189L
7	176	188L	188L/180L/170L/189L
7	186	188L	188L/180L/170L/189L
7	178	188L	188L/180L/170L/189L
7	175	188L	188L/180L/170L/189L
7	187	188L	188L/180L/170L/189L

Table 7: continued

Retention Times (RT), RT References and Quantitation References

CI # (1)	IUPAC # (2,3)	Retention Time Ref. (4)	Quantitation Reference (5)
7	182	188L	188L/180L/170L/189L
7	183	180L	188L/180L/170L/189L
7	185	180L	188L/180L/170L/189L
7	183/185	180L	188L/180L/170L/189L
7	174	180L	188L/180L/170L/189L
7	177	180L	188L/180L/170L/189L
7	181	180L	188L/180L/170L/189L
7	171	180L	188L/180L/170L/189L
7	173	180L	188L/180L/170L/189L
7	171/173	180L	188L/180L/170L/189L
7	172	180L	188L/180L/170L/189L
7	192	180L	188L/180L/170L/189L
7	193	180L	188L/180L/170L/189L
7	180	180L	180L
7	180/193	180L	180L
7	191	180L	188L/180L/170L/189L
7	170	170L	170L
7	190	170L	188L/180L/170L/189L
7	189	189L	189L

Octachlorobiphenyls

8	202	202L	202L
8	201	202L	202L/205L
8	204	202L	202L/205L
8	197	202L	202L/205L
8	200	202L	202L/205L
8	197/200	202L	202L/205L
8	198	202L	202L/205L
8	199	202L	202L/205L
8	198/199	202L	202L/205L
8	196	205L	202L/205L
8	203	205L	202L/205L
8	195	205L	202L/205L
8	194	205L	202L/205L
8	205	205L	205L

Nonachlorobiphenyls

9	208	208L	208L
9	207	208L	206L/208L
9	206	206L	206L

Table 7: continued

Retention Times (RT), RT References and Quantitation References

CI # (1)	IUPAC # (2,3)	Retention Time Ref. (4)	Quantitation Reference (5)
Decachlorobiphenyls			
10	209	209L	209L
Labeled Compounds			
7	188L	138L	138L
7	180L	194L	194L
7	170L	194L	194L
7	189L	194L	194L
8	202L	194L	194L
8	205L	194L	194L
9	208L	194L	194L
9	206L	194L	194L
10	209L	194L	194L
Labeled clean-up standards			
3	28L	52L	52L
5	111L	101L	101L
7	178L	138L	138L
Labeled Field Spike (Audit) Standards			
3	31L	52L	52L
5	95L	101L	101L
6	153L	138L	138L
Labeled injection internal standards			
2	9L	138L	138L
4	52L	138L	138L
5	101L	138L	138L
6	138L	138L	138L
8	194L	138L	138L

- (1) Number of chlorines on congener
- (2) Suffix "L" indicates labeled compound.
- (3) Multiple congeners in a box indicate a group of congeners that co-elute or may not be adequately resolved on a 30-m SPB-Octyl column. Congeners included in the group are listed as the last entry in the box.
- (4) Retention time reference that is used to locate target compounds
- (5) Labeled congeners that form the quantitation reference. Areas from the exact m/z's of the congeners listed in the quantitation reference are summed, and divided by the number of congeners in the quantitation reference. For example, for congener 10, the areas at the exact m/z's for 4L and 15L are summed and the sum is divided by 2 (because there are 2 congeners in the quantitation reference).

Table 8: PCB Congeners (bold in spike solution)

IUPAC No.	Congener
1	2-Monochlorobiphenyl
2	3-Monochlorobiphenyl
3	4-Monochlorobiphenyl
4	2,2'-Dichlorobiphenyl
5	2,3-Dichlorobiphenyl
6	2,3'-Dichlorobiphenyl
7	2,4-Dichlorobiphenyl
8	2,4'-Dichlorobiphenyl
9	2,5-Dichlorobiphenyl
10	2,6-Dichlorobiphenyl
11	3,3'-Dichlorobiphenyl
12	3,4-Dichlorobiphenyl
13	3,4'-Dichlorobiphenyl
14	3,5-Dichlorobiphenyl
15	4,4'-Dichlorobiphenyl
16	2,2',3-Trichlorobiphenyl
17	2,2',4-Trichlorobiphenyl
18	2,2',5-Trichlorobiphenyl
19	2,2',6-Trichlorobiphenyl
20	2,3,3'-Trichlorobiphenyl
21	2,3,4-Trichlorobiphenyl
22	2,3,4'-Trichlorobiphenyl
23	2,3,5-Trichlorobiphenyl
24	2,3,6-Trichlorobiphenyl
25	2,3',4-Trichlorobiphenyl
26	2,3',5-Trichlorobiphenyl
27	2,3',6-Trichlorobiphenyl
28	2,4,4'-Trichlorobiphenyl
29	2,4,5-Trichlorobiphenyl
30	2,4,6-Trichlorobiphenyl
31	2,4',5-Trichlorobiphenyl
32	2,4',6-Trichlorobiphenyl
33	2,3',4'-Trichlorobiphenyl
34	2,3',5'-Trichlorobiphenyl
35	3,3',4-Trichlorobiphenyl
36	3,3',5-Trichlorobiphenyl
37	3,4,4'-Trichlorobiphenyl
38	3,4,5-Trichlorobiphenyl
39	3,4',5-Trichlorobiphenyl
40	2,2',3,3'-Tetrachlorobiphenyl

IUPAC No.	Congener
41	2,2',3,4-Tetrachlorobiphenyl
42	2,2',3,4'-Tetrachlorobiphenyl
43	2,2',3,5-Tetrachlorobiphenyl
44	2,2',3,5'-Tetrachlorobiphenyl
45	2,2',3,6-Tetrachlorobiphenyl
46	2,2',3,6'-Tetrachlorobiphenyl
47	2,2',4,4'-Tetrachlorobiphenyl
48	2,2',4,5-Tetrachlorobiphenyl
49	2,2',4,5'-Tetrachlorobiphenyl
50	2,2',4,6-Tetrachlorobiphenyl
51	2,2',4,6'-Tetrachlorobiphenyl
52	2,2',5,5'-Tetrachlorobiphenyl
53	2,2',5,6'-Tetrachlorobiphenyl
54	2,2',6,6'-Tetrachlorobiphenyl
55	2,3,3',4-Tetrachlorobiphenyl
56	2,3,3',4'-Tetrachlorobiphenyl
57	2,3,3',5-Tetrachlorobiphenyl
58	2,3,3',5'-Tetrachlorobiphenyl
59	2,3,3',6-Tetrachlorobiphenyl
60	2,3,4,4'-Tetrachlorobiphenyl
61	2,3,4,5-Tetrachlorobiphenyl
62	2,3,4,6-Tetrachlorobiphenyl
63	2,3,4',5-Tetrachlorobiphenyl
64	2,3,4',6-Tetrachlorobiphenyl
65	2,3,5,6-Tetrachlorobiphenyl
66	2,3',4,4'-Tetrachlorobiphenyl
67	2,3',4,5-Tetrachlorobiphenyl
68	2,3',4,5'-Tetrachlorobiphenyl
69	2,3',4,6-Tetrachlorobiphenyl
70	2,3',4',5-Tetrachlorobiphenyl
71	2,3',4',6-Tetrachlorobiphenyl
72	2,3',5,5'-Tetrachlorobiphenyl
73	2,3',5',6-Tetrachlorobiphenyl
74	2,4,4',5-Tetrachlorobiphenyl
75	2,4,4',6-Tetrachlorobiphenyl
76	2,3',4',5'-Tetrachlorobiphenyl
77	3,3',4,4'-Tetrachlorobiphenyl
78	3,3',4,5-Tetrachlorobiphenyl
79	3,3',4,5'-Tetrachlorobiphenyl
80	3,3',5,5'-Tetrachlorobiphenyl
81	3,4,4',5-Tetrachlorobiphenyl
82	2,2',3,3',4-Pentachlorobiphenyl

IUPAC No.	Congener
83	2,2',3,3',5-Pentachlorobiphenyl
84	2,2',3,3',6-Pentachlorobiphenyl
85	2,2',3,4,4'-Pentachlorobiphenyl
86	2,2',3,4,5-Pentachlorobiphenyl
87	2,2',3,4,5'-Pentachlorobiphenyl
88	2,2',3,4,6-Pentachlorobiphenyl
89	2,2',3,4,6'-Pentachlorobiphenyl
90	2,2',3,4',5-Pentachlorobiphenyl
91	2,2',3,4',6-Pentachlorobiphenyl
92	2,2',3,5,5'-Pentachlorobiphenyl
93	2,2',3,5,6-Pentachlorobiphenyl
94	2,2',3,5,6'-Pentachlorobiphenyl
95	2,2',3,5',6-Pentachlorobiphenyl
96	2,2',3,6,6'-Pentachlorobiphenyl
97	2,2',3,4',5'-Pentachlorobiphenyl
98	2,2',3,4',6'-Pentachlorobiphenyl
99	2,2',4,4',5-Pentachlorobiphenyl
100	2,2',4,4',6-Pentachlorobiphenyl
101	2,2',4,5,5'-Pentachlorobiphenyl
102	2,2',4,5,6'-Pentachlorobiphenyl
103	2,2',4,5',6-Pentachlorobiphenyl
104	2,2',4,6,6'-Pentachlorobiphenyl
105	2,3,3',4,4'-Pentachlorobiphenyl
106	2,3,3',4,5-Pentachlorobiphenyl
107	2,3,3',4,5'-Pentachlorobiphenyl
108	2,3,3',4,6-Pentachlorobiphenyl
109	2,3,3',4',5-Pentachlorobiphenyl
110	2,3,3',4',6-Pentachlorobiphenyl
111	2,3,3',5,5'-Pentachlorobiphenyl
112	2,3,3',5,6-Pentachlorobiphenyl
113	2,3,3',5',6-Pentachlorobiphenyl
114	2,3,4,4',5-Pentachlorobiphenyl
115	2,3,4,4',6-Pentachlorobiphenyl
116	2,3,4,5,6-Pentachlorobiphenyl
117	2,3,4',5,6-Pentachlorobiphenyl
118	2,3',4,4',5-Pentachlorobiphenyl
119	2,3',4,4',6-Pentachlorobiphenyl
120	2,3',4,5,5'-Pentachlorobiphenyl
121	2,3',4,5',6-Pentachlorobiphenyl
122	2,3,3',4',5'-Pentachlorobiphenyl
123	2,3',4,4',5'-Pentachlorobiphenyl
124	2,3',4',5,5'-Pentachlorobiphenyl

IUPAC No.	Congener
125	2,3',4',5',6-Pentachlorobiphenyl
126	3,3',4,4',5-Pentachlorobiphenyl
127	3,3',4,5,5'-Pentachlorobiphenyl
128	2,2',3,3',4,4'-Hexachlorobiphenyl
129	2,2',3,3',4,5-Hexachlorobiphenyl
130	2,2',3,3',4,5'-Hexachlorobiphenyl
131	2,2',3,3',4,6-Hexachlorobiphenyl
132	2,2',3,3',4,6'-Hexachlorobiphenyl
133	2,2',3,3',5,5'-Hexachlorobiphenyl
134	2,2',3,3',5,6-Hexachlorobiphenyl
135	2,2',3,3',5,6'-Hexachlorobiphenyl
136	2,2',3,3',6,6'-Hexachlorobiphenyl
137	2,2',3,4,4',5-Hexachlorobiphenyl
138	2,2',3,4,4',5'-Hexachlorobiphenyl
139	2,2',3,4,4',6-Hexachlorobiphenyl
140	2,2',3,4,4',6'-Hexachlorobiphenyl
141	2,2',3,4,5,5'-Hexachlorobiphenyl
142	2,2',3,4,5,6-Hexachlorobiphenyl
143	2,2',3,4,5,6'-Hexachlorobiphenyl
144	2,2',3,4,5',6-Hexachlorobiphenyl
145	2,2',3,4,6,6'-Hexachlorobiphenyl
146	2,2',3,4',5,5'-Hexachlorobiphenyl
147	2,2',3,4',5,6-Hexachlorobiphenyl
148	2,2',3,4',5,6'-Hexachlorobiphenyl
149	2,2',3,4',5',6-Hexachlorobiphenyl
150	2,2',3,4',6,6'-Hexachlorobiphenyl
151	2,2',3,5,5',6-Hexachlorobiphenyl
152	2,2',3,5,6,6'-Hexachlorobiphenyl
153	2,2',4,4',5,5'-Hexachlorobiphenyl
154	2,2',4,4',5,6'-Hexachlorobiphenyl
155	2,2',4,4',6,6'-Hexachlorobiphenyl
156	2,3,3',4,4',5-Hexachlorobiphenyl
157	2,3,3',4,4',5'-Hexachlorobiphenyl
158	2,3,3',4,4',6-Hexachlorobiphenyl
159	2,3,3',4,5,5'-Hexachlorobiphenyl
160	2,3,3',4,5,6-Hexachlorobiphenyl
161	2,3,3',4,5',6-Hexachlorobiphenyl
162	2,3,3',4',5,5'-Hexachlorobiphenyl
163	2,3,3',4',5,6-Hexachlorobiphenyl
164	2,3,3',4',5',6-Hexachlorobiphenyl
165	2,3,3',5,5',6-Hexachlorobiphenyl
166	2,3,4,4',5,6-Hexachlorobiphenyl

IUPAC No.	Congener
167	2,3',4,4',5,5'-Hexachlorobiphenyl
168	2,3',4,4',5',6-Hexachlorobiphenyl
169	3,3',4,4',5,5'-Hexachlorobiphenyl
170	2,2',3,3',4,4',5-Heptachlorobiphenyl
171	2,2',3,3',4,4',6-Heptachlorobiphenyl
172	2,2',3,3',4,5,5'-Heptachlorobiphenyl
173	2,2',3,3',4,5,6-Heptachlorobiphenyl
174	2,2',3,3',4,5,6'-Heptachlorobiphenyl
175	2,2',3,3',4,5',6-Heptachlorobiphenyl
176	2,2',3,3',4,6,6'-Heptachlorobiphenyl
177	2,2',3,3',4,5',6'-Heptachlorobiphenyl
178	2,2',3,3',5,5',6-Heptachlorobiphenyl
179	2,2',3,3',5,6,6'-Heptachlorobiphenyl
180	2,2',3,4,4',5,5'-Heptachlorobiphenyl
181	2,2',3,4,4',5,6-Heptachlorobiphenyl
182	2,2',3,4,4',5,6'-Heptachlorobiphenyl
183	2,2',3,4,4',5',6-Heptachlorobiphenyl
184	2,2',3,4,4',6,6'-Heptachlorobiphenyl
185	2,2',3,4,5,5',6-Heptachlorobiphenyl
186	2,2',3,4,5,6,6'-Heptachlorobiphenyl
187	2,2',3,4',5,5',6-Heptachlorobiphenyl
188	2,2',3,4',5,6,6'-Heptachlorobiphenyl
189	2,3,3',4,4',5,5'-Heptachlorobiphenyl
190	2,3,3',4,4',5,6-Heptachlorobiphenyl
191	2,3,3',4,4',5',6-Heptachlorobiphenyl
192	2,3,3',4,5,5',6-Heptachlorobiphenyl
193	2,3,3',4',5,5',6-Heptachlorobiphenyl
194	2,2',3,3',4,4',5,5'-Octachlorobiphenyl
195	2,2',3,3',4,4',5,6-Octachlorobiphenyl
196	2,2',3,3',4,4',5,6'-Octachlorobiphenyl
197	2,2',3,3',4,4',6,6'-Octachlorobiphenyl
198	2,2',3,3',4,5,5',6-Octachlorobiphenyl
199	2,2',3,3',4,5,5',6'-Octachlorobiphenyl
200	2,2',3,3',4,5,6,6'-Octachlorobiphenyl
201	2,2',3,3',4,5',6,6'-Octachlorobiphenyl
202	2,2',3,3',5,5',6,6'-Octachlorobiphenyl
203	2,2',3,4,4',5,5',6-Octachlorobiphenyl
204	2,2',3,4,4',5,6,6'-Octachlorobiphenyl
205	2,3,3',4,4',5,5',6-Octachlorobiphenyl
206	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl
207	2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl
208	2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl

