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Portland Harbor RI/FS

ROUND 2
QUALITY ASSURANCE PROJECT PLAN
ADDENDUM 1: SURFACE WATER

DRAFT

August 13, 2004

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Prepared for:
The Lower Willamette Group

Prepared by:
Integral Consulting, Inc.

EPA Region 10 Superfund
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SECTION A: PROJECT MANAGEMENT

A1 TITLE AND APPROVAL SHEET

PORTLAND HARBOR RI/FS
ROUND 2 SURFACE WATER

Quality Assurance Plan Approvals

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CAS Project Manager:	Abbie Spielman	______________	Date:	________
CAS Laboratory QA Manager:	Lee Wolf	______________	Date:	________
NEA Project Manager:	Robert Wagner	______________	Date:	________
NEA Laboratory QA Manager:	William Kotas	______________	Date:	________
Axys Laboratory Project Manager:	Georgina Brooks	______________	Date:	________
Axys Laboratory QA Manager:	Dale Hoover	______________	Date:	________

A2 TABLE OF CONTENTS

A2.1 List of Tables

A2.2 LIST OF ACRONYMS

ACG	analytical concentration goals
CAS	Columbia Analytical Services
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
COI	chemicals of interest
CVAA	cold vapor atomic absorption spectrometry
DOC	dissolved organic carbon
DQO	data quality objective
EPA	U.S. Environmental Protection Agency
ERA	ecological risk assessment
FSP	field sampling plan
GC/ECD	gas chromatography/electron capture detector
GC/FPD	gas chromatography/flame photometric detection
GC/LRMS	gas chromatography/low resolution mass spectrometry
GC/MS	gas chromatography/mass spectrometry
HHRA	human health risk assessment
HRGC/HRMS	high resolution gas chromatography/high resolution mass spectrometry
ICP	inductively coupled plasma
ICP-AES	Inductively coupled plasma – atomic emission spectrometry
ICP/MS	inductively coupled plasma/mass spectrometry
ISA	initial study area
LWG	Lower Willamette Group
LWR	lower Willamette River
μg/L	micrograms per liter
μg/kg	micrograms per kilogram
MDL	method detection limit
mg/kg	milligrams per kilogram
mg/L	milligrams per liter
MID	multiple ion detection
MRL	method reporting limit
MSD	matrix spike duplicate
NEA	Northeast Analytical
PAH	polycyclic aromatic hydrocarbon
PARCC	precision, accuracy, representativeness, completeness, and comparability
PCB	polychlorinated biphenyl
PCP	pentachlorophenol
QA/QC	quality assurance/quality control
QAPP	quality assurance project plan
RI/FS	remedial investigation/feasibility study
RM	river mile
RPD	relative percent difference
SIM	selected ion monitoring
SOP	standard operating procedure
SVOC	semivolatile organic compound
TIC	tentatively identified compound
VOC	volatile organic compound

A3 DISTRIBUTION LIST

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Oregon Department of Human Services	Dave Stone
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A4 INTRODUCTION AND PROJECT ORGANIZATION

A4.1 Introduction

This quality assurance project plan (QAPP) addendum describes procedures that will be used to complete the surface water investigation for Round 2 of the remedial investigation and feasibility study (RI/FS) for the Portland Harbor Superfund Site (Site) in Portland, Oregon. This addendum supplements the Round 2 QAPP (Integral and Windward 2004). The Round 2 QAPP describes procedures and requirements for the generation of data of documented acceptable quality that will be used for the RI/FS, including the ecological and human health risk assessments. This QAPP addendum addresses procedures that will be used for the surface water investigation that are not described in the Round 2 QAPP.

Supplemental information to Sections A and B of the Round 2 QAPP is provided in this QAPP addendum. Documents and records are described in Section A9 of the Round 2 QAPP and are not addressed further in this QAPP addendum.

Procedures for project assessment and oversight (Section C of the Round 2 QAPP) will be completed as described in the Round 2 QAPP, with one exception: Additional routine technical systems audits of analytical laboratories will not be required because all of the laboratories selected for this work have been audited in connection with sample analyses for Round 1 or for Round 2 sediment analyses. Laboratories will only be audited if serious problems are encountered, as described in the Round 2 QAPP.

Procedures for data validation (Section D of the Round 2 QAPP) will be completed as described in the Round 2 QAPP with one addition. The following protocol will be used for data validation in addition to protocols itemized in the Round 2 QAPP: *Guidance on the Documentation and Evaluation of Trace Metals Data Collected for Clean Water Act Compliance Monitoring (Draft)* (EPA 1996b).

The section numbers in this QAPP addendum correspond to U.S. Environmental Protection Agency (EPA) guidance for QAPP preparation (EPA 2002) and, in most cases, correspond to the Round 2 QAPP.

A4.2 PROJECT AND TASK ORGANIZATION

The organizational structure for activities associated with the Round 2 investigation is provided in Section A4.2 and Figure A4-1 of the Round 2 QAPP. Contact information related to the surface water study is provided in Table A4-1 of this QAPP addendum.