IUPAC No.	Congener
209	2,2',3,3',4,4',5,5',6,6'- Decachlorobiphenyl

Table 9: PCB Homologues

PCB Homologue
Monochlorobiphenyl
Dichlorobiphenyl
Trichlorobiphenyl
Tetrachlorobiphenyl
Pentachlorobiphenyl
Hexachlorobiphenyl
Heptachlorobiphenyl
Octachlorobiphenyl
Nonachlorobiphenyl
Decachlorobiphenyl

Experiment: 1668A (7 Functions)

Operator : User
Date : 12-JAN-2015 16:13:15
Instrument : Autospec-UltimaE

Function 1

Type : SIR Voltage
Calibration file used : M2150112_1
High mass : 236.0
Low mass : 188.0
Resolution : 10000
Ionisation mode : EI+
Accelerating Voltage : 8000.0V
Magnet 1 control : Current
Start Time : 8:30
End Time : 10:50
Fast lock : On
Number of channels : 10
Cycle time (ms) : 735

Channel	Mass	Ch Time (ms)	I/ch Time (ms)
1	188.0393	100	25
2	190.0363	80	10
3	200.0795	50	10
4	202.0766	50	10
5	218.9856	30	10
6 (Lock)	218.9856	50	10
Primary Span Lock (Peaks) 2.00			
Secondary Span Lock (Peaks) 2.00			
Lock Level (mV) 5			
Step Lock (Peaks) 0.040			
7	222.0003	80	10
8	223.9974	80	10
9	234.0406	50	10
10	236.0376	50	10
Septum flow	: Off		

Experiment: 1668A (7 Functions)

Operator : User
Date : 12-JAN-2015 16:13:15
Instrument : Autospec-UltimaE

Function 2

Type : SIR Voltage
Calibration file used : M2150112_2
High mass : 304.0
Low mass : 222.0
Resolution : 10000
Ionisation mode : EI+
Accelerating Voltage : 8000.0V
Magnet 1 control : Current
Start Time : 10:50
End Time : 13:37
Fast lock : On
Number of channels : 16
Cycle time (ms) : 1240

Channel	Mass	Ch Time (ms)	I/ch Time (ms)
1	222.0003	120	30
2	223.9974	80	10
3	234.0406	50	10
4	236.0376	50	10
5	241.9224	80	10
6	242.9856	30	10
7 (Lock)	242.9856	50	10
Primary Span Lock (Peaks) 2.00			
Secondary Span Lock (Peaks) 2.00			
Lock Level (mV) 5			
Step Lock (Peaks) 0.020			
8	243.9194	80	10
9	255.9614	80	10
10	257.9584	80	10
11	268.0016	50	10
12	269.9986	50	10
13	289.9224	80	10
14	291.9194	80	10
15	301.9626	50	10
16	303.9597	50	10
Septum flow	: Off		

Experiment: 1668A (7 Functions)

Operator : User
 Date : 12-JAN-2015 16:13:15
 Instrument : Autospec-UltimaE

Function 3

Type : SIR Voltage
 Calibration file used : M2150112_3
 High mass : 339.9
 Low mass : 256.0
 Resolution : 10000
 Ionisation mode : EI+
 Accelerating Voltage : 8000.0V
 Magnet 1 control : Current
 Start Time : 13:37
 End Time : 17:09
 Fast lock : On
 Number of channels : 14
 Cycle time (ms) : 1070

Channel	Mass	Ch Time (ms)	I/ch Time (ms)
1	255.9614	120	30
2	257.9584	80	10
3	268.0016	50	10
4	269.9986	50	10
5	289.9224	80	10
6	291.9194	80	10
7	292.9824	40	10
8 (Lock)	292.9824	50	10
Primary Span Lock (Peaks) 2.00			
Secondary Span Lock (Peaks) 2.00			
Lock Level (mV) 5			
Step Lock (Peaks) 0.020			
9	301.9626	50	10
10	303.9597	50	10
11	325.8805	80	10
12	327.8775	80	10
13	337.9207	50	10
14	339.9178	50	10
Septum flow	: Off		

Experiment: 1668A (7 Functions)

Operator : User
 Date : 12-JAN-2015 16:13:15
 Instrument : Autospec-UltimaE

Function 4

Type : SIR Voltage
 Calibration file used : M2150112_4
 High mass : 373.9
 Low mass : 289.9
 Resolution : 10000
 Ionisation mode : EI+
 Accelerating Voltage : 8000.0V
 Magnet 1 control : Current
 Start Time : 17:09
 End Time : 22:48
 Fast lock : On
 Number of channels : 14
 Cycle time (ms) : 1055

Channel	Mass	Ch Time (ms)	I/ch Time (ms)
1	289.9224	120	25
2	291.9194	80	10
3	301.9626	50	10
4	303.9597	50	10
5	325.8805	80	10
6	327.8775	80	10
7	330.9792	30	10
8 (Lock)	330.9792	50	10
Primary Span Lock (Peaks) 2.00			
Secondary Span Lock (Peaks) 2.00			
Lock Level (mV) 5			
Step Lock (Peaks) 0.020			
9	337.9207	50	10
10	339.9178	50	10
11	359.8415	80	10
12	361.8385	80	10
13	371.8817	50	10
14	373.8788	50	10

Septum flow : Off

Experiment: 1668A (7 Functions)

Operator : User
Date : 12-JAN-2015 16:13:15
Instrument : Autospec-UltimaE

Function 5

Type : SIR Voltage
Calibration file used : M2150112_5
High mass : 407.8
Low mass : 325.9
Resolution : 10000
Ionisation mode : EI+
Accelerating Voltage : 8000.0V
Magnet 1 control : Current
Start Time : 22:48
End Time : 28:24
Fast lock : On
Number of channels : 14
Cycle time (ms) : 1055

Channel	Mass	Ch Time (ms)	I/ch Time (ms)
1	325.8805	120	25
2	327.8775	80	10
3	337.9207	50	10
4	339.9178	50	10
5	354.9792	30	10
6 (Lock)	354.9792	50	10
Primary Span Lock (Peaks) 2.00			
Secondary Span Lock (Peaks) 2.00			
Lock Level (mV) 5			
Step Lock (Peaks) 0.020			
7	359.8415	80	10
8	361.8385	80	10
9	371.8817	50	10
10	373.8788	50	10
11	393.8025	80	10
12	395.7995	80	10
13	405.8428	50	10
14	407.8398	50	10

Septum flow : Off

Experiment: 1668A (7 Functions)

Operator : User
 Date : 12-JAN-2015 16:13:15
 Instrument : Autospec-UltimaE

Function 6

Type : SIR Voltage
 Calibration file used : M2150112_6
 High mass : 441.8
 Low mass : 359.8
 Resolution : 10000
 Ionisation mode : EI+
 Accelerating Voltage : 8000.0V
 Magnet 1 control : Current
 Start Time : 28:24
 End Time : 35:53
 Fast lock : On
 Number of channels : 14
 Cycle time (ms) : 1060

Channel	Mass	Ch Time (ms)	I/ch Time (ms)
1	359.8415	120	30
2	361.8385	80	10
3	371.8817	50	10
4	373.8788	50	10
5	393.8025	80	10
6	395.7995	80	10
7	404.9760	30	10
8 (Lock)	404.9760	50	10
Primary Span Lock (Peaks) 2.00			
Secondary Span Lock (Peaks) 2.00			
Lock Level (mV) 5			
Step Lock (Peaks) 0.020			
9	405.8428	50	10
10	407.8398	50	10
11	427.7635	80	10
12	429.7606	80	10
13	439.8038	50	10
14	441.8008	50	10

Septum flow : Off

Experiment: 1668A (7 Functions)

Operator : User
 Date : 12-JAN-2015 16:13:15
 Instrument : Autospec-UltimaE

Function 7

Type : SIR Voltage
 Calibration file used : M2150112_7
 High mass : 511.7
 Low mass : 393.8
 Resolution : 10000
 Ionisation mode : EI+
 Accelerating Voltage : 8000.0V
 Magnet 1 control : Current
 Start Time : 35:53
 End Time : 46:30
 Fast lock : On
 Number of channels : 18
 Cycle time (ms) : 1360

Channel	Mass	Ch Time (ms)	I/ch Time (ms)
1	393.8025	120	30
2	395.7996	80	10
3	405.8428	50	10
4	407.8398	50	10
5	427.7635	80	10
6	429.7606	80	10
7	439.8038	50	10
8	441.8008	50	10
9	454.9728	30	10
10 (Lock)	454.9728	50	10
Primary Span Lock (Peaks) 2.00			
Secondary Span Lock (Peaks) 2.00			
Lock Level (mV) 5			
Step Lock (Peaks) 0.020			
11	461.7246	80	10
12	463.7216	80	10
13	473.7648	50	10
14	475.7619	50	10
15	497.6826	80	10
16	499.6797	80	10
17	509.7229	50	10
18	511.7199	50	10

Septum flow : Off

Attachment 2

CFIA - PCB Separation Documentation

Reported PCB #	Typical Retention Time (min)	Column	Separated / Coeluted
1	9.12	SPB Octyl	Separated
3	10.32	SPB Octyl	Separated
4	10.43	SPB Octyl	Separated
8	11.51	SPB Octyl	Separated
10	11.72	SPB Octyl	Separated
15	13.14	SPB Octyl	Separated
18	16.53	DB-5	Separated
19	11.84	SPB Octyl	Separated
22	15.00	SPB Octyl	Separated
28	18.45	DB-5	Separated
33/21	14.78	SPB Octyl	Coelution
37	16.99	SPB Octyl	Separated
40/41/71	16.88	SPB Octyl	Coelution
41/40/71	16.88	SPB Octyl	Coelution
44	21.09	DB-5	Separated
49/69	15.92	SPB Octyl	Coelution
52	15.65	SPB Octyl	Separated
54	13.28	SPB Octyl	Separated
60	19.61	SPB Octyl	Separated
66	18.95	SPB Octyl	Separated
70	23.05	DB-5	Separated
74	22.52	DB-5	Separated
77	22.30	SPB Octyl	Separated
81	21.85	SPB Octyl	Separated
87/117	26.02	DB-5	Coelution
95	18.11	SPB Octyl	Separated
99	24.43	DB-5	Separated
101	20.18	SPB Octyl	Coelution
104	16.23	SPB Octyl	Separated
105	25.34	SPB Octyl	Separated
110	26.25	DB-5	Separated
114	24.77	SPB Octyl	Separated
118	24.27	SPB Octyl	Separated
119	25.05	DB-5	Separated
123	23.99	SPB Octyl	Separated
126	28.25	SPB Octyl	Separated

Reported PCB #	Typical Retention Time (min)	Column	Separated / Coeluted
128/166	28.35	SPB Octyl	Coelution
129	31.18	DB-5	Separated
137	26.75	SPB Octyl	Separated
138/129/163	27.16	SPB Octyl	Coelution
141	26.15	SPB Octyl	Separated
149/147	23.28	SPB Octyl	Coelution
151	26.17	DB-5	Separated
153	29.10	DB-5	Separated
155	20.05	SPB Octyl	Separated
156	33.53	DB-5	Separated
157	34.15	DB-5	Separated
158	27.52	SPB Octyl	Separated
167	30.10	SPB Octyl	Separated
168/153	25.88	SPB Octyl	Coelution
169	34.72	SPB Octyl	Separated
170	34.08	SPB Octyl	Separated
171	33.52	DB-5	Separated
177	29.73	SPB Octyl	Separated
178	27.57	SPB Octyl	Separated
180	34.55	DB-5	Separated
183	29.08	SPB Octyl	Separated
187	28.46	SPB Octyl	Separated
188	24.76	SPB Octyl	Separated
189	37.52	SPB Octyl	Separated
191	33.13	SPB Octyl	Separated
193	35.05	DB-5	Separated
194	39.90	SPB Octyl	Separated
199	37.20	DB-5	Separated
201	30.82	SPB Octyl	Separated
202	29.87	SPB Octyl	Separated
203	35.80	SPB Octyl	Separated
205	40.45	SPB Octyl	Separated
206	42.47	SPB Octyl	Separated
208	37.01	SPB Octyl	Separated
209	44.33	SPB Octyl	Separated

EXTRACTION AND CLEAN-UP OF CHLORINATED BIPHENYLS (PCBs)



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Document Identity	
Document Categorization	
Campobello Departments	Environmental HRMS

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Release and Audit Schedule	
Release Schedule	When Approved <input type="checkbox"/> Allow Administrator to Release Document Early
Expiration Schedule	When Superseded or Obsoleted
Audit Schedule	12 Month(s)
Special Handling on Release	
<input checked="" type="checkbox"/> Update Completed Trainee Records	

Insert Text	
<ul style="list-style-type: none"> BRL SOP-00409 CTA-safety 	

Associated Documents

Associated External Documents

- Method 1668, Revision A

Document Control Documents

- Burlington SOP BRL SOP-00408 : PCB Congeners Analysis by HRGC HRMS in Water, Soil and Air - EPA1668 A+B
- Corporate WI Publish to All COR WI-00010 : Corporate Procedure for Nonconformances
- Corporate WI Publish to All COR WI-00011 : Corporate Corrective and Preventive Actions Procedure
- Corporate WI Publish to All COR WI-00012 : Definitions
- Corporate WI Publish to All COR WI-00040 : Corporate Procedure for Policy Deviation Forms
- Campobello WI CAM WI-00095 : Environmental Method Validation (NELAC + DOD requirements)
- Campobello WI CAM WI-00121 : Maxxam Lab QM Supplement to Meet Requirements of DoD QSM Version 4.1
- Burlington SOP BRL SOP-00003 : GPC Cleanup (Based on EPA SW846 3640A)
- Burlington SOP BRL SOP-00009 : Preparation of Stack Testing and Ambient Air Trains and TOPS Modules
- Burlington SOP BRL SOP-00212 : Extraction of Sample Trains
- Campobello SOP CAM SOP-00445 : Determination of Moisture Content in Solids by Gravimetry
- Ultra Trace Air Toxics WI BRL WI-00006 : Air HRMS - ING - SVOC - VOC labs - Glassware Washing
- Ultra Trace Air Toxics FCD BRL FCD-00087 : Water Tracking Form

-  Ultra Trace Air Toxics FCD BRL FCD-00092 : Air Tracking Sheet
-  Ultra Trace Air Toxics FCD BRL FCD-00102 : HR Soil/Tissue/Food Tracking sheet
-   Campobello WI CAM WI-00018 : Waste Disposal
-   Campobello SOP CAM SOP-00704 : Sample Preparation - Food
-   Campobello SOP CAM SOP-00105 : Archiving, Retrieval and Disposal of Samples

Reason for Change

Date of Change May 23, 2006	Version 2
Section Changed SOP header	
Change Made Corrected SOP header for pagination and presence of SOP ID on pages 2 to 12.	
Date of Change January 9, 2012	Version 3
Section Changed 1.0, 3.1, 4.1, 4.2, 6.2.1, 6.3.4, 6.3.6, 6.4.1, 6.4.10, 7.1.3, 7.2.2, 7.3.1, 7.4.1, 8.0, 10.4, 12.0,	
Change Made 1.0 Changed to HRMS Prep lab as current lab's name 3.1 Changed to CAM WI-00095 4.1 Added modification on cleaning of Sodium Sulphate 4.2 Removed listed SOPs instead referenced to associated documents in the QSI 6.2.1 remove overhead fume hood since current lab setting does not have it over the sink 6.3.4 Changed to "vacuum pump" 6.3.6 updated information to current GPC unit 6.4.1 Added clarification on cleaning Na2SO4 6.4.10 Added clarification on cleaning glass wool 7.1.3 Clarified color-labeling of syringes used for the method 7.2.2. changed batch size from 14 to 20 7.2.2. & 7.2.3 removed notes referring to projects: NYCPCB and NYCPCBHR since they are no longer applicable 7.3.1 Added information on which lab performs % moisture 7.4.1 Changed the solvent to DCM and volume to 40 mL 8.0 changed batch size from 14 to 20 throughout the section 10.4 added COR WI-00040 for Policy Deviation procedure 12.0 removed appendix to eliminate duplication it is build in to the QSI template	
Date of Change February 19, 2015	Version 4
Section Changed 2.0, 2.2, 4.1, 5.0, 6.1, 6.2.1, 6.3.3.1, 6.3.5, 6.3.7, 6.4.5, 6.4.6, 6.4.7, 6.4.8, 6.4.11, 7.0.1, 7.1.1, 7.1.2, 7.1.3, 7.1.4, 7.2, 7.3, 7.4.1, 7.4.2, 7.4.3, 7.4.4, 10.1, 11.0	
Change Made 2.0 - clarified matrices 2.2 - added food 4.1 - added centrifuge tubes 5.0 - added sampling details for biota and food 6.1 - added centrifuge tubes 6.2.1 - added reference to BRL WI-00006 6.3.3.1 - added extraction apparatus 6.3.5 - added centrifuge apparatus 6.3.7 - added centrifuge tubes 6.4.3 - added storage details for solvents 6.4.5 - added details for silica gel cleaning 6.4.6, 6.4.7, 6.4.8 - added desiccator 6.4.11 - updated steps 1 and 3 7.0.1 - added steps 1 and 2 7.1.1 - added note and updated step 2 7.1.2 - added note and updated step 2 7.1.3 - updated steps 3 and 4 7.1.4 - added nonane and centrifuge tube; spiking to be witnessed 7.2 - updated extraction of particulates 7.3 - updated extraction of solids 7.4.1 - updated sulphuric acid extraction 7.4.2 - updated H2SO4 Acid/Silica Gel Column 7.4.3 - updated 3% Water Deactivated Florisil 7.4.4 - updated Sample Concentration 10.1 - updated documentation requirements 11.0 - added safety and waste management details added CTA	
Optional Field A reviewed associated documents - added BRL WI-00006 and CAM SOP-00445 Removed redundant items	
Date of Change February 23, 2015	Version 5
Section Changed 2.0, 3.0, 3.1, 5.0, 5.1, 6.3.3.1, 6.3.3.2, 7.2, 7.2.1, 7.2.1.1, 7.3, 7.3.1, 7.3.2.1, 7.3.3, 7.4, 8.2, 9.0, 11.3	
Change Made 2.0 - added eggs to food matrices and included processed food; added statement regarding validation. 3.0 - included food and other matrices 3.1 - added details for water MDLs 5.0 - added shipping and storage conditions 5.1 - included food 6.3.3.1 - added liquid 6.3.3.2 - added Soil, Sediment, Meat, Processed food, Cheese, Egg, Ash, etc.) 7.2 - included Water, Liquid Drinks	