A5 PROBLEM DEFINITION AND BACKGROUND

An overview of the Portland Harbor RI/FS is provided in Section A5.1 of the Round 2 QAPP. The objectives of the Round 2A surface water sampling program are to assess water quality conditions in the initial study area (ISA) and adjacent areas under different flow conditions, provide water quality data for use in the ecological and human health risk assessments, and provide water quality data for the assessment of recontamination potential during the FS.

The phasing and anticipated schedule of the Round 2 surface water sampling efforts are discussed in detail in the Surface Water Sampling Field Sampling Plan (FSP) (Integral 2004). In summary, samples will be collected at 23 stations in the lower Willamette River (LWR). Three types of samples will be collected, depending on the data needs for that particular station, using two different sampling methods (see FSP Table 2-2):

- **Single-Point Near-Bottom Samples.** Surface water will be collected in water less than 20 feet deep as close to 1 foot off the river bottom as practicable, and in no case more than 3 feet off the bottom, at 17 ecological risk assessment (ERA) sampling stations by either peristaltic pump or the Infiltrex 300 system (XAD-2) described further below.

- **Cross-Sectional River Transect Water-Column Samples.** Composite samples from the water column will be collected at three river transects using both a peristaltic pump and the XAD-2 system. The river transect samples at RM 4, 6.3, and 11 will be spatially integrated across the entire width and depth of the channel. Details on the river transect sampling approach are provided in the Surface Water Sampling FSP (Integral 2004).

- **Single-Point Water-Column Samples.** A peristaltic pump will be used to sample the three quiescent human health risk assessment (HHRA) stations: W-14 (Willamette Cove), W-20 (Swan Island Lagoon), and W-10 (Cathedral Park). Samples of the water column will be integrated vertically from 1 foot below the water surface to within 1-3 feet of the river bottom.

Most samples will be collected using the peristaltic pump method. However, certain chemicals of interest (COIs) in the LWR are hydrophobic and found at very low concentrations in the water column, and they are frequently undetected in surface water using standard analytical methods. They have the potential to accumulate in aquatic biota at concentrations that may pose a threat to human health and piscivorus wildlife. Therefore, very low analytical method reporting limits (MRLs) are needed to detect some of these chemicals at concentrations that can be compared to water quality criteria established for aquatic biota and the human health protection of ingestion of fish. Conversely, relatively standard analytical MRLs are adequate to detect concentrations of most of these COIs for comparison to water quality criteria established for the protection of ecological receptors and for human ingestion of water.

Collection of high volumes of water is the typical sampling approach used to achieve the very low MRLs for surface water. By passing high volumes of surface water (e.g., 1,000 liters) through XAD-2 resin columns, these very dilute COIs will be concentrated as they adsorb to the resin beads. Subsequently, the target compounds can be extracted from the resin and then analyzed.

EPA has identified two surface water sample locations [W-13 (Willamette Cove) and W-15 (Rhone Poulenc)] as well as the three river transect sample locations that will require the high-volume, XAD-2 system surface water sampling method for analysis of dioxins/furans. EPA also identified two additional surface water sample locations, W-16 (ATOFINA) and W-18 (Portland Shipyard), that require high-volume sampling for analysis of pesticides and polychlorinated biphenyls (PCBs) (see FSP Figure 2-1 and Table 2-2).

All high-volume water samples collected with an XAD-2 column will be filtered. The associated pumping system has an inline filter placed before water passes through the XAD-2 resin column. The filter will be extracted and analyzed separately from the XAD-2 column extract to determine the concentrations of COIs sorbed to entrained sediment particles. The filter and XAD-2 resin analytical results can be combined to determine the total analyte concentration in the water column.

Surface water samples will be collected at three different river flow regimes to measure seasonal variability of COI concentrations. Surface water sampling is scheduled to occur during 1) low-flow conditions in the early fall, 2) the early rainy season in mid-late fall, and 3) late winter high-flow period when amphibian egg masses are typically released.

A6 TASK DESCRIPTION

The tasks to be completed for Round 2 include sample collection, laboratory analyses, data quality evaluation, data management, and report preparation. Summaries of field and laboratory tasks and references to detailed descriptions are provided in this section. Procedures for data quality evaluation, data management, and report preparation are described in the Round 2 QAPP.

A6.1 Field Tasks

Two methods of surface water collection will be used during Round 2A:

1. A peristaltic pump and Teflon™ tubing will be used to collect bulk water samples.

2. An Infiltrex 300 sampling device designed by Axys Environmental Systems, which includes a stainless-steel column packed with XAD-2 resin, will be used to collect high-volume samples.

The peristaltic pump will be used to collect samples for determination of conventional analytes, metals, butyltin compounds, chlorinated herbicides, and semivolatile organic compounds (SVOCs) at all applicable sampling stations. Samples for determination of organochlorine pesticides and PCB Aroclors will be collected using the peristaltic pump or the Infiltrex 300 system, depending on reporting limit requirements for each location. Samples for analysis of chlorinated dioxins and furans, low-level polycyclic aromatic hydrocarbons (PAHs) and phthalate esters, and PCB congeners will be collected using the Infiltrex 300 system. Details regarding the sampling program and sample collection procedures are provided in the Surface Water Sampling FSP. Sample collection procedures are summarized below in Section B2.

A6.2 Laboratory Analyses and Deliverables

Chemical analysis of bulk and high-volume surface water samples will be completed by three laboratories:

- Northeast Analytical (NEA; Schenectady, NY) will complete analyses for pesticides in bulk water samples and for PCB Aroclors in bulk water samples and in XAD extracts.
- Axys Analytical (Axys; Sidney, BC, Canada) will prepare XAD extracts and will complete analyses for pesticides, PAHs, phthalate esters, chlorinated dioxins and furans, and PCB congeners in XAD extracts.
- Columbia Analytical Services (CAS; Kelso, WA) will complete all other analyses on bulk water samples (i.e., conventional analyses, metals, butyltin compounds, chlorinated herbicides, and SVOCs).

Laboratories and analyses for surface water samples are provided in Table A6-1. A complete analyte list with analytical concentration goals (ACGs) and method reporting limits (MRLs) is provided in Table A6-2.

Analyses will be completed using EPA methods and other established methods as indicated in Table A6-1. Laboratory data deliverables are described in the Round 2 QAPP.

A6.3 Project Schedule

Round 2 surface water sampling will be initiated following EPA's approval of the Surface Water Sampling FSP and this QAPP addendum. It is anticipated that Round 2 surface water sampling will take place in fall 2004 and late winter 2005.

Schedules for delivery of data and reports are described in the Programmatic Work Plan (Integral et al. 2004).

A7 QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

A7.1 The Data Quality Objective (DQO) Process

DQOs for the surface water study are described in the Round 2 QAPP. ACGs have been established to identify analytical sensitivity levels that will be sufficient to determine risks to ecological and human health. Although ACGs can be met for many analytes, modifications to optimize laboratory MRLs are not sufficient to meet the ACGs in all cases. MRLs and ACGs for Round 2A surface water are provided in Table A6-2.

A7.2 Data Quality Indicators

The overall quality objective for Round 2 is to develop and implement procedures that will ensure the collection of representative data of known and acceptable quality. The QA procedures and measurements that will be used for this project are based on EPA guidance (EPA 1983, 1994b, 1999, 2004) and on established laboratory methods from other sources (Unger et al. 1986; APHA 1997).

QC samples and procedures are specified in each method protocol that will be used for this project. Methods are summarized in Table A6-1. All QC requirements will be completed by each laboratory as described in the protocols and in the Round 2 QAPP. Laboratory control limits for quality control samples and procedures are provided in Tables A7.1 and A7.2 and in the laboratory QA manuals (Appendix C of the Round 2 QAPP and Appendix A of this QAPP addendum). Data validation criteria and procedures are described in Sections D1 and D2 of the Round 2 QAPP. PARCC parameters (i.e., precision, accuracy or bias, representativeness, completeness, comparability) are described in the Round 2 QAPP.

Target MRLs for this study are summarized in Table A6-2. Laboratory methods are described in Section B4. Method detection limits (MDLs) will be determined by each laboratory for each analyte, as described in the Round 2 QAPP. When available, MDLs are provided in Table A6-2. MDL studies will be completed for all remaining analyses and provided to EPA before project samples are analyzed.

Analyte concentrations for this investigation will be reported to the MDL, as described in the Round 2 QAPP. For analyses completed by Axys (i.e., pesticides, PAHs, phthalate esters, chlorinated dioxins and furans, and PCB congeners in high-volume samples), sample-specific detection limits will be reported as described in EPA methods 1613B and 1668A.

A8 SPECIAL TRAINING/CERTIFICATION

In addition to requirements for experience and training provided in Section A8 of the Round 2 QAPP, requirements for surface water sampling include experience with water sample collection for low-level analytes and training on the use of the Infiltrex 300 system. Ian Stupakoff, the field coordinator for surface water sampling, and Susan Fitzgerald have the requisite experience in collection of water samples for low-level constituents, including the use of EPA Method 1669. Mr. Stupakoff will conduct or supervise all surface water sample collection. Ms. Fitzgerald will be available if needed. Axys will provide the requisite training on the use of their sampling system prior to the first surface water sampling event.

SECTION B: DATA GENERATION AND ACQUISITION

Section B of this Round 2 QAPP addendum includes the following supplemental sections:

- B1 Sampling Process Design
- B2 Sampling Methods
- B3 Sample Handling and Custody
- B4 Field and Laboratory Methods
- B5 Quality Control.

Procedures related only to the instrumentation that will be used for field measurements of water quality conditions are additionally addressed in the following sections, while laboratory instrumentation is discussed in the Round 2 QAPP:

- B6 Instrument/Equipment Testing, Inspection, and Maintenance
- B7 Instrument/Equipment Calibration and Frequency.

The following information is provided in the Round 2 QAPP and is not addressed further in this QAPP addendum:

- B8 Inspection/Acceptance of Supplies and Consumables
- B9 Non-direct Measurements
- B10 Data Management.