7.2.1 and 7.2.1.1 - replaced water with liquid
 7.3 - added specific matrices
 7.3.1 - added steps 7 and 8
 7.3.2.1 - added steps 7 and 8
 7.3.3 - added matrix details and details in steps 2, 15, 16 and 17
 7.4 - added conditions for GPC clean-up
 8.2 - added blank prep details
 9.0 - referenced BRL SOP-00408
 11.3 - referenced CAM SOP-00105 and CAM WI-00018
Optional Field A reviewed associated documents - added CAM WI-00018, BRL FCD-00087, BRL FCD-00092, BRL FCD-00102, CAM SOP-00704 and CAM SOP-00105

Approval Status Table			
Approver	Source	Role for Approvers	Parallel-Everybody Segment
Approver	Action	Date	Comment
Betsy Cliffe	Approve	February 23, 2015 1:23 PM GMT-5	
Karen Nicol	Approve	February 23, 2015 11:08 AM GMT-5	
Sue Bigg	Approve	February 23, 2015 10:33 AM GMT-5	

EXTRACTION AND CLEAN-UP OF CHLORINATED BIPHENYLS (PCBs)

1.0 LOCATION:

This procedure is performed in the HRMS Prep Laboratory.

2.0 PURPOSE:

This method is used for the extraction and clean-up of liquids, solids and air samples for follow up analysis of chlorinated biphenyl homologues by Hi-Res Mass Spectrometry.

This method has been validated for all matrices stated in the document.

Note: For the purpose of this procedure's clarity on matrices, use the following reference:

Water Matrix – ground water, drinking waters, surface waters, wastewaters, etc.

Food Matrix – could include, but is not limited to, biota, dairy, meat, eggs, processed food and seafood.

Soil Matrix – solids, chemical materials, sludge, sediments and other solid wastes

2.1 Principle of the Method: chlorinated biphenyls are widely found substances in the environment and consist of 209 homologues varying in level of biphenyl chlorination from mono through deca. Some of the homologues have no ortho chlorine substitution or a single ortho chlorine substitution and have been found to exhibit greater toxicity. These compounds are often targeted in the analytical scheme.

Chlorinated biphenyls are removed from a soil or water through a process of solvent extraction. In the case of solids, they are also removed by solvent extraction. Once the sample extract has been concentrated, it goes through a series of cleanup procedures as required by the sample to remove potential chemical interferences.

2.2 Nature of the Samples: samples may be many types; groundwaters, surface waters, industrial effluents, incinerator ashes, ambient air, stack emissions, food and soils. The laboratory should be made aware of any past history involving the samples or the presence of potentially interfering substances at elevated levels, (e.g. aliphatic hydrocarbons). This allows the prep staff to take a smaller aliquot of sample so that internal standards are not diluted out during analysis

2.3 Safety Considerations: the toxicity or carcinogenicity of each compound or reagent used in this method has not been established precisely. Each compound should be treated as a potential health hazard and exposure should be reduced to the lowest possible level. On the basis of the available toxicological and physical properties of the homologue, these compounds should only be handled by highly trained personnel thoroughly familiar with handling and cautionary procedures, and who understand the associated risks. All work related to the analysis of chlorinated biphenyls should be carried out within a specially designed laboratory.

Take the same precautions used for the analysis of PCDD/DFs. This includes purchasing dilute standards where possible as opposed to the purchase of neat standards.

3.0 SCOPE:

This method is applicable to the extractions of 209 chlorinated biphenyl homologues in water, soil, sediment, sludge, food and air samples. The method can also be adapted to include additional matrices after appropriate validation procedures are done. The homologues most frequently requested include the following compounds by IUPAC number:

<u>Compound Identity</u>	<u>BZ Number</u>
3,3',4,4'-Tetrachlorobiphenyl	77
2,3,3',4,4'-Pentachlorobiphenyl	105
2,3,4,4',5-Pentachlorobiphenyl	114
2,3',4,4',5-Pentachlorobiphenyl	118
2',3,4,4',5-Pentachlorobiphenyl	123
3,3',4,4',5-Pentachlorobiphenyl	126
2,3,3',4,4',5-Hexachlorobiphenyl	156
2,3,3',4,4',5'-Hexachlorobiphenyl	157
2,3',4,4',5,5'-Hexachlorobiphenyl	167
3,3',4,4',5,5'-Hexachlorobiphenyl	169
2,3,3',4,4',5,5'-Heptachlorobiphenyl	189

3.1 Method Precision and Bias: See also CAM WI-00095 Method Validation procedure. Method precision is based upon homologue analysis from the MDL determinations for solid and aqueous blank spikes, (replicates of 8-10 of each). MDL's are determined annually. Soil MDLs are determined based upon 8 to 10 replicate of 10 g Ottawa sand samples analyzed at a final volume of 100 µL. Water MDLs are determined based upon 8-10 replicate analyses of blank water spikes at a final volume of 100 µL.

3.2 Interferences: the sensitivity of this method is dependent upon the level of interferences within a given matrix. Solvents, reagents, glassware and other sample processing hardware may yield artifacts or elevated baselines that may cause misinterpretation of the data. Proper cleaning of glassware is extremely important. Note that glassware may not only contaminate the samples, but may also remove the analytes of interest by adsorption on the glass surface. Method blanks must be analyzed in order to demonstrate that all laboratory materials are free from interference under the conditions of the analysis. The use of high purity reagents and solvents helps to minimize interference problems.

Numerous interferences can be found including chlorinated hydrocarbons and aliphatic hydrocarbons. Although the aliphatics do not exhibit masses that are used in quantitation of the higher chlorinated biphenyls, the presence of excessive levels can impact the chromatography and

suppress ionization. Often the compounds responsible for interferences may be present at concentration levels several orders of magnitude higher than any chlorinated biphenyl, which may be present. Cleanup procedures are used to reduce or eliminate these interferences to the maximum extent practicable in order to ensure reliable quantitation at trace levels. Despite rigorous cleanup procedures, the possibility of matrix interference may still exist. Sample extracts may have to be re-processed using alternative cleanup techniques or reported at elevated detection levels.

4.0 **REFERENCES:**

4.0.1 EPA Method 1668, Revision A, Office of Water, EPA-821-R-00-002, Dec. 1999, "Chlorinated Biphenyl Congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS"

4.1 **Modifications and/or Improvements from Referenced Methods:**

- Reference stores extracts in the dark at <-10°C until analyzed. Maxxam stores extracts on the bench in clear glass centrifuge tubes.
- Sodium Sulphate (**Na₂SO₄**) used for soxhlet extraction is cleaned by cleaning overnight on the soxhlet extractor.
- Silica gel cleanup: Maxxam does not use basic silica
- Maxxam uses 44% H₂SO₄ instead of 30% H₂SO₄
- Maxxam pre-elutes the silica cleanup column with 30 mL hexane instead of 50-100 mL hexane
- Maxxam uses the Rotovap instead of a Snyder column for concentrating the extract in the 500 mL flask
- Maxxam uses Rotovap instead of Kuderna-Danish concentrator

4.2 **Other Relevant SOPs:**

- CAM WI-00095 Method Validation
- COR WI-00012 Corporate Definitions
- BRL SOP-00408 Determination of Individual and Total Chlorinated Biphenyl Homologues in Liquid, Solid and Air Samples by Hi-Res Mass Spectrometry (based on EPA Method 1668A)
- BRL SOP-00003 Cleanup of Sample Extracts Using GPC, (based on EPA 3640A)

4.3 **Analytical Test Codes:**

Other test codes may be created as necessary

Test Code:	Analysis
PCBCONH-IP	PCB Congeners in Air samples
PCBCONH-S	PCB Congeners in Soils
PCBCONH-W	PCB Congeners in Waters
PCBCONHR-T	PCB Congeners in Tissues
PCBHRMS-S	WHO List PCB's in Solids
PCBHRMS-F	WHO List PCB's in Air samples

PCBHRMS-W WHO List PCB's in Waters
PCBHRMS-TI WHO List PCB's in Tissues

5.0 SAMPLE HANDLING AND PRESERVATION:

Due to the fragile nature of the containers, the samples should be well wrapped with protective packaging during shipment from the field site to the laboratory. Biota or food samples are shipped either refrigerated or frozen and upon receipt they are frozen until extraction. All other samples should be maintained at 2-6 °C during shipment and until analysis. Samples that exceed the hold time will be flagged on the Certificate of Analysis. Different hold times may be imposed by other regulating agencies or as determined by client specific projects. Project specific and regulatory requirements for preservation method and reporting criteria, (required detection limit, dry or wet weight basis), must be examined and made clear prior to sample analysis.

5.1 Hold Times for Samples: in general, chlorinated biphenyl samples are stable for at least one (1) year when stored as indicated, i.e. refrigeration for water, soil and air and freezing for tissues and food.

<u>Matrix</u>	<u>Container</u>	<u>Min. Vol.</u>
Waters *	1L amber glass	800 mL
Soils +	250mL amber glass	20 g
Oils	vial/jar	1 mL
Biological	120mL amber jars	20 g

* for waters, sludges and similar materials containing ≤5% solids, use amber glass bottles, 1 L minimum, with screw cap, pre-cleaned to EPA specifications

+ for food, soils, sediments, sludges, paper pulps, filter cake, compost, and similar materials that contain >5% solids use wide mouth, amber glass, 200 mL minimum, pre-cleaned to EPA specifications. Caps must be Teflon lined.

5.2 Storage Time for Sample Extracts: store extracts in clear glass vials at room temperature for up to 1 yr. prior to analysis

6.0 APPARATUS AND MATERIALS:

6.1 Sample Containers: 5mL centrifuge tubes with Teflon-lined screw or crimp cap or Reacti-vials with Teflon-lined screw caps.

6.2 Miscellaneous Equipment:

6.2.1 For Glassware Cleaning: Refer to BRL WI-00006 – “General Glassware Cleaning”

6.3 Sample Preparation Equipment: Laboratory fume hood of sufficient size to contain the sample preparation equipment listed below.

6.3.1 Equipment for Determining Percent Moisture:

- oven capable of maintaining a temperature of 105 ± 5 °C

6.3.2 Balances and Ovens:

- analytical balance capable of weighing 0.1 mg
- top-loading balance capable of weighing 10 mg
- oven capable of maintaining a constant temp. (± 5 °C), at 105 °C for baking/storage of absorbents

6.3.3 Extraction Apparatus:

6.3.3.1 Water or Liquid Samples:

- graduated cylinder, 1-L capacity
- liquid/liquid extraction - Separatory funnels 250, 500 and 2000 mL, with Teflon stopcocks
- 500mL flat bottom flasks
- Allihn filters or filter funnels

6.3.3.2 Solid Samples (Soil, Sediment, Meat, Processed food, Cheese, Egg, Ash, etc.):

- Soxhlet: 50 mm ID, 200 mL capacity with 500 mL flask, (Cal-Glass LG-6900, or equivalent, except substitute 500 mL round-bottom flask for 300 mL flat-bottom Bask).
- Heating mantle: flat steel, with variable transformer for heat control, capable of supplying heat to boil toluene and solvents of lower BP in flat bottomed flasks
- Dean Stark extraction apparatus
- 250 mL glass jars with lids for mixing solids with Na_2SO_4 if required

6.3.4 Filtration Apparatus:

- 125-250 mL glass funnel
- 15 cm Buchner funnel
- glass-fiber filter paper for Buchner funnel above Whatman GF/D, (or equivalent)
- 1.5-2 L side-arm filtration flasks
- vacuum pump

6.3.5 Centrifuge Apparatus:

- centrifuge capable of rotating 40mL borosilicate centrifuge tubes at 3000 rpm
- 40mL glass vial with teflon lined screw cap to fit centrifuge

6.3.6 Cleanup Apparatus:

- J2 Scientific Accuprep with MPS GPC System with Accuprep software
- 600-700 mm long x 25 mm ID column, packed with 70 g of SX-3 Bio-beads, (Bio-Rad Laboratories, Richmond, CA, or equivalent)
- disposable 9 inch Pasteur pipettes, Fisher Scientific or equivalent
- disposable $5\frac{3}{4}$ inch Pasteur pipettes, Fisher Scientific or equivalent

- disposable 10 mL serological pipettes
- ~40 cm x 15 mm ID glass chromatographic columns with tapered ends. (from a commercial glass blower)
- 40 mL disposable borosilicate vials

6.3.7 Concentration Apparatus:

- rotary evaporator-Buchi/Brinkman-American Scientific No. E5045-10 or equivalent, equipped with a variable temperature water bath
- vacuum source for rotary evaporator equipped with shutoff valve at the evaporator and vacuum gauge. Water aspiration is acceptable for DCM extracts.
- 500 mL flat-bottom flasks, with ground-glass fitting compatible with the rotary evaporator.
- Nitrogen Evaporation apparatus, equipped with water bath controlled in the range of 30-60 °C, (N-Evap, Organomation Associates), installed in a fume hood
- disposable 5³/₄ inch Pasteur pipettes, Fisher Scientific or equivalent
- Reacti-vials: clear glass, 1 mL, rinsed with DCM prior to use purchased from Kimble or 5mL disposable centrifuge tubes with teflon lined screw caps

6.4 Reagents:

6.4.1 Sodium Sulfate (Na₂SO₄): granulated reagent grade. This is cleaned by soxhlet extracting overnight using the Soxhlet extraction tube. The solvent is discarded and then the sample is placed in the extraction tube.

6.4.2 Sulfuric Acid (H₂SO₄): concentrated reagent grade

6.4.3 Solvents (Pesticide Grade): hexane, dichloromethane (DCM), toluene, iso-octane, nonane. Store in original container at ambient temperature for up to 1 year

6.4.4 RODI: Reverse Osmosis De-ionized Water, >16MΩ purity, produced in house

6.4.5 Silica Gel: 100-200 mesh, 60 A. from ICN Biomedicals, Cat. No. 02761 or equivalent

The Silica gel must be washed as follows before use:

1. Place approx. 300mL of ICN Silica Gel into a 600mL Buchner funnel and connect to a vacuum pump
2. Cover the silica gel with approx. 300mL of hexane
3. Stir the silica with a spatula or glass rod and let it settle for 2 minutes
4. Turn on the vacuum pump to remove the solvent
5. Repeat steps 2,3 & 4 2 more times using hexane – total washing with hexane = 3
6. Repeat steps 2,3 & 4 using DCM – this is also repeated 3 times
7. Transfer the washed Silica gel into a pyrex dish lined with foil (rinsed with DCM)
8. Cover pyrex dish with rinsed foil (put some vent holes in the foil cover)
9. Allow to dry in a fumehood overnight to remove solvent

Once the solvent is removed, place the silica in the pyrex dish in the oven at 200°C overnight

6.4.6 Acid Silica Gel (44% H₂SO₄):

- Step 1* tare an empty 1 L clear glass bottle with a Teflon lined closure, marked for 44% H₂SO₄
- Step 2* add ~270-300 g silica gel
- Step 3* the amount of H₂SO₄ needed is calculated by:

$$\text{Wt. H}_2\text{SO}_4 \text{ needed (g)} = \text{wt. Silica Gel (g)} \times (44/56)$$

- Step 4* carefully add the H₂SO₄ to the bottle, on the balance, and allow it to be absorbed
- Step 5* put the lid on the bottle and shake by hand to loosen up the silica gel before placing on the tumbler
- Step 6* tumble for a minimum of 18 hours
- Step 7* record the prep date, expiry date and prep person's name on the bottle and in the Adsorbent Logbook.
- Step 8* store in a desiccator for up to one month.