Details regarding field documentation for surface water sampling are provided in the Surface Water Sampling FSP.

B1 SAMPLING PROCESS DESIGN

Composite water samples will be collected at 23 stations during each of three surface water sampling events that represent low-flow conditions (late summer or early fall), the early rainy season (fall), and high-flow conditions (winter). The 23 stations include:

- Three cross-sectional transects at the upstream (RM 11), middle (RM 6.3), and downstream (RM 4) boundaries of the ISA, to support site characterization
- Fourteen stations in areas providing amphibian habitat to support the ERA
- Three stations in human use contact areas to support the HHRA
- Three stations in beach areas to support the ERA.

Samples collected for the ERA and HHRA will also be used to support the site characterization and source evaluation. Details regarding the sampling design for surface water are provided in the Surface Water Sampling FSP (Integral 2004).

Field QC samples to be collected for each sampling event are summarized in Table B4-3. Replicate water samples and field splits of samples collected by peristaltic pump will be collected at approximately 5% of the water sampling stations. Equipment rinsate blanks will be collected for the peristaltic pump near the beginning and again near the end of each sampling event. Storage blanks will also be collected near the beginning and end of each sampling event. These will be analyzed if contaminants are found in the equipment blanks at levels above 20% of analyte concentrations in any sample (i.e., the analyte concentration in any sample is less than 5 times the concentration in a related equipment blank) to evaluate the source of the contamination. Prior to the start of fieldwork for each sampling event, decon blanks will be analyzed to ensure that the decontamination procedure used for the peristaltic pump equipment is adequate. The field blank for the XAD-2 system will consist of blank resin columns that will be shipped with the samples. These columns will be analyzed, if needed, to evaluate results obtained for surface water samples.

B2 SAMPLING METHODS

This section outlines sample collection methods, equipment, and sample requirements for Round 2 surface water samples. Additional details not provided here are included in Surface Water Sampling FSP (Integral 2004). Sample containers, sample size requirements, preservation, and holding times for surface water samples and equipment rinse blanks are summarized in Table B2-1. Corrective actions are addressed in Sections B2.3 and C1 of the Round 2 QAPP.

B2.1 Sample Collection

Surface water samples will be collected by peristaltic pump at all locations. The Infiltrex 300 system will additionally be used to collect high-volume samples at seven locations for the low-flow and early rainy season sampling events and at three locations for the high-flow sampling event.

Surface water sampling will follow the guidelines in EPA Method 1669, *Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels* (EPA 1996a), and in the *Field Sampling Manual for the Regional Monitoring Program for Trace Substances* (David et al. 2001). High-volume surface water sampling will follow guidelines established in EPA's SOP MSL-M-090-00 (EPA 1994a) and in *Total Maximum Daily Loads for Dioxins in the Houston Ship Channel Quality Assurance Project Plan* (Houston and TNRCC 2002). A single composite sample will be collected at each of the three transect stations (i.e., downstream boundary of the ISA, mid-ISA, and upstream of the ISA). The composite sample will be collected in a manner that reflects the cross-sectional area and flow regime of the river transect.

Details regarding surface water sample collection are provided in the Surface Water Sampling FSP (Integral 2004).

B2.2 Surface Water Sampling by Peristaltic Pump

Surface water samples for standard chemical and conventional analyses will be collected using a peristaltic pump with an extended sampling tube lowered to the desired depth. Samples will be collected using the two-person "clean hands – dirty hands" method (EPA 1996a). The peristaltic pump's water intake will be placed 15 feet away from the bow of the boat with a long pole. The outflow of the pump will be directed through a Y-splitter into two composite mixing containers for sampling.

Equal volumes will be pumped into two large, pre-cleaned, 10-L or 20-L mixing containers equipped with magnetic stirring devices. The first container, made of polycarbonate, will be used for compositing and mixing samples for subsequent analysis of trace metals, butyltin species, and conventional analytes. The second container, made of stainless steel or glass, will be used for compositing and mixing samples for subsequent analysis of organic compounds. Following sample compositing in the mixing containers, appropriate sample bottles will be filled using a second peristaltic pump, with the outflow directed into the bottle. The sample jar will be held near the pump outlet, and the sample container will be rinsed several times and then filled. The sample containers will be capped, labeled, and placed in clean, double Ziploc™ bags, and then placed inside a cooler.

Two types of surface water samples will be collected by peristaltic pump: unfiltered and filtered [for metals and dissolved organic carbon (DOC)]. For filtered metals and DOC samples, the filter will be placed in-line near the tubing outlet to filter samples immediately before the water is discharged into the sample bottle. A 0.45 μm filter will be used for dissolved metals samples. The filter size for DOC will be selected in consultation with EPA.

Samples for total suspended solids (TSS) and total dissolved solids (TDS) will filtered at the laboratory. The filter size to be used for these analyses will be determined by EPA and LWG.