6.4.7 3% Water Deactivated Silica Gel: add 3 mL of RODI water for every 97 g silica in a glass jar with a Teflon lined closure, (Woelm Silica, 100-200 mesh, 60A, dried overnight at ~105 °C). Shake by hand until all lumps are broken up. Tumble for at least 18 hours. Store in a tightly closed glass jar in a desiccator. Replace monthly.

6.4.8 3% Water Deactivated Florisil: add 3 mL of RODI water for every 97 g Florisil in a glass jar with a Teflon lined closure. Shake by hand until all lumps are broken up. Tumble for at least 18 hours. Store in a desiccator. Replace monthly.

6.4.9 Sand, White Quartz, -50+70 mesh: Soxhlet the sand for 16-18 hours with toluene. Air dry in a fume hood then store in a glass jar with a lid until use.

6.4.10 Glass Wool: 8 μ fiberglass. The glass wool is cleaned by adding it to the soxhlet extraction tube before the Na₂SO₄ and both are cleaned by soxhlet extraction overnight with the appropriate solvent (DCM or Toluene).

6.4.11 Copper Powder: reagent grade

6.4.11.1 Activated Copper Powder: Caution: prepare within a fumehood

- Step 1* add ~1 mL of reagent grade copper powder to a cleaned 40 mL vial, rinsed with DCM
- Step 2* add ~20 mL of concentrated HCl
- Step 3* cap with a teflon lined cap and shake for ~ 1 minute
- Step 4* after settling remove the HCl with the pipette
- Step 5* rinse three times with RODI water, followed by three rinses of acetone and three rinses of hexane
- Step 6* dry using a stream of N₂

Note: prepare fresh and use within one hour.

6.4.12 Compressed Gases: Ultra High Purity nitrogen

6.5 Standards: information regarding the concentration, source, lot number, preparation date, expiry date and analyst responsible is written on the label of the bottle used to store the solutions and in the Standard and Reagent Log Book located in the instrument lab. Equivalent standards may be purchased from other suitable suppliers as available. Other volumes of a standard may be prepared by modifying the amount of stock used appropriate to the final volume required.

6.5.1 Internal, Clean-up and Matrix Spike Standards: prepare standards as per BRL SOP-00408. Refer to Section 7.1 for the spiking amounts.

7.0 ANALYTICAL PROCEDURE:

In most cases the following procedures for sample extractions and clean-ups are followed. Clients may occasionally request a specific method to be followed. Contact the Project Mgr. if there is a doubt. Prepare the spikes as per BRL SOP-00408.

7.0.1 Sample ID Check:

- Step 1* check that the MAXXAM laboratory label and the original container label have identical Client Ids
- Step 2* **Step 2** Print a LIMS worksheet containing all sample Ids and appropriate QC for the batch.

7.1 Spiking:

7.1.1 Internal Standard (Surrogate):

- Step 1* use the syringe dedicated for spiking the internal standard
- Step 2* rinse the syringe several times with acetone prior to spiking
- Step 3* add the internal standard (green label), to the method blank, the blank spike(s) samples, duplicates and matrix spikes, (5 µL/split)

Note: If GPC 1 is being used the GPC clean up consumes half of the sample so double the final volume if it will be used. If GPC 2 is used the entire extract will be loaded onto the GPC column and double spiking is not required.

- Step 4* record all volumes used and the split if any on the tracking sheet
- Step 5* rinse the syringe thoroughly with acetone after use

7.1.2 Matrix Spike (Native, OPR):

- Step 1* use the syringe dedicated for matrix spiking
- Step 2* rinse the syringe several times with acetone prior to spiking
- Step 3* add the matrix spike (red label), to the blank spike(s) and the matrix spike samples (10 µL/split)

Note: If GPC 1 is being used the GPC clean up consumes half of the sample so double the final volume if it will be used. If GPC 2 is used the entire extract will be loaded onto the GPC column and double spiking is not required.

- Step 4* record all volumes used and the split if any on the tracking sheet
- Step 5* rinse the syringe with acetone after use

7.1.3 Cleanup Spike:

- Step 1* all sample extracts require the cleanup spike unless a client specifies otherwise
- Step 2* always use the cleanup standard syringe
- Step 3* rinse the syringe several times with acetone prior to spiking
- Step 4* add the clean up spike (5 uL) to the samples, blank, blank spike(s), duplicates and matrix spikes before any cleanups are started, including the acid back-extraction procedure if required
- Step 5* record all volumes used on the tracking sheet
- Step 6* rinse the syringe with acetone after use

7.1.4 Method Spike: prepare a method spike with each batch of samples extracted. Using procedures given in Sections 7.1.1 to 7.1.3, spike a clean calibrated 5mL centrifuge tube containing with the internal standard, matrix spike and clean-up spike add nonane to a final volume of 100 µL. Use only one aliquot of spikes even if the sample was spiked double or more for a split or a GPC run. Hand this in with the samples.

Note: SPIKING MUST BE WITNESSED BY A SECOND STAFF MEMBER FAMILIAR WITH THE PROCEDURE. Both the person spiking the solution and the witness must sign off the tracking sheet

7.2 Extraction Procedures for Liquid Samples (Water, Liquid Drinks etc.): For samples without particulate proceed to section 7.2.2

7.2.1 Visible Particulates: if particulate is visible the sample must be filtered using the apparatus described in Section 6.3.4. The filter containing the residue is not dried and is extracted as a solid – no Internal standard is added to this prior to Soxhlet extraction.

Extraction of Particulates from a Liquid Sample:

- Step 1* rinse a pre-washed 1 L vacuum flask 3x with DCM
- Step 2* rinse a 90 mm Buchner funnel 3x with DCM
- Step 3* Carefully pour the sample into the funnel with the vacuum applied. Use additional filters, which have been weighed, if there is a large amount of solid material.
- Step 4* rinse the bottle with minimal RODI, ensure particulates are transferred, if required
- Step 5* keep sample bottle for extraction, keep water portion for extraction
- Step 6* continue suction until the flow stops completely
- Step 7* Carefully transfer the filter(s) used to a portion of pre-rinsed aluminum foil. All filters used will be combined and extracted in one Soxhlet body as per Section 7.2.1.1.

Note: Samples requiring filtration will be noted on the worksheet.

- Step 8* Transfer the filtered liquid contents of the flask to a clean labeled separatory funnel. Rinse the flask and the Buchner funnel with DCM and add this to the separatory funnel and proceed to 7.2.3

7.2.1.1 Extraction of the Solids Portion of the Liquid Sample:

- Step 1* Prepare a Soxhlet apparatus according to Section 7.3.2, steps 3, 5, 6 and label glassware.
- Step 2* add all filters used for the for each sample to the same Soxhlet body. Cover with ~1.5 cm of anhydrous Na₂SO₄. Note: the filters are not spiked with any standards.
- Step 3* Once solid portion has extracted for 16 hours, rotary evaporate the extract to ~2 mL and combine with rotovaped extract of the water portion. Concentrate combined extracts to ~2 mL prior to cleanup.

7.2.2 Preparation of Liquid Samples not requiring filtration:

Prior to any liquid extractions, cleaned glassware must be thoroughly rinsed as follows:

- Step 1* Separatory funnels are rinsed 3 times with ~100-150 mL of DCM, shaking for 2 minutes each time and releasing the pressure as required.
- Step 2* Prepare Allihn filters/ conical funnel by placing them on the flasks and filling the filter ~1/3 to 1/2 full with anhydrous Na₂SO₄ or ~10-20 grams of Na₂SO₄ for the funnel respectively. Rinse the 500mL flask and filter combination 3 times with ~100-150 mL of DCM, shaking for 2 minutes each time.
- Step 3* Label flasks and separatory funnels with sample number

Perform the following for each sample:

- Step 1* Mark the position of the meniscus on the bottle to allow the initial volume determination.
- Step 2* Label cleaned flasks and separatory funnels with sample number.
- Step 3* Fill the method blank and blank spike separatory funnel with ~1L of RODI water for the QC. Note: prepare one of each for every batch of 20 samples, or less, depending on the client's requirements
- Step 4* Pour the samples into their marked 2L separatory funnel.
- Step 5* Add the internal standard as described in Sections 7.1.1.
- Step 6* Spike the blank and matrix spikes as described in Sections 7.1.2 and record start time on tracking sheet, as well as the unique glassware numbers on the worksheet for each sample.
- Step 7* Add ~150 mL of DCM to each sample bottle and shake vigorously for ~30 sec and add this DCM to each respective sample separatory funnel. For method blank, blank spike and matrix spike add ~ 150mL of DCM directly to the separatory funnel.
- Step 8* For the first extraction of the aqueous phase, shake the separatory funnel vigorously for ~ 4-5 minutes, with occasional venting.
- Step 9* Allow the layers to stand for ~5-10 minutes to achieve separation.
- Step 10* If necessary break up any emulsions as per Section 7.2.3.
- Step 11* Drain the lower DCM of each sample and QC from the separatory funnel through their

respective pre-rinsed and labeled Allihn filter/conical funnel flask combination.

- Step 12* Extract the aqueous phase a second time with ~100 mL of DCM added to the separatory funnel, shaking vigorously for ~3 minutes and occasionally venting.
- Step 13* Drain the lower DCM of each sample and QC from the separatory funnel through their respective pre rinsed and labeled Allihn filter/conical funnel flask combination.
- Step 14* Extract the aqueous phase a third time with ~100 mL of DCM added to the separatory funnel, shaking vigorously for ~1 minute and occasionally venting.
- Step 15* Drain the lower DCM of each sample and QC from the separatory funnel through their respective pre rinsed and labeled Allihn filter/conical funnel flask combination.
- Step 16* Add an additional ~50mL of DCM to the Allihn filter or funnel of each sample and QC to rinse the Na₂SO₄. Note: A bulb can be used on the filter to ensure collection of the remaining DCM.
- Step 17* Add ~3-5 mL of iso-octane and rotary evaporate the extract to ~2 mL. Note: transfer samples directly from the flask to the first clean up column if no splits are required

Measure the sample volume by pouring the remaining sample after extraction into a 1000 mL graduated cylinder. Record the volume on the tracking sheet and record QC volume of 1000mL.

7.2.3 Emulsions: emulsions covering >1/3 of the organic layer must be broken up. The following techniques may help to break up the emulsified layer

Option 1:

- Step 1* use a glass rod to break up the emulsion or
- Step 2* Drain the organic layer into multiple DCM rinsed centrifuge tubes, if required, and centrifuge the sample for ~5 minutes at 3000 rpm.
- Step 3* if the emulsion still exists add ~2 drops of conc. H₂SO₄ and shake gently, (use caution!), then re-centrifuge the layer
- Step 4* Using a pipette, transfer the separated DCM layer to the samples respective Allihn filter or funnel. Carefully pour the centrifuge tube(s) contents back to the appropriate separatory funnel. If performing tumbler extraction, drain the funnel back into the sample bottle once the centrifuge material has been added back.
- Step 5* If performing a tumbler extraction, rinse the tubes with a total of ~50 mL of DCM and add to the sample bottle to continue extraction. If performing a manual extraction, rinse the tubes with a total of ~100 mL of DCM and continue extraction.
- Step 6* Repeat if necessary before completing the third extraction.

Option 2:

- Step 1* Drain the organic layer into 250 mL wide mouth clear glass jar, well rinsed with DCM and add an additional ~10 mL of DCM.
- Step 2* Shake for ~1 min to achieve separation. If necessary, add additional DCM to separate the organic layer.
- Step 3* Using a pipette, transfer the separated DCM layer to the samples respective Allihn filter or funnel. Carefully pour the jars' contents back to the appropriate separatory funnel. If performing tumbler extraction, drain the funnel back into the sample bottle once the centrifuge material has been added back.
- Step 4* If performing a tumbler extraction, rinse the jar with a total of ~50 mL of DCM and add

to the sample bottle to continue extraction. If performing a manual extraction, rinse the jar with a total of ~100 mL of DCM and continue extraction.

Repeat if necessary before completing the third extraction.

7.3 Preparation of Solid Samples (Soil, Sediment, Meat, Processed food, Cheese, Egg, Ash, etc.):

Note: All soxhlet apparatus with added glass wool and ~ 2-3cm of Na₂SO₄ are put overnight to cycle prior to usage.

7.3.1 For dry weight reporting - Moisture Determination is completed using CAM SOP-00445 in the pre-processing lab. The results for % moisture can be found in MaxLIMS.

7.3.2 Extraction of Solids: (Soils, Filters, Sediment)

- Step 1* Do not dry samples, analytes of interest may be lost
- Step 2* thoroughly rinse all glassware, flasks and Soxhlet apparatus three times [~ 2 minutes each time] with ~ 100mL DCM, discard the rinsate
- Step 3* prepare a Soxhlet apparatus each for the blank, blank spike(s), samples, duplicates and matrix
- Step 4* Add ~300-350mL DCM to the flask, enough for the sample to cycle for 16-18 hours and not go dry.
- Step 5* label the Soxhlets and flasks with the sample ID numbers
- Step 6* prepare 250 mL clear glass jars, which are rinsed 3 times with DCM
- Step 7* make sure the samples are homogenized prior to weighing to get a representative sample.
- Step 8* accurately weigh into the glass jars 10-25 g of sample. If required, use the moisture of the sample to obtain an equivalent of ~10 g dry weight for each and record the weights on the tracking sheet
- Step 9* Gradually add ~ 10-25g of Na₂SO₄ and mix thoroughly until the sample is free flowing.
- Step 10* Transfer the mixture to the labeled soxhlet and add another ~ 1cm of Na₂SO₄ to cover the top of the sample
- Step 11* spike all the samples, blank and blank spike(s), duplicates and matrix spikes with the internal spiking solution as in Section 7.1.1 and record on the tracking sheet
- Step 12* spike only the blank spike(s) and matrix samples with the matrix spiking solution as in Section 7.1.2 and record on the tracking sheet
- Step 13* rinse the sides of the Soxhlet with DCM to ensure all of the spike solutions has reached the sample
- Step 14* extract for at least 16-18 hours with ~300 mL DCM, the flasks do not need to be covered with aluminum foil
- Step 15* after 16-18 hours remove from burners and rinse the sides of the soxhlet with additional DCM to cycle the Soxhlet into the flask
- Step 16* rotary evaporate the extract to ~2 mL with solvent exchange into isoctane

Note: DO NOT LET THE EXTRACT GO DRY AT ANY TIME

7.3.2.1 Optional Extraction Using Dean Stark Apparatus:

Note: do not use Na_2SO_4 with the Dean Stark Apparatus

- Step 1* do not dry samples, analytes of interest may be lost
- Step 2* thoroughly rinse all glassware, flasks and Soxhlet apparatus 3x [~ 2minutes each time] with ~100mL toluene, discard the rinsate
- Step 3* prepare a Soxhlet apparatus for each blank, blank spike(s), sample, duplicate and matrix spike rinse through with toluene
- Step 4* add ~300-350mL of toluene to each flask, enough for the sample to cycle 16-18 hours and not go dry.
- Step 5* label the Soxhlets and flasks with the sample ID numbers
- Step 6* prepare a thimble with a ~5 g silica layer and 100 g of clean sand
- Step 7* make sure the samples are homogenized prior to weighing to get a representative sample.
- Step 8* accurately weigh into the glass jars 10-25 g of sample. If required, use the moisture of the sample to obtain an equivalent of ~10 g dry weight for each and record the weights on the tracking sheet
- Step 9* mix the sample into the sand thoroughly without disturbing the silica layer
- Step 10* insert the thimbles into the Soxhlets
- Step 11* spike all the samples, blank and blank spike(s), duplicates and matrix spikes with the internal spiking solution as in Section 7.1.1 and record on the tracking sheet
- Step 12* spike only the blank spike(s) and matrix samples with the matrix spiking solution as in Section 7.1.2 and record on the tracking sheet
- Step 13* rinse the sides of the Soxhlet with toluene to ensure all of the spike solutions has reached the sample
- Step 14* fill the Dean Stark with ~100-175 mL toluene
- Step 15* place on the burners, set at high, and wrap the entire apparatus except for the Dean Stark reservoir with aluminum foil to ensure that boiling temperature is achieved
- Step 16* extract for 16-18 hours with toluene , (do not let the extract go dry at any time)
- Step 17* remove from burners and rinse the sides of the soxhlet body with solvent to cycle the Soxhlet into the flask