B2.3 High-Volume Surface Water Sampling by XAD-2 Columns

High-volume surface sampling will be accomplished using an Infiltrex 300 system with XAD-2 resin columns. This sampling method will be used to collect hydrophobic organic compounds from water at locations that require ultra-low analytical detection methods.

Approximately 1,000 L of water will be pumped through Teflon™ tubing, glass fiber filter cartridges, and Amberlite XAD-2 resin beads packed inside stainless-steel canisters. Suspended particles will be retained on the filters and dissolved organic contaminants will be adsorbed onto the resin. This method eliminates the need to collect, store, and transport large volumes of water. The minimum filter pore size to be used will be determined in consultation with EPA and its partners before sampling is initiated.

Samples will be collected using the "clean hands – dirty hands" method. Once the desired volume is pumped, the column assembly will be removed and any residual water will be drained out. XAD-2 canisters will be labeled, wrapped appropriately, and then placed in a cooler with wet ice. Any additional glass fiber filters will be removed, placed in glass jars, and stored in a cooler containing dry ice.

At the analytical laboratory, the column and filters will be analyzed individually to determine the dissolved and particulate concentrations of analytes in the samples. The sum of the dissolved and particulate concentrations will represent the total analyte concentration in the surface water samples.

B3 SAMPLE HANDLING AND CUSTODY

Sample custody procedures are described in Section B3 of the Round 2 QAPP. Sample preservation and storage requirements and holding times for the surface water samples are provided in Table B2-2 of this QAPP addendum.

Samples collected by the Infiltrex 300 system will be analyzed for PCB Aroclors. In order to allow possible future analysis of these samples for PCB congeners, a portion of each sample extract will be stored frozen at Axys. Portions of extracts from both the XAD-2 resin (for dissolved PCBs) and the filters (for PCBs bound to particulates) will be archived in this manner.

B4 FIELD AND LABORATORY METHODS

B4.1 Field Measurements

In situ measurements of general water quality characteristics will be taken at all sampling stations, including conductivity, pH, temperature, dissolved oxygen, and oxidation-reduction potential. Measurements will be taken using a YSI 650/600XLM Multi Probe lowered into the water column. Details regarding the operation of this instrument, including calibration, measurement, quality control procedures, and decontamination, are provided in the *YSI 650/600XLM Multi Probe SOP*, provided as Appendix E of the Surface Water Sampling FSP.

B4.2 Laboratory Analyses

Laboratory methods to be used for Round 2 are consistent with requirements provided in EPA methods (EPA 1983, 1994b, 1999, 2004) and other widely accepted protocols (Unger et al. 1986). Modifications will be made to these methods, as necessary and technically feasible, to improve MRLs. Methods and modifications are described below. Analytes, MRLs, and ACGs for sediment samples are provided in Table A6-2. Method modifications will not be sufficient to reduce MRLs to the level of the

ACGs for several analytes, and ACGs will not be attained in these cases. Laboratory methods are described below for surface water samples.

Surface water samples collected by peristaltic pump will be analyzed for the following:

- Conventional analyses
- Total and dissolved metals
- Butyltin compounds
- Chlorinated herbicides
- Organochlorine pesticides
- PCB Aroclors
- SVOCs.

Surface water samples collected by the Infiltrex 300 system will be analyzed for the following:

- Organochlorine pesticides
- PCB Aroclors
- PAHs
- Phthalate esters
- Chlorinated dioxins and furans
- PCB congeners (extract archived for potential analysis).

The total number of samples and the analyses that will be conducted on each sample are indicated in the Surface Water Sampling FSP. The laboratory methods for sample preparation and analysis are summarized in Table A6-1. Samples to be analyzed for PCB congeners and the suite of congeners to be analyzed will be selected by EPA and LWG after data for PCB Aroclors are available.

B4.2.1 Conventional Analyses in Surface Water

Conventional analyses of surface water samples will include total suspended solids, total dissolved solids, total organic carbon, dissolved organic carbon, and perchlorate. EPA methods will be used as shown in Table A6-1.

TSS and TDS will be determined gravimetrically according to EPA Methods 160.2 and 160.1, respectively. The filter pore size to be used at the laboratory for these analyses will be determined by EPA and LWG.

Total and dissolved organic carbon will be analyzed by EPA Method 415.1. Organic carbon in the samples will be oxidized and the evolved CO_2 will be analyzed using an infrared detector. Samples will be pretreated with hydrochloric acid to remove inorganic carbon.

Perchlorate will be analyzed according to EPA Method 314.0. Samples will be filtered at the laboratory as specified in the method and analyzed by ion chromatography.

B4.2.2 Metals and Butyltin Compounds in Surface Water

Three methods will be used to analyze surface water samples for total and dissolved metals (Table A6-1). Digestion with nitric and hydrochloric acids will be used to prepare samples for analysis of metals other than mercury and hexavalent chromium. Analysis for these metals will be completed by inductively coupled plasma/mass spectrometry (ICP/MS). Samples for analysis of arsenic will be concentrated by a factor of 10 prior to analysis as described above.