Note: this procedure may be required by other clients, consult the Project Manger

7.3.3 Soxhlet Extraction of Food (Meat, Processed food, Cheese, Egg)

- Step 1* do not dry samples, analytes of interest may be lost
- Step 2* Make sure each sample is homogenized prior to sub sampling
 - Samples with particle sizes greater than 5mm are subjected to grinding, homogenization or blending. The method of reducing the particle size to less than 5mm is matrix dependent. In general, hard particles can be reduced by grinding them with a mortar and pestle. Softer particles can be reduced in size by using a meat grinder. (Reference CAM SOP 00704)

- Step 3* Thoroughly rinse all glassware, flasks and Soxhlet apparatus three times with DCM [~ 2 minutes each time] with ~ 100mL DCM, discard the rinsate
- Step 4* Prepare a Soxhlet apparatus each for the blank, blank spike(s), samples, duplicates and matrix spikes
- Step 5* Add ~300 – 350mL of DCM to the flask, enough for the samples to cycle for 16-18 hours and not go dry.
- Step 6* Label the Soxhlets and flasks with the sample ID numbers
- Step 7* Prepare 250mL jars by rinsing 3 times with DCM
- Step 8* Accurately weigh sample, (~5-20g) into the rinsed jars-record the accurate weights on the tracking sheet
- Step 9* Gradually add ~10-25g of Na₂SO₄ to the jars and mix thoroughly until the sample is free flowing
- Step 10* Transfer the mixtures to the labeled Soxhlets and add ~1 cm of Na₂SO₄ to the top of the sample
- Step 11* Spike all the samples, blank and blank spike(s), duplicates and matrix spikes with the internal spiking solution as in Section 7.1.1 and record on the tracking sheet
- Step 12* Spike only the blank spike(s) and matrix samples with the matrix spiking solution as in Section 7.1.2 and record on the tracking sheet
- Step 13* Rinse the sides of the Soxhlet with DCM to ensure all of the spiking solution has been added to the sample
- Step 14* Extract for at least 16-18 hours with ~300 mL **50/50 DCM/hexane**, flasks don't need to be covered with aluminum foil
- Step 15* Do not let the extract go dry at any time
- Step 16* Remove from burners and rinse the sides of the soxhlet with solvent into the flask
- Step 17* Prepare the sample for GPC clean-up, all biota samples require GPC prior to clean-up, refer to BRL SOP-00003

7.4 Cleanup Procedures: the following is a summary of the cleanup strategy.

All food extracts containing greater than 1% lipids are subjected to GPC before proceeding to column cleanup (starting at Section 7.4.2). Refer to BRL SOP-00003 for GPC cleanup. Solid and post-GPC lipid containing samples may undergo a sulphuric acid extraction before proceeding to column cleanup (Section 7.4.1). The sulphuric acid extraction must also be performed on any water samples that are cloudy, discoloured or suspected to be heavily contaminated with dissolved organic interferents.

7.4.1 Sulphuric Acid Extraction:

- Step 1* Quantitatively transfer the 2mL extract from the flask to a pre-rinsed 40mL vial labeled 'A' and rinse the flask 4 times with ~2mL of DCM –add each rinse to vial 'A'
- Step 2* Concentrate the extract to ~ 10mL.

- Step 3* Add ~10 ml of concentrated H₂SO₄ to the extract in vial 'A'. Shake and vent several times to release the pressure. Then shake vigorously for ~2minutes. Allow the vial 'A' to stand for ~10minutes.
Note: Using a centrifuge after shaking for ~2 minutes at a setting of 3000rpm for ~4minutes will speed up the process.
- Step 4* When 2 distinct layers are formed, transfer the DCM layer (top layer) using a Pasteur pipet into another pre-rinsed 40mL vial labeled as 'B'. If the H₂SO₄ portion in vial 'A' is highly coloured, add ~10mL of H₂SO₄ to vial 'B' and repeat step 3.
Note: If an emulsion forms and 2 distinct layers are not observed, transfer the entire contents of the vial to a 250mL jar or a small separatory funnel and increase the volume of H₂SO₄ to ~50mL and DCM to ~75mL.
- Step 5* If colour is still present in the acid portion, repeat steps 3 and 4. The DCM portion to be transferred to another pre-rinsed vial labeled 'C'. Repeat the extractions with H₂SO₄ until no further colour is noticed. Label the last re-rinsed vial as 'F' (Final)
- Step 6* For vial 'A' acid portion, rinse 2 times with ~ 10mL of DCM and shake each time for ~ 2 minutes. Add the rinsate to vial 'B', then the rinsates from 'B' should be added to vial 'C' and the rinsate from vial 'C' will be transferred to vial 'F'
- Step 7* Concentrate the extract, vial 'F' under a gentle stream of N₂ to ~ 2mL
- Step 8* Process the extract as per 7.4.2

7.4.2 H₂SO₄ Acid/Silica Gel Column:

- Step 1* prior to application of the extract, add the cleanup spike as described in section 7.1.3
- Step 2* add activated copper powder to the extract until it no longer turns black
- Step 3* pack the tapered end of a 15 mm ID x 40 cm glass column with a small piece of glass wool, add in the following sequence;
- ~1/2 mL sodium sulphate
 - ~1/2 mL silica gel
 - 9 mL of 44% H₂SO₄ in silica gel
 - ~1/2 mL silica gel
 - ~1/2 mL sodium sulphate
- Step 4* pre-wash the column with ~30 mL of hexane and discard the hexane
- Step 5* using a disposable pipet, transfer the extract to the column just as the rinse reaches the top of the column bed
Transfer steps are critical. Loss of any of the extract will seriously affect recoveries.
- Step 6* Rinse the flask/vial with ~ 2mL of hexane and transfer the rinsate to the column. Discard the eluent from the waste vial and switch to a pre-rinsed 40mL collection vial that has been labeled appropriately.
- Step 7* Quantatively rinse the flask/vial several times with additional hexane, adding each rinsate to the column just as the previous rinse reaches the top of the column bed.
- Step 8* Add additional hexane in small amounts to rinse down the sides of the column
- Step 9* When the vial is ~ half full, the hexane can be added in larger amounts (~10mL)
- Step 10* Continue addition of hexane until the collection vial is filled to the top
- Step 11* Concentrate the total eluent to ~ 2mL final volume under a gentle stream of N₂ @ room temperature, adding ~ 1mL of iso-octane as a keeper during concentration
- Step 12* Cover the eluent with a teflon-lined cap if the extract is not to be processed immediately.

Note: If the rate of concentration is too fast, analyte loss may occur

Note: If the entire sulphuric acid/ silica gel layer is coloured, the column has been overloaded. Reprocess the concentrated eluent on a fresh column.

7.4.3 3% Water Deactivated Florisil:

Step 1 pack the tapered end of a disposable graduated pipette with glass wool and add in the following sequence;

- ~1/2 mL sodium sulphate
- 1 mL 3% H₂O in SiO₂
- 1 mL 3% H₂O in Florisil
- 2.5 mL 44 % H₂SO₄ in SiO₂
- ~1/2 mL sodium sulphate

Step 2 rinse the packed column with ~ 10mL of hexane and discard the eluent from the waste vial and switch to a pre-rinsed 40mL collection vial that has been properly labeled

Step 3 using a disposable pipet, add the extract to the column just as the solvent reaches the top of the column bed

Step 4 quantitatively rinse the vial several times, adding each rinsate to the column just as the previous rinse reaches the top of the column bed

Step 5 when the vial is approximately half full, the hexane can be added in larger amounts (~7 mL)

Step 6 collect ~30-40 mL

Step 7 place the vial on the N-Evap and concentrate under a gentle stream of N₂ at room temperature to ~1 mL, adding ~ 1mL of iso-octane as a keeper during concentration

Note: If the rate of concentration is too fast, analyte loss may occur

7.4.4 Sample Concentration (Vialing):

Step 1 Pre-rinse a 5mL centrifuge tube, calibrate the tube to 100uL and add ~ 100uL of nonane – label all the tubes appropriately

Step 2 Load ~ 1mL of the extract from the 40mL vial to the centrifuge tube, rinse the vial with ~ 0.5mL of hexane and add the rinsate to the centrifuge tube.

Step 3 Place the centrifuge tube on the N-Evap at room temperature and a gentle stream of N₂

Step 4 rinse the 40 mL vial at 2 more times with ~0.5 mL hexane, adding each rinse to the centrifuge tube

Step 5 concentrate the extract to 100 µl

Note: if highly contaminated, analysts may want the extract vialled in 1 mL of iso-octane using a 15 mL centrifuge tube.

8.0 QUALITY CONTROL:

8.1 Internal Standard Recoveries: refer to BRL SOP-00408 for details

8.2 Method Blank Analysis: Prepare a method blank for each batch of 20 samples using blank matrix

8.3 Blank Matrix Spike: an aliquot, equal to the method blank aliquot is spiked with the matrix spike solution. One blank spike is extracted for every 20 samples unless regulations or contracts require or allow a different frequency.

8.4 Laboratory Duplicates: extract a duplicate from a randomly selected sample at a frequency of 1 in 20 or 1 per sample batch if projects require. This is not required if an MS/MSD is prepared.

8.5 Matrix Spike/Matrix Spike Duplicate: if the sample batch size is 20 or more then two separate sub-aliquots of one randomly selected sample is spiked with an appropriate level, (dependent on the expected sample concentration), of chlorinated biphenyl homologues, (Matrix Spike). Spike at a level 2-5x higher than the sample if possible. If a regulatory limit is involved, spike at the regulatory limit. If there is insufficient sample, this step may be omitted.

8.6 Additional QC Requirements: the exact requirements of the QC for any given project should be discussed with the project manager to ensure that project contractual requirements are met. For example, certain regions of EPA require MDL verification studies, triplicate analysis and other special QC requirements not identified in this SOP.

9.0 DATA ANALYSIS:

Not applicable to this SOP. Refer to the analytical SOP BRL SOP-00408 for data calculations.

10.0 DOCUMENTATION:

10.1 Preparation/Extraction Documentation: A LIMS worksheet and a tracking sheet needs to accompany all sample. This sheet includes details of the Job number, lab sample number, client sample ID, QC samples analyzed in the batch, spiking solutions used and their concentrations, preparation date and lot #, dates of analysis and cleanup, analysts initials. A copy of the tracking/work sheet is maintained with analytical data.

10.2 Analyst Logbook: the analyst must record, at a minimum, the following information in their logbook

- deviations from normal procedures required for problematic samples, (deviations must be discussed and signed off by the appropriate lab manager), trouble shooting records with full descriptions of the actions taken to resolve the problem. This is required for all instances in which acceptance criteria are not achieved. Alternatively, these may also be recorded on the sample tracking / work sheet.

Sample Deviation Records: these deviations are recorded in the Job comment fields in LIMS. The entries listed appear on the Certificate of Analysis as part of the final report sent to the client. Some examples are as follows:

- analyzed past hold time
- matrix interference suspected,
- sample is not homogeneous

10.4 Method Deviation Records: See COR WI-00040 for Corporate Policy Deviation procedure and CAM FCD-00328 for Bench Level Deviation/Non-Conformance Form.

10.3 Reagent Preparation Logbooks: all preparations of reagents are recorded in the Reagent Preparation Logbook. All records must contain, at a minimum, the following information.

- supplier Lot Number
- concentration and date of preparation and expiry
- name of analyst who prepared the reagent

11.0 WASTE MANAGEMENT

Safety & Disposal

General Safety requirements for this SOP are provided in the critical task analysis (CTA). In addition to the CTA, additional guidance on Maxxam's Environment, Health and Safety (EHS) program are found in various Safe Work Procedures, Safety Policies, and the Safety Guide (See MEHS WI-00013).

- 11.1 The use of personal protective equipment (PPE), including safety glasses and lab coats are mandatory in all Maxxam labs. It is the responsibility of the analyst to read and understand the CTA associated with this SOP and ensure that any additional identified hazard controls are used (e.g. nitrile gloves, splash goggles, fume hoods, respirators, etc).
- 11.2 Material safety data sheets for all chemical reagents are available to personnel using this method. Training on the interpretation of MSDS sheets is provided during WHMIS training upon hire. Staff performing this method shall review the associated MSDS sheets for chemicals used in this procedure and ensure they understand the associated hazards and safety controls required to work safely with each chemical.
- 11.3 Disposal of all samples, extracts and reagents must be done in accordance with local, provincial and federal laws and regulations. Chemical wastes and sample disposal protocols are described in CAM SOP-00105 and CAM WI-00018.
- 11.4 All waste must be disposed of as hazardous waste and may not be discarded in the sink.

Ultra Trace Air Toxics SOP BRL SOP-00415 / 5

Ultra Trace Air Toxics

OC Pesticides by HRMS in Liquid, Solid and Tissue



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Document Identity	
Document Categorization	
Ultra Trace Air Toxics Departments Hidden	Environmental HRMS

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Release and Audit Schedule	
Release Schedule	When Approved <input type="checkbox"/> Allow Administrator to Release Document Early
Expiration Schedule	When Superseded or Obsolete
Audit Schedule	12 Month(s)
Special Handling on Release	
<input checked="" type="checkbox"/> Update Completed Trainee Records	

Insert Text	
BRL SOP-00415 r5	

Associated Documents
Document Control Documents
<ul style="list-style-type: none"> Burlington WI BRL WI-00011 : Review and Validation of Analytical Data Burlington SOP BRL SOP-00003 : GPC Cleanup Burlington SOP BRL SOP-00010 : Extraction Organochlorine Pesticides from Liquids and Solids Burlington FCD BRL FCD-00052 : MDL Template for Multi-Analyte Tests - NELAC Corporate WI Publish to All COR WI-00010 : Corporate Procedure for Nonconformances Corporate WI Publish to All COR WI-00011 : Corporate Procedure for Corrective and Preventative Actions Corporate WI Publish to All COR WI-00012 : Definitions Corporate WI Publish to All COR WI-00018 : Determination of Estimation of Analytical Uncertainty of Measurement Corporate WI Publish to All COR WI-00040 : Corporate Procedure for Policy Deviation Forms Corporate WI Publish to All COR WI-00044 : Manual Integration of Chromatographic Peaks Corporate WI Publish to All COR WI-00049 : Continuing Calibration Verification (CCV) Acceptance Criteria Corporate WI Publish to All COR WI-00050 : Environmental Chemistry Method Validation Corporate WI Publish to All COR WI-00055 : Corporate Procedure for Control Charting Campobello WI CAM WI-00095 : Environmental Method Validation (NELAC + DOD requirements) Campobello WI CAM WI-00121 : Maxxam Lab QM Supplement to Meet Requirements of DoD QSM Version 4.2

Reason for Change	
<p>Date of Change July 14, 2009</p> <p>Section Changed 1.0, 3.5, 4.1.1, 6.2.2, 7.3.4.1, 7.3.4.2, 8.1, 8.3, 9.3, 10.2.2, Table 2, Table 4</p> <p>Change Made 1.0 updated to current location 3.5 removed the list to eliminate redundancy 4.1.1 referenced to Associated Documents section 6.2.2 added DDT & Endrin Breakdown Solution 100ng/mL 7.3.4.1 + 7.3.4.2 added: DDT/Endrin Breakdown Check 8.1 added: DDT/Endrin Breakdown Check, and renumbered 8.1-8.10 8.3 change limits to +/-35% for ion abundance ratios 9.3 referenced to BRL WI-00011 to reflect current practice 10.2.2 referenced to the QSI Deviation policy Form to reflect current practice Table 2 added reference to the EPA 1699 current ratios Table 4 replaced p,p'-DDD-ring d8 with p,p'-DDD-ring 13C12</p>	Version 2
<p>Date of Change July 15, 2009</p> <p>Section Changed Table 1</p> <p>Change Made Table 1 replaced d8-pp-DDD with 13C12-pp-DDD</p>	Version 3
<p>Date of Change August 5, 2010</p> <p>Section Changed 3.2, 3.3, 4.0, 8.5, 10.2, 10.6.1</p> <p>Change Made 3.2+3.3 redefined correlation between MDL and detection limit, as well as Maxxam's RDL and LOQ, added performance of quarterly LOD and LOQ 4.0 updated reference section by listing reference methods used in this SOP 8.5 added method blank criteria & corrective actions for DoD related projects 10.2 updated to reflect current practice re: use of COR WI-00040, Corporate Procedure for Policy Deviation Forms 10.6.1. updated storage of records offsite to reflect current practice</p>	Version 4
<p>Date of Change December 5, 2012</p> <p>Section Changed 3.2, 8.3, 8.9</p> <p>Change Made 3.2 revised to refer to CAM WI-00095 for method validation; refer to CPro for the maintenance of validation records 8.3 updated section with respect to Continuing Cal. Standards,%RSD was changed to %D (% difference). In addition, overall grammatical and spelling corrections. 8.9 added two more analytes to be control charted and referenced current COR WI-00055 for control charting procedure</p> <p>Optional Field A Associated documents have been reviewed, and where required the CPro links were updated to reflect most current procedures in use by the HRMS laboratory</p>	Version 5

Approval Status Table			
Approver	Source	Role for Approvers	Parallel-Everybody Segment
Approver	Action	Date	Comment
Ewa Koniczna	Approve	November 30, 2012 5:16 PM GMT-5	
Owen Cosby	Approve	December 5, 2012 8:57 PM GMT-5	

DETERMINATION OF ORGANOCHLORINE PESTICIDES IN LIQUID, SOLID AND TISSUE SAMPLES BY HIGH-RESOLUTION GC/MS

1.0 LOCATION:

This procedure is performed in the HRMS Prep Lab and the HRMS Instrument Laboratory.