Mercury samples will be extracted with aqua regia and oxidized using potassium permanganate. Analysis will be completed by cold vapor atomic absorption spectrometry (CVAA).

Analysis for hexavalent chromium will be completed by coprecipitation of the hexavalent chromium as lead chromate with lead sulfate in a solution of acetic acid. The chromium-containing precipitate will be washed to remove trivalent chromium in solution. The precipitate will be redissolved and analyzed by ICP-AES.

The procedure for butyltins will include extraction, derivitization, and analysis of mono-, di-, tri-, and tetrabutyltin. Tropolone in methylene chloride will be used to extract the butyltins, followed by a Grignard reaction with hexylmagnesium bromide to form hexyl derivatives. The extract will be cleaned up using silica and alumina cartridge columns and analyzed by gas chromatography/flame photometric detection (GC/FPD).

B4.2.3 Organic Compounds in Surface Water

B4.2.3.1 Samples Collected by Peristaltic Pump

For analysis of chlorinated herbicides, water samples will be adjusted to a pH <2, and the herbicides in both acid and derivatized forms will be extracted with ethyl ether. Derivatives of the phenoxy acid herbicides in the extract will be hydrolyzed to the acid form by the addition of sodium hydroxide. The sample will be acidified and the acid herbicides extracted. The acids will then be converted to their methyl esters using diazomethane. Extracts will be analyzed by gas chromatography/electron capture detector (GC/ECD). Pentachlorophenol will not be included in the analyte list for this method because Method 8270C will yield a sufficiently low MRL.

Organochlorine pesticides will be extracted from samples using continuous liquid-liquid extraction procedures. Samples will be analyzed by GC/ECD. Florisil® column clean-up will be performed on the sample extracts. Pesticide detections will be confirmed at CAS by reverse search of the gas chromatography/mass spectrometry (GC/MS) data when concentrations are sufficiently high.

Solid phase extraction with an SPE-DEX 4790 extractor from Horizon Technologies and styrene divinylbenzene extraction disks will be used for PCB analyses. Four liters of sample will be extracted to provide MRLs that meet the ACGs for this project. Acid cleanup will be performed on the sample extract followed by Florisil® cleanup. Samples will be analyzed for PCB Aroclors by GC/ECD. The surrogate compounds, tetrachloro-*m*-xylene and decachlorobiphenyl, will be added to every sample and QC sample and to continuing calibration standards. NEA will complete an MDL study and initial demonstration of proficiency using the proposed method modifications prior to analysis of project samples.

Sample extractions for SVOCs will be completed using continuous liquid-liquid extraction. SVOCs will be analyzed by GC/MS with a large-volume injector to enhance sensitivity. Tentatively identified compound (TICs) will not be reported. Analyses for PAHs will be completed by GC/MS with selected ion monitoring (SIM).

B4.2.3.2 Samples Collected by the Infiltrex 300 System

Samples collected using the Infiltrex 300 system with XAD-2 resin and glass fiber filters will be extracted at Axys by Soxhlet extraction. Each extract will be divided into six portions and analyzed as follows:

- One sixth of the extract each will be used for analysis of pesticides, PCB Aroclors, PAHs, and phthalate esters
- Two sixths of the extract will be used for analysis of chlorinated dioxins and furans

Analyses for pesticides, PAHs, phthalate esters, and chlorinated dioxins and furans in the XAD-2 and glass fiber filter sample extracts will be completed by Axys. All of these analyses will be completed by GC/MS using isotope dilution methodology using multiple ^{13}C labeled surrogate standards. Analyses for PAHs and phthalate esters will be completed by GC/LRMS, while analyses for pesticides, chlorinated dioxins and furans, and PCB congeners will be completed by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS).

Cleanup procedures for chlorinated dioxins and furans will include sulfuric acid cleanup and silica/carbon column cleanup. Additional cleanup procedures will be used, as necessary, to remove analytical interferences. As described in EPA Method 1613B, detection limits are calculated on an individual compound and sample basis and depend on the signal-to-background ratio for the specific labeled isomer. The detection limits listed in Table A6-2 are representative of MDLs typically obtained when using the described procedure and sample volume.

The extract for pesticide analyses will be cleaned up and fractionated by absorption column chromatography to produce two fractions. The first fraction, called E1, contains the PCBs and non-polar and moderately polar pesticides. The E1 fraction will be analyzed by HRGC/HRMS for chlorinated pesticides. The second fraction, E2, contains the most polar chlorinated pesticides and will be analyzed by HRGC/HRMS separately from fraction E1.

The extract for PAH analyses will be fractionated on silica gel into slightly polar (F1), moderately polar (F2), and highly polar (F3) fractions. The F1 fraction contains the alkane and hopane compounds. This fraction will be discarded. The F2 fraction contains PAHs. This fraction will be analyzed as described below. The third fraction (F3) contains polar hydrocarbons such as sterols. This fraction will be discarded.

Analysis will be completed by HRGC/LRMS in the multiple ion detection (MID) mode to enhance sensitivity. At least two ions will be monitored for each target compound or labeled standard. Isotope dilution quantification protocols will be used to calculate analyte concentrations.