2.0 PURPOSE:

This method is used to measure the concentration of Organochlorine Pesticides, (OCs) in liquid, solid and tissue samples.

2.1 Principal of the Method: OCs are Soxhlet extracted from solid samples with dichloromethane (DCM) and from tissue samples with 50:50 DCM/hexane. An optional Dean Stark extraction using toluene may be used for solids. Liquid-liquid extraction with DCM is used for aqueous samples. Following extraction, the samples are cleaned up and passed through a series of columns that remove, by reaction and/or selective adsorption, the bulk of the organic matrix co-extracted with the OCs. The resulting fraction is concentrated to a known volume for analysis. Qualitative/quantitative analysis for OCs is performed using separation by high-resolution capillary gas chromatography, (HRGC), and measurement by high-resolution mass spectrometry (HRMS). OCs are identified by comparing gas chromatograph (GC) retention times and the ion abundance ratios of the m/z s with the corresponding values obtained for authentic standards.

The GCMS system is calibrated and the analyte concentration is determined using an isotope dilution technique. Quantitation is based on the use of internal standards and relative response factors (RRFs).

2.2 Nature of Samples: samples can be from many different sources including incinerator ashes, soils, sediments and effluents. The laboratory should be made aware of any past history involving the samples or the presence of potentially interfering substances at elevated levels (e.g. PCB). This can allow the preparation technician to take a smaller aliquot of sample so that internal standards are not diluted out during analysis.

2.3 Safety:

2.3.1 General Considerations: the toxicity or carcinogenicity of each compound or reagent used in this method has not been established precisely. Each compound should be treated as a potential health hazard and exposure should be reduced to the lowest possible level. On the basis of the available toxicological and physical properties of the OCs, only highly trained personnel thoroughly familiar with handling and cautionary procedures should handle these compounds, and who understand the associated risks. All work related to the analysis of OCs should be carried out within a specially designed laboratory.

3.0 SCOPE:

This is a HRGC/HRMS method for the determination of OCs at picogram to nanogram levels in liquid, solid, and tissue samples.

3.0.1 Chemical Abstracts No.: refer to Table 4 in the Appendix for a listing of the CAS No.

3.1 Linear Range: the method is calibrated over the following linear ranges of calibration solutions.

5.0 pg/ μ L to 2000 pg/ μ L

3.2 Detection Limit: detection Limit is also referred to as Method Detection Limits (MDL): an MDL is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. MDLs are determined by the procedure outlined in CAM WI-00095, for Method Validation procedure.

Target MDLs are verified annually by spiking water/soil replicates in respective clean matrices. These samples are carried through the full extraction and cleanup procedure. MDLs are determined by multiplying the standard deviation of the results by the Student's t -Value for the number of replicates used. If Target Limits are not achieved, the exercise is repeated spiking at a lower level. An MDL study is used to determine if the target limits outlined in test methods have been achieved. These are maintained on file in the CPro MDL Module as well as at the instrument.

Estimated Detection Limit (EDL): EDLs are sample specific and are calculated on a case specific basis for all analytes. If a signal produced is not at least 2.5 times the average background level at the expected retention time for specific isomers, the area response for the noise is calculated as follows.

$$2.5 \times \text{peak intensity of background noise} \times \frac{\text{area of internal standard}}{\text{height of internal standard}}$$

This is done for either the quantitation ion or the confirmation ion. Using theoretical ratios for the specific degree of chlorination an area for the second ion is generated. These areas are then totaled and applied to the same calculation scheme as for “positive” hits. (see Section 9). EMPCs (Estimated Maximum Possible Concentrations) are calculated whenever peaks are detected that meet all criteria except for ratios. The area in this case is recalculated (factored up or down) to meet the classical ratio and the result is flagged as an EMPC (NDR, not detected because of ratios, for Canadian Method).

3.3 Reporting Detection Limit (RDL): Reporting Detection Limit is also referred to as Limit of Quantitation (LOQ), equivalent to the Low Level Standard.

3.4 Interferences: interferences co-extracted from the sample material will vary considerably with the matrix and the diversity of the site being sampled. OCs are often associated with other chlorinated organics that may potentially interfere with the analysis. These include polychlorinated biphenyls, polychlorinated dibenzodioxins and furans, polychlorinated hydroxy diphenyl ethers, polychlorinated benzylphenyl ethers, polychlorinated diphenyl ethers, polychlorinated naphthalenes, polychlorinated xanthenes, and polynuclear aromatics.

Often the compounds responsible for interferences may be present at concentration levels several orders of magnitude higher than any OCs that may be present. Cleanup procedures can be used to reduce or eliminate these interferences to the maximum extent practicable in order to ensure reliable quantitation of OCs at trace levels. Despite rigorous cleanup procedures, the possibility of matrix interference will still exist. If the excessive background seriously elevates detection limits, the sample extract will have to be re-processed using alternative cleanup techniques.

3.5 Definitions:

Refer to Corporate Definitions procedure: COR WI-00012

4.0 REFERENCES:

EPA Method 1699, December 2007, Pesticides in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS. Method 1699 is performance-based method, any modifications made to it as per current BRL SOP-00415 must meet the method's equivalency requirements stated in section 9.1.2.

Maxxam's method meets EPA 1699 method performance and prior to the release of the reference method 1699 it has been developed in conjunction, and with the approval of the NYS Department of Environmental Conservation and is derived from the proposed NYSDEC Method HRMS-2.

4.1 Additional Information Sources:

- Draft Analytical Procedure for Organochlorine Pesticides by Isotope Dilution HRGC/HRMS, NYSDEC Method HRMS-2.
- Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples, Section 3A [required for cleaning glass components of the sampling train].
- For further information contact Gary McAlister or Roger Shigehara, Emission Measurement Branch (MD-19), Technical Support Division, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, USA 27711, telephone (919)-541-1062.
- Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS
- USEPA Method 1699: Pesticides in Water, Soil, Sediment, Biosolids and Tissue by HRGC/HRMS. Brian Englehart, Ph. D., Engineering & Analytical Support Branch, Engineering and Analysis Division (4303T), Office of Science and Technology, Office of Water, U.S.E.P.A, 1200 Pennsylvania Avenue NW, Washington, DC, 20460.
- EPA SW-846 3540C, Soxhlet Extraction, (SW-846 PROPOSED UPDATE III Revision 3, January 1995)

- EPA SW-846 3510C, Separatory Funnel Liquid-Liquid Extraction (SW-846 PROPOSED UPDATE III Revision 3, January 1995),
- EPA SW-846 3620C, Fluorisil Cleanup, Revision 3, February 2007.
- EPA SW-846 3640A, Gel-Permeation Cleanup, (SW-846 Update II, September 1994)

4.1.1 Other Standard Operating Procedures:

Refer to CPro section Associated Documents for links to related methods

4.3 Analytical Test Codes:

Other test codes may be created as necessary

Waters: **Analysis:**
 PESTOCHR-W OCs In Water By HRMS

Solids: **Analysis:**
 PESTOCHR-S OCs In Solids By HRMS

Tissues: **Analysis:**
 PESTOCH-TI OCs In Tissues By HRMS

5.0 SAMPLE HANDLING AND PRESERVATION:

When feasible, samples should be maintained at 2-6 °C from the time of collection until the point of extraction. Due to the fragile nature of the containers, the samples should be well wrapped with protective packaging during shipment from the field site to the laboratory. Samples that exceed the hold time will be flagged on the Certificate of Analysis. Different hold times may be imposed by other regulating agencies or as determined by client specific projects. Project specific and regulatory requirements for preservation method and reporting criteria, (required detection limit, dry or wet weight basis), must be examined and made clear prior to sample analysis. **Note:** sample containers should have Teflon liners in the caps.

<u>Matrix</u>	<u>Container</u>	<u>Min. Vol.</u>	<u>Time to Extract</u>	<u>Time to Analysis</u>
Waters	4x1 L amber glass	800 mL	30 days	45 days
Soils/Sludge	100 mL amber glass	2x5 gram	30 days	45 days
Pulp	100 mL amber glass	2x15 gram	30 days	45 days
Biological	100 mL amber glass	2x20 gram	30 days	45 days

6.0 APPARATUS AND MATERIALS:

6.1 Reagent Preparation: all reagent preparation information, lot numbers, and supplier are documented in the reagent preparation logbook kept in the sample preparation laboratory. Equivalent quality reagents and standards may be purchased from other suppliers as appropriate

6.1.1 Solvents: hexane, dichloromethane (DCM), toluene, isooctane, , nonane, ethyl acetate, petroleum ether, Distilled in Glass quality from Fisher or Caledon

6.1.2 RODI Water: Reverse Osmosis Deionised Water, (RODI), >16MΩ purity, produced in house

6.1.3 Compressed Gases: UHP Grade nitrogen

6.2 Standard Preparations: all standards preparations, lot numbers, supplier information, pertinent dates are documented by the analyst in the Standard Preparation Log Book located in the instrumentation laboratory. Store stock standards as per manufacturer's directions.

After preparation, use a permanent fine-tip marker to mark a line at the liquid level.

This allows monitoring loss due to evaporation. (Loss is greatly reduced by using refrigerated storage.)

6.2.1 Calibration Standards: refer to Appendix: Table 3 for the volumes of the stock standards to use for preparing calibration standards. Current suppliers and lot numbers are in the Standards Prep Logbook in the Instrument Lab. Stock (neat) standards are stored in the freezer compartment of the standards fridge.

6.2.1.1 Native Intermediate (20 ng/uL): add the volumes of stocks to a 5 mL volumetric flask and dilute to volume with nonane.

6.2.1.2 Native Dilution (0.2 ng/uL): dilute 10 uL of the native intermediate to 1 mL with nonane

6.2.1.3 Matrix Spiking Solution (5 ng/uL): add 1250 uL of the native intermediate to a 5 mL volumetric flask and dilute to volume with nonane

6.2.2 Method Spiking or Internal Standard Solution (4 ng/uL): a 10 mL nonane working level internal standard solution, is prepared once every two years or as required containing isotopically labeled OCs stock solutions. The volume of stock standards used is recorded in the Standard Preparation Log Book, located in the Instrument laboratory. Manufacturer Certified Stock standards are purchased from Cambridge Isotope Laboratories, Andover, MA, USA -

Component	Stock Conc. (ng/μL)	Final Conc. (pg/μL)	Vol. Added (μL)
Aldrin ¹³ C ₁₂	100	4000	400
BHC-beta ¹³ C ₆	50	4000	800
Chlordane ¹³ C ₁₀	100	4000	400
cis-Nonachlor ¹³ C ₁₀	100	4000	400
Dieldrin ¹³ C ₁₂	100	4000	400
Endrin ¹³ C ₁₂	100	4000	400
Heptachlor ¹³ C ₁₀	100	4000	400
Heptachlor Epoxide ¹³ C ₁₀	100	4000	400
Lindane ¹³ C ₆ d ₆	100	4000	400
Methoxychlor-ring ¹³ C ₁₂	100	4000	400
Mirex ¹³ C ₁₀	100	4000	400
Oxychlordane ¹³ C ₁₀	100	4000	400
p,p'-DDD-ring ¹³ C ₁₀	100	4000	400
p,p'-DDE-ring ¹³ C ₁₂	100	4000	400
p,p'-DDT-ring ¹³ C ₁₂	100	4000	400
trans-Nonachlor ¹³ C ₁₀	100	4000	400
Endosulfan-I- ¹³ C ₉	100	4000	400
Endosulfan-II- ¹³ C ₉	100	4000	400
HXB ¹³ C ₆	100	4000	400
Endrin Ketone ¹³ C ₁₂ **	50	4000	800
Endrin Aldehyde ¹³ C ₁₂ **	50	4000	800

** Obtained in solid form and reconstituted as per manufacturers instructions. The stability of these compounds in solution is unknown and not certified and they have been included on a trial basis

Recovery or Injection Standard (5 ng/uL) a 5 mL final volume, nonane working level solution, is prepared once every two years or as required and are purchased from Cambridge Isotope Laboratories, Andover, MA, USA , or Wellington Labs, Guelph, Ontario, Canada.

The volumes of stock standards used for the current set of working level standards in use are documented in the Standard Preparation Log Book, located in the Instrument laboratory.

DDT and ENDRIN Breakdown Check Solution (100 ng/mL) a 10 mL final volume, nonane working level solution, is prepared once every two years or as required and are purchased from a reputable supplier such Accustandard or Ultra Scientific. The volumes of stock standards used for the current set of working level standards in use are documented in the Standard Preparation Log Book, located in the Instrument laboratory.

6.2.3 Use the following for 5 ng/μL stocks.

Component	Stock Conc. (ng/μL)	Final Conc. (pg/μL)	Vol. Added (μL)
BHC-delta ¹³ C ₆	100	5000	250
¹³ C ₁₂ -Tetrachlorobiphenyl (BZ 52)	50	5000	500
¹³ C ₁₂ -Pentachlorobiphenyl (BZ 101)	50	5000	500
¹³ C ₁₂ -Heptachlorobiphenyl (BZ 178)	50	5000	500

6.3 Apparatus: autosampler vials; assorted gas-tight micro syringes; assorted screw cap amber vials with teflon-lined caps. Equivalent labware and equipment may be purchased from other suppliers as available.

6.3.1 Glassware Quality Control: all extraction glassware is engraved with a specific serial number. Glassware used for processing samples is tracked using this number. All glassware is subjected to a proven, rigorous cleaning procedure after which it is acceptable for reuse. Method Blank analyses confirm the acceptability of this procedure.

- Soxhlet apparatus that were exposed to samples resulting in highly coloured extracts are soaked in a soap solution, (Extran), overnight
- After soaking they are rinsed thoroughly with successive rinses of RODI water and acetone
- All Soxhlets are then cycled with toluene overnight
- Rotovap glassware is rinsed thoroughly with appropriate solvents after each use

6.4 Instrumentation: High Resolution GCs coupled to High Resolution Mass Spectrometers

HR Gas Chromatographs:

Associated HR Mass Spectrometers:

HP6890A	(S/NUS000034029)	Micromass AutoSpec Ultima	(S/N M384)
HP6890	(S/N US00029754)	Micromass Autospec Ultima	(S/N M230)
HP6890D	(S/N US00030341)	Micromass Autospec Ultima	(S/N M449)
HP6890N	(S/N US10131086)	Micromass Autospec Ultima	(S/N M536)
HP5890 Series II	(S/N3203G16149)	VG AutoSpec "S"	(S/N S1800)
HP6890A Plus	(S/NUS00038736)	Micromass AutoSpec Ultima	(S/N M526)

6.4.1 Gas Chromatographs: gas chromatographs consist of the following components

- **Oven:** capable of maintaining a temp. ± 1 °C and performing programmed temp. rate increases of at least 3 °C/min
- **Temperature Gauge:** to monitor column oven, detector, & exhaust temperature ± 1 °C
- **Gas Flow Metering System:** to measure sample, fuel, combustion gas, & carrier gas flows
- **Capillary Column:** the primary column is a fused silica column, 60 m x 0.25 mm inside diameter (ID) x 0.25 μ m film thickness, coated with CP Sil 8CB (Varian or equivalent)

6.4.2 Mass Spectrometers: capable of routine operation at 1:10000 resolution with ± 5 ppm stability with a compatible data system capable of monitoring at least five groups of 25 ions. Because of the extensive mass range covered in each function, it may not be possible to maintain 10,000 resolution throughout the mass range during the function; therefore, resolution must be $\geq 8,000$ throughout the mass range and must be $\geq 10,000$ in the center of the mass range for each function.