The sample extract for phthalate esters will be fractionated on a silica gel column into non-polar and polar fractions. The polar fraction will be analyzed for phthalate esters. Analysis will be completed by HRGC/LRMS as described above for PAHs..

Analyses for PCB Aroclors in the XAD-2 extracts will be conducted at NEA by GC/ECD. Cleanup and analysis procedures will be completed as described above in Section B4.3.1 for samples collected by peristaltic pump.

The samples to be analyzed and the analyte list for PCB congeners will be determined by LWG and EPA data users when PCB Aroclor data are available. The E1 fraction collected during Florisil® fractionation for pesticides will be used to analyze for PCB congeners. The E1 fraction will be subjected to further cleanup procedures and analyzed by HRGC/HRMS following protocols provided in EPA Method 1668A.

B5 QUALITY CONTROL

Quality control samples will be prepared in the field and at the laboratories to monitor the bias and precision of the sample collection and analysis procedures.

Field QC samples for this study will include field replicates, field splits, equipment rinse blanks, storage blanks, decon blanks, and temperature blanks. A summary of field QC samples that will be collected for each surface water sampling event is provided in Table B4-3.

Field replicates, field splits, equipment rinse blanks, and temperature blanks are described in the Round 2 QAPP. Storage blanks are sample jars that are filled directly with the water that is used to decontaminate equipment and to collect equipment rinse blanks without passing the water over any sampling equipment. Storage blanks are kept with the samples during shipping and storage at the laboratory. Storage blanks are collected to evaluate the source of the contamination. They will only be analyzed if contaminants are found in the equipment blanks at levels above 20% of analyte concentrations in any sample (i.e., the analyte concentration in any sample is less than five times the concentration in a related equipment blank). Prior to the start of sample collection activities for each sampling event, a decon blank will be generated by the laboratory that conducts decontamination of the peristaltic pump sampling equipment. To ensure that the decontamination procedure in Appendix B is adequate, the decon blank will be analyzed by the laboratories identified in Table A6-1 for metals and organic parameters, as indicated in Table B4-3.

Laboratory quality control samples and procedures will be completed as described in the Round 2 QAPP.

B6 INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

Maintenance of the YSI 650/600XLM Multi Probe that will be used for field measurements will be completed as described in the manufacturer's instructions and the SOP for its use (Appendix E of the Surface Water Sampling FSP).

Testing, inspection, maintenance, setup, and calibration of laboratory instruments are described in the Round 2 QAPP.

B7 INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY

A YSI 650/600XLM Multi Probe will be used for field measurements (i.e., conductivity, pH, temperature, dissolved oxygen, and oxidation reduction potential). This instrument will be shipped to the field pre-calibrated by Hoskin Scientific, Vancouver, BC. Calibration checks will be performed on the Multi Probe prior to use each day that measurements will be made, as described in the SOP for use of the YSI 650/600XLM Multi Probe (Appendix E of the Surface Water Sampling FSP) and in the manufacturer's instructions. Calibration checks will be completed twice daily at a minimum. The unit will be checked for calibration before each daily sampling begins and again at the end of the day. If measurements are made at more than 10 stations in a single day, calibration checks will be made after every 10 stations are measured and at the end of the day. Calibration information will be recorded in the field logbook.

Calibration procedures for laboratory instruments are described in the Round 2 QAPP.

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Appendix A

APPENDIX A

AXYS'S QUALITY ASSURANCE MANUAL

(The Axys QA Manual will be supplied to the EPA QA Manager under separate cover.)

Appendix B

APPENDIX B

DECONTAMINATION OF FIELD SAMPLING EQUIPMENT FOR SURFACE WATER SAMPLING SOP

DECONTAMINATION OF FIELD SAMPLING EQUIPMENT FOR SURFACE WATER SAMPLING

The purpose of this standard operating procedure (SOP) is to define and standardize the methods for decontamination of field sampling equipment for the collection of surface water samples using a peristaltic pump and Teflon™ tubing to ensure sample integrity and minimize contamination during sample handling. Details on surface water sampling techniques and equipment setup are described in Appendix C "Surface Water Sampling SOP" of the Portland Harbor RI/FS Round 2 Field Sampling Plan, Surface Water Sampling (Integral, 2004).

This SOP utilizes and augments the procedures outlined in the *Interagency Field Manual for the Collection of Water-Quality Data* (USGS 2000) and U.S. Environmental Protection Agency (EPA) Method 1669, *Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels* (EPA 1996). Clean sampling techniques designed for trace metals will be used for the collection of filtered and unfiltered water samples. Samples will be analyzed for organic compounds, metals, and conventionals for the surface water sampling events.

SUMMARY OF METHOD

Preparation of the Teflon™ sample tubing will be completed in the laboratory 3-4 weeks before the start of a sampling event. All sample tubing, filters and containers will be decontaminated, pre-assembled and packed for the field in double bagged polyethylene bags.