6.5 Miscellaneous Equipment: analytical balance capable of measuring within 0.1 mg

7.0 ANALYTICAL PROCEDURE:

7.1 Sample Extraction: refer to BRL SOP-00010 "for the Extraction and Clean-up of Organochlorine Pesticides from Liquid and Solid Samples.

7.2 Sample Clean Up and Fractionation: refer to BRL SOP-00010 "for the Extraction and Clean-up of Organochlorine Pesticides from Liquid and Solid Samples.

7.3 Analysis: analyze the sample extract by HRGC/HRMS using the instrumental parameters in section 7.3.1 and 7.3.2.

- Step 1** Add 4 μ L of Recovery Standard to the 200 μ L sample extract in the 1 mL Reacti-vial
- Step 2** Vortex for ~30 seconds and allow to equilibrate for at least 3 minutes
- Step 3** Transfer a portion to an amber autosampler vial using a micropipettor
- Step 4** Seal with an aluminum teflon lined crimp cap
- Step 5** Inject 1 or 2 μ L of the extract into the GC

Analyze the sample using a GC/MS with the instrument parameters given in Section 7.3.1 and 7.3.2. Some samples, at a 200 μ L final volume, may contain high levels of the compounds of interest, interfering compounds, or polymeric

materials, and may crystallize out of solution at room temperature. A 10-fold dilution is performed to address this issue, as well as the anomalies observed with recoveries of the internal standard. A 1-2 μl aliquot of both extracts is injected into the GC to determine the concentration of each target analyte.

7.3.1 Typical GC Operating Conditions (these are typical conditions and are optimized for each individual column to maximize performance.

- **Injector:** configured for capillary column, splitless, 250 °C
- **Carrier Gas:** helium at 1-2 ml/min
- Initial Temperature 100 °C for 2 minutes
- 20 °C/minute to 150 °C
- 5 °C/min to 285 °C
- hold at 285 °C for 2 minutes

7.3.3 High Resolution Mass Spectrometer

- Resolution of 8,000 minimum
- Ionization Mode: Electron impact, 35-40 eV, (optimize)
- Source Temperature: 290 °C, (optimize)
- Monitoring mode: Selected ion recording - see Table 1 for a list of the ions to be monitored

7.3.4 Run Sequence: at the beginning and the end of a run sequence, a hardcopy of the Resolution check is printed out. The operator manually verifies that a minimum resolution of 1:8,000 has been achieved for each multi group experiment; see the descriptor groups in see Table 1.

7.3.4.1 Initial Calibration: (process takes ~ 4 to 5 hours to perform)

- DDT/ENDRIN Breakdown Check
- CS1_OC
- CS2_OC
- CS3_OC
- CS4_OC
- CS5_OC
- Solvent
- OC_Ref_Std (optional 2nd source standard, if available)
- Solvent

7.3.4.2 Typical Sample Analysis Sequence: (process takes ~12 hours to perform). At the beginning and the end of a run sequence a hardcopy of the Resolution check is printed out. The operator manually verifies that a minimum resolution of 1:8,000 has been achieved for each multi group experiment, see the descriptor groups in Table 1. After this verification is complete the run can proceed as follows:

- DDT/ENDRIN Breakdown Check
- CS3_OC
- Solvent (optional)
- OPR
- Solvent
- Method Blank
- Sample 1
- Sample 2
- Sample 3
- Sample 4
- Sample 5
- Sample 6
- Sample 7
- ...
- Sample 20
- Solvent
- CS3_OC (post analysis calibration verification)
- Method Spike (the method spike is not used in any calculations but serves only as an aid to determine the

source of potential problems for internal and matrix recovery.)

7.4 Identification Criteria: the following preliminary identification criteria shall be used for characterization of OCs.

- The integrated ion-abundance ratio shall be within ± 20 percent of the theoretical value or the value obtained from that days calibration standard
- Retention time for the analytes must be within 3 seconds for the corresponding labeled internal, surrogate or alternate standard
- The monitored ions shown in Table 1 for a given analyte shall reach their maximum within 2 seconds of each other
- The identification of specific analytes that do not have corresponding labeled standards is done by comparing the relative retention time, (RRT), of the analyte to the nearest internal standard retention time with reference, (i.e. within 0.005 RRT units), to the comparable RRT's found in the continuing calibration
- The signal to noise for all monitored ions must be >2.5

7.4.1 Quantification: the peak areas for the two ions monitored for each analyte are summed to yield the total response for each analyte.

7.5 Maintenance: Maxxam staff or a manufacturer's Service Engineer will perform emergency maintenance. Preventative maintenance is performed annually through a service contract.

7.6 Troubleshooting and Common Problems: the analyst may perform the following checks if he/she is capable. Otherwise call a Manufacturer's Service Engineer. Check for the following conditions:

- System is fully powered on and is in the Operate mode
- Vacuum is in acceptable range, i.e. 10^{-6} mbar or better, if not check for leaks
- Filament is "ON" and the trap is regulating
- Source and transfer line heaters are at the proper operating temperature, the source temperature affects the fragmentation of the sample
- GC in good working order, adequate supply of carrier gas with respect to oven heater and temperature regulation
- Injector system is clean with a properly installed column, liner and septum. Leaks and contamination may cause performance problems
- Capillary column Helium head pressure is adjusted to proper setting, i.e. ~ 25 psi for a 60 m x 0.25 mm ID column
- Autosampler syringe is in good condition, not leaking nor plugged
- Data system is running and is controlling and communicating with the instrument

7.6.1 Loss of Beam: may be caused by any of the following

- A defective source, collector or alpha slit may be obstructing the beam
- The isolation valve may not be completely open, check the pneumatic valve
- Check the compressed air tank line pressure
- Broken or blocked PFK jet or capillary line, replace if necessary

7.6.2 Loss of Filament Current, Trap Current and Electron Energy: may be caused by any of the following

- Remove the source, check for short circuits, dirty or defective parts. Clean or replace if needed
- Check the filament alignment in the source when replacing it
- If the filament comes on and there is no Trap current, this could indicate that a trap contact problem has occurred
- Check the electrical contacts and the alignment of the source magnets

7.6.3 Loss of Magnet: may be caused by any of the following

- High voltage breaker switch tripped due to a power interruption or surge
- High voltage breaker switch tripped due to a loss of the cooling water supply. When cooling water supply is lost or is too warm the magnet unit and the diffusion pumps overheat. The heat sinks on the power supply board cause the power to shut down and may trip the breaker on the power distribution panel on the front of the instrument. These must all be reset before the magnet can be turned back on

7.6.4 Loss of High Voltage: may be caused by any of the following

- An electronic fault and may be brought on by a discharge of a dirty lens or ceramics or arcing of the flight tube
- These regions must be cleaned to restore voltages and to re-establish control of the beam
- Electronics and S10S interface will also have to be reset to restore communications and control of the beam control and source control PCBs

8.0 QUALITY CONTROL:

8.1 DDT/ENDRIN Breakdown Check: This test is to be run at the beginning of every run before an initial calibration or continuing calibration. Its purpose is assess the activity of the injection port will eventually which cause Endrin and 4,4'-DDT to breakdown into Endrin Aldehyde and Ketone and 4,4'-DDD and 4,4'-DDE, respectively. The percent breakdowns are calculated as follows:

$$4,4'\text{-DDT Breakdown (\%)} = \frac{\text{(Sum of areas for 4,4'\text{-DDD} + \text{sum of areas for 4,4'\text{-DDE)}}}{\text{Sum of areas for 4,4'\text{-DDT}}} \times 100$$

$$\text{Endrin Breakdown (\%)} = \frac{\text{(Sum of areas for Endrin Aldehyde + Endrin Ketone)}}{\text{Sum of areas for Endrin}} \times 100$$

- A percent breakdown of $\geq 20\%$ indicates Endrin breakdown into Endrin Aldehyde and Ketone and similarly for 4,4'-DDT into 4,4'-DDD and DDE.
- If $\geq 20\%$ breakdown is observed, the injection port must be cleaned and reconditioned. This means cooling the injector, wiping surfaces clean with Kim Wipe and methanol, replacing the septum, inlet liner and gold seal.
- Pyrex liners dual tapered are recommended for this test, as they are believed to be less active.
- Liners can be made to be inactive through re-silanization then capping with methanol. Consult a senior analyst or supervisor before attempt this as the silanizing compound dichlorodimethyl silane is corrosive.

8.2 Initial Calibration: calibrate the GC/MS system using the set of five standards, (Table 3). These working level standards are used for a period up to 2 years. If available, an "injection ready" standard from a second source supplier is also run as part of the initial calibration. Instrument parameters are adjusted and standards are analyzed until the following QC criteria are achieved.

- Relative standard deviation, (RSD), of the mean response factor for each unlabeled analytes should be $\pm 35\%$.
- RSD of the mean response factor for each of the labeled standards should be $\pm 35\%$
- Signal to noise ratio for the GC signal present in every selected ion current profile shall be ≥ 10 for both labeled and unlabeled analytes
- The ion abundance ratios shall be within the control limits in Table 2

8.3 Continuing Calibration Verification: inject 1 μL of solution CS3, (see Table 3). At the beginning of each 12 hour sequence, calculate the relative response factors, (RRFs), for each compound and compare each of them to the corresponding mean RRF obtained during the initial multi-point calibration. The following requirements should be met before sample analysis can begin.

- The measured %D (% difference) of the RRF for the labeled analytes for the daily run must be $\pm 50\%$ except for $^{13}\text{C}_{12}$ -Endrin and the natives that use it as an internal standard (Endosulfan Sulfate). As this compound is extremely susceptible to GC injector activity, its' response will increase as the liner is used. Calculations may use the daily RF for these compounds to correct for this.
- The measured %D of the RRF for the unlabeled analytes for the daily run must be $\pm 50\%$
- The ion abundance ratios must be within the limits given in Table 2 or within $\pm 35\%$ of the value obtained from that days calibration standard

The CS3 standard is analyzed at the end of the run sequence. The %D of the RRFs are again compared to the initial calibration and should satisfy the above criteria. As another indicator of breakdown, a decrease in the RF of the ^{13}C -4,4'-DDT of $>50\%$ compared to the initial calibration is an indicator of injector liner degradation and GC inlet maintenance must be performed.

8.4 Internal Standards: are added to all samples and QC samples.

Recoveries must be 10-200% for the labeled compounds

8.4.1 Corrective Actions: if the above criterion is not achieved

- The data will still be acceptable provided that the signal is equal to or greater than ten times the noise level
- This will be flagged in the Case Narrative section of the final report
- The extract may be diluted and rerun. Complex matrices may mask or enhance the response of several compounds (Aldrin, methoxychlor, 4,4'-DDT)

- The sample may be re-extracted if nothing can be found to explain the low or high recoveries and no obvious interference is causing the problem.

8.5 Method Blanks: a method blank is run in every batch, and a minimum of one for every 20 samples.

Method Blank must be <CS1 Standard concentration (RDL)

NOTE: for DoD samples, the method blank will be considered to be contaminated if:

- The concentration of any target analyte in the blank exceeds 1/2 the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater);
- The concentration of any common laboratory contaminant in the blank exceeds the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater); or
- The blank result otherwise affects the samples results as per the test method requirements or the project-specific objectives

8.5.1 Corrective Actions: if the above criteria are not met then

- Investigate possible source of contamination by checking at a minimum: instrument Spike Standard Solutions, Recovery Standards, proofing of glassware, proofing of solvent and absorbents used in clean-up.
- All of the samples must be re-prepared and reanalyzed
- If sufficient sample is not available then any positive sample data must be flagged as possibly contaminated to the level found in the Method Blank

8.6 Blank Matrix Spike: must be prepared and analyzed at a frequency of 1 Blank Spike for every batch of samples up to a maximum batch size of 20 samples. Calculate the recovery as:

$$\text{Spike Recovery (\%)} = \frac{\text{Spiked Blank Result}}{\text{Spike Added}} \times 100$$

Native analyte recoveries should be 40-200%

Internal Standard recoveries should be 10-200%

8.6.1 Corrective Actions:

- Check calculations and reanalyse if recoveries are outside of these limits
- If the blank spike is outside of limits but the matrix spike is acceptable then the blank spike may have been spiked incorrectly. Review the data with the Team or Group Leader. All data may be accepted but must be flagged as exceeding acceptance criteria
- If both the blank spike and the matrix spikes exceed their respective limits re-prepare and reanalyze the samples providing sufficient sample is available
- If sufficient sample is not available the data must be flagged in Tester's Comments

8.7 Matrix Duplicate: must be prepared and analyzed using randomly selected samples, at a frequency of 1 matrix duplicate for every batch of samples up to a maximum batch size of 20 samples. The RPD is calculated as:

$$\% \text{ RPD} = \frac{\text{first sample result} - \text{duplicate sample result}}{(\text{First sample result} + \text{duplicate sample result})/2} \times 100$$

RPD between duplicates should be ±25%

8.7.1 Corrective Actions:

- Check calculations for errors
- Check solid samples for homogeneity, if not homogeneous, flag the data in Tester's Comments
- If the sample is homogeneous, re-prepare and reanalyze the sample

8.8 Matrix Spike/Matrix Spike Duplicate Recoveries: if sufficient sample is available, spike two separate aliquots of a sample in each batch of 20 samples or less with an appropriate level, (2-5 times the sample concentration if possible), of native OCs. Calculate the recoveries as follows:

$$\text{Matrix Spike Recovery (\%)} = \frac{\text{spiked sample result} - \text{sample result}}{\text{Amount spike added}} \times 100$$

Recoveries of matrix spiked internal standards must be between 10-200%

Native analyte recoveries should be 40-200%

RPD between duplicates should be $\pm 25\%$

8.8.1 Corrective Actions:

- Check calculations for errors
- If recovery calculations aren't possible, (due to high sample concs.), flag the data in Tester's Comments
- If the blank spike is acceptable then flag the data as a possible Matrix interference
- Check solid samples for homogeneity, if not homogeneous, flag the data in Tester's Comments
- If the sample is homogeneous, re-prepare and reanalyze the sample
- if both the blank spike and the matrix spikes exceed their respective limits re-prepare and reanalyze the sample the sample if sufficient sample is available
- if sufficient sample is not available flag the data in Tester's Comments

8.9 Control Charts: plot the blank spike recovery of 4,4'-DDT, Heptachlor Epoxide, and 4,4'-DDD for waters, soils, and tissues on separate control charts. Update the chart immediately after the analysis of the QC point used or in the morning after an overnight run, prior to reporting of data. Monitor the chart for the development of trends on the chart. Take actions, if necessary, as defined in the COR WI-00055 for Control Charting. If an "Out of Control" point is found, terminate the analysis and resolve the problem. Note the resolution directly on the chart or code the point to a reference in the analyst's workbook.

8.9.1 Possible Causes:

- Deterioration of standard, reagents or injector liner activity
- Standard, QC sample or reagent preparation error
- Standard contamination or evaporation
- Improper sample introduction
- Poor analyst technique or insufficient training
- Deviation from SOP procedure
- Imprecise measuring devices, i.e. pipettors, syringes

8.9.2 Corrective Actions: if "out of control points" are encountered

- Check the other run QC, if acceptable report the data
- If not acceptable, reanalyze the QC samples and if acceptable, report the data
- If not acceptable, find and resolve the cause, re-extract and reanalyze the samples
- If insufficient sample exists report the data, flagged as "out of statistical control"
- If hold times will be exceeded upon re-extraction and reanalysis, flag the data
- If no reason can be found, report the data as "out of statistical control"

Note the resolution on the Control Chart or reference it to the Analyst's Workbook.

8.10 Additional QC: in addition to the QC samples listed above, blind replicates, audit and performance evaluation samples may be submitted. These samples may have specific instructions that must be followed, however, analysis is to proceed as for any other sample. Any USACE project has an Analytical Data Review Checklist, documented in the QA Manual, completed and submitted with the final data report.

9.0 DATA ANALYSIS:

9.1 Calculations: the internal standard method is used to quantify OCs. It relies upon consistent linearity of MS response over time and over the calibration range represented by the standard solutions defined in Table 3. This internal standard method is easily integrated into an automated routine for data quantification. Internal standard quantification is based on the use of Relative Response Factors, (RRF). For native standards, the RRF is the ratio of analyte response factor to the response factor of the corresponding labeled surrogate, (internal standard). These RRFs remain unchanged over the range of concentration for which MS response is linear. Using these RRFs, along with native and surrogate

responses from the sample run, recovery-corrected concentrations of OCs are calculated directly. Internal standard recoveries are calculated separately and reported. These values reflect the overall data quality.

Relative response factors for the native standard (RRFn) and for the Internal standard (RRFs) are calculated using the following equations:

$$RRFn = \frac{Ac * Csc}{Asc * Cc} \quad \text{and} \quad RRFs = \frac{Asc * Crc}{Arc * Csc}$$

Where:

- RRFn = relative response factor, Native Standard to Internal Standard
- RRFs = relative response factor, Internal Standard to Recovery Standard
- Ac = quantification ion (single or both ions) peak area for Native Standard
- Asc = quantification ion (single or both ions) peak area for the appropriate Internal Standard
- Arc = quantification ion (single or both ions) peak area for the appropriate Recovery Standard
- Cc = concentration of the Native Standard (pg/μl)
- Csc = concentration of the appropriate Internal Standard (pg/μl)
- Crc = concentration of the appropriate Recovery Standard (pg/μl)

Using the RRFs, sample concentrations of OCs (C) and internal standard recoveries (%R) can be calculated as follows:

$$C(X) = \frac{\sum_{k=1}^n Ak \cdot Qss}{Ass \cdot RRFn} /Ws \text{ or } Vs \quad \text{and} \quad \%R(X) = \frac{Ass * Qrs * 100}{Ars * Qss * RRFs}$$

Where:

- C(X) = recovery-corrected quantity of analyte X (ng/g for solids, ng/L in liquids)
- Ak = quantification ion (single or both ions) peak area for the “kth” homologous isomer of analyte X (n=1 for isomer-specific analysis)
- Qss = amount of internal standard X added to the sample (ng)
- Ass = quantification ion (single or both ions) peak area for internal standard X in extract
- %R(X) = percent recovery of internal standard X
- Qrs = amount of the appropriate Recovery Standard in sample extract (ng)
- Ars = quantification ion (single or both ions) peak area for the appropriate Recovery Std in the sample extract
- Ws = weight of dry sample in grams
- Vs = volume of sample in litres

9.2 Data Transfer: data is processed using a custom application macro developed internally. An excel spreadsheet is generated which incorporates weights, dilution factors, splits, internal standard amounts added, recovery standard amounts added and estimated detection limits. The result file, once completed and checked by authorized personnel is electronically transferred to the MaxxLIMS and approved.

9.3 Data Validation: Refer to BRL WI-00011 Review and Validation of Analytical Data and corresponding Data Review Checklist (BRL FCD-00002) to perform a primary and a secondary analytical data review and validation prior to issuance of the Certificate of Analysis. If the data and report are acceptable the Certificate of Analysis is signed by the Project Manager and sent to the client.

9.4 Data Storage: sample data is transferred to a separate computer system as required. The back up computer is maintained by the systems group and is also backed up regularly.

10.0 DOCUMENTATION:

10.1 Tracking Sheet: before samples are prepared, a GC-MS sample tracking /work sheet is completed. This sheet includes details of the Job number, lab sample number, client sample ID, QC samples analyzed in the batch, spiking solutions used and their concentrations, preparation date and lot #, dates of analysis and cleanup, analyst’s initials. A copy of the tracking /work sheet is maintained with analytical data

10.2.1 Instrument Logbook:

- Troubleshooting records with full descriptions of the actions taken to resolve the problem. This is required for all instances in which there is an acceptance criterion that is not achieved. Alternatively these may also be recorded on a separate tracking sheet designed for the analysis.
- Record of Instrument Service by the Supplier with the associated paperwork

10.2.2 Method Deviation Records: instances may arise in which the standard operating procedure may not be applicable to the nature of the sample and may require modifications to the normal methodology. These deviations must be discussed with the Supervisor or Operation Manager prior to application. Approval must be obtained as per COR WI-00040 and documented using QSI module for Policy Deviation Form. These deviations must also be described in the comment section of MaxxLIMS.

10.2.3 Sample Deviation Records: these deviations must be recorded in MaxxLIMS Comments.

10.4 Maintenance Tracking: analysts maintain logbooks/tracking sheets to include the following minimum information

- Record of Instrument Service by the Supplier with the associated paperwork
- Records of all maintenance performed indicating the date performed and by who

10.5 Standard and Reagent Preparation Tracking: record all preparations of standards and reagents in the Standard Preparation and the Reagent Preparation Logbooks. All records must contain at a minimum the following information

- Supplier Identification and Lot Number
- Date of Preparation and Expiry
- Concentration, and name of Analyst who prepared the standard

10.6 Certificates of Analysis for Standards and Reagents: certificate of analyses are kept for all inorganic salts and solutions utilized in this SOP. These records will contain at a minimum the following information.

- Supplier information and Lot Number
- Date received

10.7 Storage of Records:

10.7.1 Paper Records: raw and calculated data, including calibrations and QC results are stored chronologically in file folders in the laboratory. These files are archived on-site for a period of one year and then transferred to an off-site storage for 5 years, unless otherwise instructed.

Electronic Media: data entered into LIMS is backed up daily.

11.0 WASTE MANAGEMENT:

All efforts are taken to prevent or reduce to a minimum the effect of waste disposal on the environment. All solvents are collected for shipment to a recycling facility. All recyclable plastic, glass and paper products are shipped to an appropriate recycling facility. The disposal of waste materials and samples are to be carried out in accordance with protocols outlined in the SOP for the Preparation, Storage and Disposal of Reagents and Standards and the SOP for the Receipt, Handling and Disposal of Hazardous Wastes. All waste disposal will comply with the Ontario Ministry of the Environment and Energy's Sewer Guidelines and Regulation 558.

11.1 Specific Disposal Issues: contaminated sample extracts are collected and sent for disposal to an approved hazardous waste subcontractor. Excess contaminated samples are either returned to the client or submitted for disposal as noted.

12.0 APPENDIX:

- Table 1: Exact Masses of the Ions Monitored by Hi-Resolution Mass Spectrometry
- Table 2: Theoretical Ion Abundance Ratios and their Control Limits
- Table 3: Hi Res OC Calibration Standards
- Table 4: Quantitation References For Organochlorine Pesticides

TABLE 1:
EXACT MASSES OF THE IONS MONITORED BY HI-RESOLUTION MASS SPECTROMETRY

Descriptor No:	Accurate Mass		Analyte
1	216.9145	M	a-BHC, b-BHC, d-BHC, g-BHC
	218.9116	M+2	a-BHC, b-BHC, d-BHC, g-BHC
	222.9347	M	13C6-beta BHC, 13C6-delta BHC
	224.9317	M+2	13C6-beta BHC, 13C6-delta BHC
	227.9662	M	13C6-d6-gamma BHC (Lindane)
	229.9632	M+2	13C6-d6-gamma BHC (Lindane)
	283.8102	M	Hexachlorobenzene
	285.8072	M+2	Hexachlorobenzene
	289.8303	M	13C6-Hexachlorobenzene
	291.8273	M+2	13C6-Hexachlorobenzene
	230.9856	LOCK MASS	PFK
	2	262.857	M
264.854		M+2	Aldrin
269.8806		M	13C12-Aldrin
271.8102		M	Heptachlor
271.8776		M+2	13C12-Aldrin
273.8072		M+2	Heptachlor
276.8272		M	13C10-Heptachlor
278.8242		M+2	13C10-Heptachlor
301.9626		M	13C-PCB 52
303.9597		M+2	13C-PCB 52
280.9824		LOCK MASS	PFK
3		352.8442	M
	354.8413	M+2	Heptachlor Epoxide
	362.8779	M	13C10-Heptachlor Epoxide
	364.8749	M+2	13C10-Heptachlor Epoxide
	377.7482	M	Octachlorostyrene
	379.7452	M+2	Octachlorostyrene
	386.8055	M	oxy-Chlordane
	388.8025	M+2	oxy-Chlordane
	396.839	M	13C10-Oxychlordane
	398.839	M+2	13C10-Oxychlordane
	380.976	LOCK MASS	PFK
	4	194.9537	M
196.9507		M+2	a-Endosulfan
201.9771		M	13C9-Endosulfan I
203.9741		M+2	13C9-Endosulfan I
234.8445		M	g-Chlordane, a-Chlordane
235.0081		M	2,4'-DDD
236.8416		M+2	g-Chlordane, a-Chlordane
237.0052		M+2	2,4'-DDD
239.8613		M	13C10-Chlordane
241.8583		M+2	13C10-Chlordane
246.0003		M	2,4'-DDE, 4,4'-DDE
247.9974		M+2	2,4'-DDE, 4,4'-DDE
258.0406		M	13C-pp-DDE
260.0376		M+2	13C-pp-DDE
262.857		M	trans-Nonachlor, Dieldrin
264.854		M+2	trans-Nonachlor, Dieldrin
265.986		M	13C-PCB 101
267.983		M+2	13C-PCB 101
269.8806		M	13C10-trans Nonachlor, 13C12-Dieldrin
271.8776		M+2	13C10-trans Nonachlor, 13C12-Dieldrin
242.9856		LOCK MASS	PFK

TABLE 1: continued

Descriptor No:	Accurate Mass		Analyte
5	194.9537	M	b-Endosulfan
	196.9507	M+2	b-Endosulfan
	201.9771	M	13C9-Endosulfan II
	203.9741	M+2	13C9-Endosulfan II
	235.0081	M	4,4'-DDD, 2,4'-DDT, 4,4'-DDT
	237.0052	M+2	4,4'-DDD, 2,4'-DDT, 4,4'-DDT
	247.0484	M	13C12-pp-DDD
	249.0454	M+2	13C12-pp-DDD
	247.0484	M	13C-pp-DDT
	247.8523	M	Endrin Aldehyde
	249.0454	M+2	13C-pp-DDT
	249.8493	M+2	Endrin Aldehyde
	262.857	M	Endrin, cis-Nonachlor
	264.854	M+2	Endrin, cis-Nonachlor
	269.8806	M	13C12-Endrin, 13C10-cis Nonachlor
	271.8102	M	Endosulfan Sulfate
	271.8776	M+2	13C12-Endrin, 13C10-cis Nonachlor
	273.8072	M+2	Endosulfan Sulfate
242.9856	LOCK MASS	PFK	
6	405.8428	M	13C-PCB 178
	407.8398	M+2	13C-PCB 178
	392.976	LOCK MASS	PFK
7	227.1072	M	Methoxychlor
	228.1106	M+2	Methoxychlor
	239.1475	M	13C-Methoxychlor
	271.8103	M	Mirex
	273.8073	M+2	Mirex
	276.8272	M	13C10-Mirex
	278.8242	M+2	13C10-Mirex
	316.9039	M	Endrin Ketone
	318.901	M+2	Endrin Ketone
	280.9824	LOCK MASS	PFK

H = 1.007825
 C = 12.000000
 13C12 = 13.003355
 F = 18.9964
 O = 15.994915
 35Cl = 34.968853
 37Cl = 36.965903

Alternate PFK lock masses may be employed in order to remove column bleed interferences should a new column not be available.

TABLE 2:
THEORETICAL ION ABUNDANCE RATIOS AND THEIR CONTROL LIMITS

Number of Cl Atoms	Ion Type	Theoretical Ratio	Control Limits *	
			Lower	Upper
4	M/M+2	0.77	0.62	0.92
5	M+2/M+4	1.55	1.24	1.86
6	M+2/M+4	1.24	0.99	1.49
6	M/M+2	0.51	0.41	0.61
7	M/M+2	0.44	0.35	0.53
7	M+2/M+4	1.04	0.83	1.25
8	M+2/M+4	0.89	0.71	1.07

* QC limits represent $\pm 20\%$ window around the theoretical ion abundance ratios. These limits are preliminary. As of 2007, the method USEPA 1699 states that the ratios are in a 25-35% window.

TABLE 3: Hi Res OC Calibration Standards

Component	Stock Conc. (ng/μl)	CS5		CS4		CS3		CS2		CS1	
		Conc. (pg/μl)	Vol. Req'd. (μl)								
Native Analytes											
OC Native Intermediate	20	2000	400	400	80	100	20	-	-	-	-
OC Native Dilution	0.2	-	-	-	-	-	-	20	400	5	100
Internal Standards											
OC Internal Standard	4	100	100	100	100	100	100	100	100	100	100
Recovery Standards											
OC Recovery Standard Mix	5	100	80	100	80	100	80	100	80	100	80

Final Volume of all standards is 4 mL.

Table 4

QUANTITATION REFERENCES FOR ORGANOCHLORINE PESTICIDES

Compound	CAS Number	Internal Standard Reference	Recovery Std Reference
2,4'-DDD	53-19-0	p,p'-DDD-ring $^{13}\text{C}_{12}$	13C-PCB 101
2,4'-DDE	3424-82-6	p,p'-DDE-ring $^{13}\text{C}_{12}$	
2,4'-DDT	789-02-6	p,p'-DDT-ring $^{13}\text{C}_{12}$	
4,4'-DDD	72-54-8		
4,4'-DDE	72-55-9	p,p'-DDE-ring $^{13}\text{C}_{12}$	13C-PCB 101
4,4'-DDT	50-29-3	p,p'-DDT-ring $^{13}\text{C}_{12}$	13C-PCB 101
Aldrin	309-00-2	Aldrin $^{13}\text{C}_{12}$	13C-PCB 52
BHC-alpha	319-84-6	BHC-beta $^{13}\text{C}_6$	
BHC-beta	319-85-7	BHC-beta $^{13}\text{C}_6$	13C6-delta BHC
BHC-delta	319-86-8	BHC-beta $^{13}\text{C}_6$	
BHC-gamma	58-89-9	Lindane $^{13}\text{C}_6 \text{ d}_6$	13C6-delta BHC
Chlordane (cis)	5103-71-9	Chlordane $^{13}\text{C}_{10}$	
Chlordane (oxy)	27304-13-8	Oxychlordane $^{13}\text{C}_{10}$	13C-PCB 52
Chlordane (trans)	5103-74-2	Chlordane $^{13}\text{C}_{10}$	13C-PCB 101
Dieldrin	60-57-1	Dieldrin $^{13}\text{C}_{12}$	13C-PCB 101
Endosulfan I	959-98-8	Endosulfan-I- $^{13}\text{C}_9$	13C-PCB 101
Endosulfan II	33213-65-9	Endosulfan-II- $^{13}\text{C}_9$	13C-PCB 101
Endosulfan Sulfate	1031-07-8	Endrin $^{13}\text{C}_{12}$	
Endrin	72-20-8	Endrin $^{13}\text{C}_{12}$	13C-PCB 101
Endrin Aldehyde	7421-36-3	Endrin $^{13}\text{C}_{12}$	
Endrin Ketone	53494-70-5	Mirex $^{13}\text{C}_{10}$	
Heptachlor	76-44-8	Heptachlor $^{13}\text{C}_{10}$	13C-PCB 52
Heptachlor Epoxide B	1024-57-3	Heptachlor Epoxide $^{13}\text{C}_{10}$	13C-PCB 52
Hexachlorobenzene	118-74-1	HXB $^{13}\text{C}_6$	13C6-delta BHC
Methoxychlor	72-43-5	Methoxychlor-ring $^{13}\text{C}_{12}$	13C-PCB 178
Mirex	2385-85-5	Mirex $^{13}\text{C}_{10}$	13C-PCB 178
Nonachlor (cis)	5103-73-1	cis Nonachlor $^{13}\text{C}_{10}$	13C-PCB 101
Nonachlor (trans)	39765-80-5	trans Nonachlor $^{13}\text{C}_{10}$	13C-PCB 101