Decontamination of tubing, filters, stir bars, and containers consists of soaking the sampling equipment in cleaning solutions for a pre-determined amount of time and then rinsing it with deionized water. A peristaltic pump is used to fill the Teflon™ sample tubing with cleaning solutions and to flush with deionized water between cleanings. In similar fashion, sampling filters are also attached in series with C-flex™ tubing, filled with cleaning solutions and flushed with deionized water between cleanings. The Teflon™ tubing ends and in-line filters are joined together with C-flex™ tubing for transport to the field.

PROCEDURES

The procedure that will be used for each type of sampling equipment is provided below. Selected equipment (e.g., tubing) will be used for collection of all target parameters. However, selected equipment (containers, filter units) will be processed separately for metals and organics.

Teflon™ and C-Flex™ Pump Tubing and Teflon™ Coated Stir Bars for Intake Water

The Teflon™ and C-Flex™ tubing used for the intake of site water and Teflon coated stir bars used in the containers will be cleaned for all target parameters. Cleaning procedures are as follows:

- Completely fill sample tubing with reagent grade methanol and let it soak for 24 hours. Soak stir bars in reagent grade methanol for 24 hours.
- Drain methanol solution from the tubing and stir bars and flush with approximately 10 liters (L) of deionized (DI) water.
- Completely fill sample tubing with dilute reagent grade nitric acid (HNO_3) and let soak for 24 hours. Soak stir bars in reagent grade HNO^3 for 24 hours.
- Drain acid and flush tubing and stir bars with DI water. Fill tubing with DI water, and let set for 24 hours. Soak stir bars in DI water for 24 hours. Drain, rinse with DI water, and drain.
- Double bag clean tubing and stir bars, label outside bag identifying cleaning process used, and store in double-bagged polyethylene bags until assembly.

Teflon™ and C-Flex™ Pump Tubing From Filtration Units to Sample Jars

The Teflon™ and C-Flex™ tubing used from the filtration units to the sample jars will be cleaned for metals or for organic and conventional parameters, as described below:

Metals, Butyltin, and Conventional Analysis

- Completely fill sample tubing with dilute reagent grade HNO_3 and let soak for 24 hours.
- Drain acid and flush tubing with DI water, fill with DI water, and let set for 24 hours. Drain, rinse with DI water, and drain.
- Double bag clean tubing, label outside bag identifying cleaning process used, and store in double-bagged polyethylene bags until assembly.

Organic Analysis

- Completely fill sample tubing with reagent grade methanol and let it soak for 24 hours.
- Drain methanol solution from the tubing and flush with approximately 10 L of DI water.

- Double bag clean tubing, label outside bag identifying cleaning process used, and store in double-bagged polyethylene bags until assembly.

Filter Cartridges

Filter cartridges (0.45 µm and 10 µm) will be used for sample collection. The 0.45 µm cartridges will be used for the collection of dissolved trace metal samples and DOC in water. The filter size for DOC will be selected in consultation with EPA. The DOC filter cartridge will be cleaned according to the same procedure used for the 0.45 µm and 10 µm cartridges. The 10 µm cartridges will be used for all samples. Normally, one filter cartridge is used per sample site, although elevated suspended solids concentrations may require using two or more cartridges per site. The following procedures are used for cleaning the 10 µm and 0.45 µm filter cartridges for metals, butyltin species, and conventionals, and the selected cartridge for DOC:

- Completely fill filter cartridge with dilute reagent grade HNO_3 and let soak for 24 hours.
- Drain acid and flush filter cartridge with DI water, fill with DI water, and let set for 24 hours. Drain, rinse with DI water, and drain.
- Double bag clean cartridges, label outside bag with cleaning process used, and store in double-bagged polyethylene bags until assembly.

The following procedures are used for cleaning the 10 µm filter cartridges for organics:

- Completely fill filter cartridge with reagent grade methanol and let it soak for 24 hours.
- Drain methanol solution from the filter cartridge and flush with approximately 10 L of DI water.
- Double bag clean catridges, label outside bag with cleaning process used, and store in double-bagged polyethylene bags until assembly .

Glass and Polycarbonate 20 Liter Containers:

The glass and polycarbonate containers will be used to composite the sample prior to distribution to the sample containers. The cleaning procedure for metals and for organic and conventional parameters is described below:

Metals, Butyltin, and Conventional Analysis

- Completely fill polycarbonate container with dilute reagent grade HNO_3 and let soak for 24 hours.
- Drain acid and flush container with DI water, fill with DI water, and let set for 24 hours. Drain, rinse with DI water, and drain.
- Assemble components of filtration unit and store in double-bagged polyethylene bags until used in the field .

Organic Analysis

- Completely fill glass container with reagent grade methanol and let it soak for 24 hours.
- Drain methanol solution from the tubing and flush with DI water.
- Assemble components of filtration unit and store in double-bagged polyethylene bags until used in the field .

ASSEMBLY

After all the components have been cleaned, the peristaltic pump collection and filtration units will be assembled by the laboratory performing the sample equipment decontamination. The assembled units will be double-bagged in polyethylene bags, labeled for identification on the outside bag, and sent to the field laboratory.

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