Lower Duwamish Waterway Group

Port of Seattle / City of Seattle / King County / The Boeing Company

BASELINE SURFACE WATER COLLECTION AND CHEMICAL ANALYSES - QUALITY ASSURANCE PROJECT PLAN

FINAL

Prepared for

Lower Duwamish Waterway Group

For submittal to

US Environmental Protection Agency

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TITLE AND APPROVAL PAGE
SURFACE WATER COLLECTION AND CHEMICAL ANALYSES
QUALITY ASSURANCE PROJECT PLAN

Windward Project Manager	Name	8/2/17 Date
Windward Field Coordinator	Name	8/2/17 Date
Windward QA/QC Manager	Name	8/2/17 Date
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EPA QA/QC Manager	Name	8/2/17 Date

Distribution List

This list identifies all individuals who will receive a copy of the approved quality assurance project plan, either in hard copy or electronic format, as well as any subsequent revisions.

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- Kathy Godtfredsen, Windward Project Manager
- Susan McGroddy, Windward Task Manager
- Thai Do, Windward Field Lead
- Donald Brown, EPA QA/QC Manager
- Amara Vandervort, Windward QA/QC Manager
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  - Jeff Stern, Debra Williston (King County)
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Table of Contents

Tables

Figures

Maps

Acronyms

%RSD	percent relative standard deviation
ALS	ALS Environmental-Kelso
AOC	Administrative Order on Consent
ARAR	applicable or relevant and appropriate requirement
ARI	Analytical Resources, Inc.
AWQC	ambient water quality criteria
Axys	Axys Analytical Services Ltd.
BHC	benzene hexachloride
CFR	Code of Federal Regulations
cfs	cubic feet per second
COC	chain of custody
cPAH	carcinogenic polycyclic aromatic hydrocarbon
CSM	conceptual site model
CV-AFS	cold vapor-atomic fluorescence spectrometry
CWA	Clean Water Act
DCM	dichloromethane
DD	decimal degrees
DDD	dichlorodiphenyldichloroethane
DDE	dichlorodiphenyldichloroethylene
DDT	dichlorodiphenyltrichloroethane
DL	detection limit
DOC	dissolved organic carbon
DQI	data quality indicator
DQO	data quality objective
EAA	early action area
Ecology	Washington State Department of Ecology
EDL	estimated detection limit
EIM	Environmental Information Management

EPA	US Environmental Protection Agency
FC	field coordinator
FLPE	fluorinated high-density polyethylene
FNU	Formazin Nephelometric Unit
FS	feasibility study
GC/ECD	gas chromatography / electron capture detection
GC/MS	gas chromatography / mass spectrometry
GC/NPD	gas chromatography / nitrogen-phosphorus detector
GPC	gel permeation chromatography
GPS	global positioning system
HDPE	high-density polyethylene
HG-AFS	hydride generation-atomic fluorescence spectrometry
HpCDD	heptachlorodibenzo-*p*-dioxin
HpCDF	heptachlorodibenzofuran
HPLC/TS/MS	high-performance liquid chromatography / thermospray / mass spectrometry
HRGC/HRMS	high-resolution gas chromatography / high-resolution mass spectrometry
HSP	health and safety plan
HxCDD	hexachlorodibenzo-*p*-dioxin
HxCDF	hexachlorodibenzofuran
ICP-MS	inductively coupled plasma-mass spectrometry
ID	identification
LCS	laboratory control sample
LDW	Lower Duwamish Waterway
LDWG	Lower Duwamish Waterway Group
MDL	method detection limit
MS	matrix spike
MSD	matrix spike duplicate
NIST	National Institute of Standards and Technology

NOAA	National Oceanic and Atmospheric Administration
OCDD	octachlorodibenzo-*p*-dioxin
OCDF	octachlorodibenzofuran
OSHA	Occupational Safety and Health Administration
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PE	polyethylene
PeCDD	pentachlorodibenzo-*p*-dioxin
PeCDF	pentachlorodibenzofuran
PM	project manager
PPE	personal protective equipment
PRC	performance reference compound
PSEP	Puget Sound Estuary Program
QA	quality assurance
QAPP	quality assurance project plan
QC	quality control
RL	reporting limit
RM	river mile
ROD	Record of Decision
RPD	relative percent difference
SDG	sample delivery group
SIM	selected ion monitoring
SM	Standard Methods
SOP	standard operating procedure
SRM	standard reference material
SVOC	semivolatile organic compound
TBT	tributyltin
TCDD	tetrachlorodibenzo-*p*-dioxin
TCDF	tetrachlorodibenzofuran

TM	task manager
TOC	total organic carbon
TSS	total suspended solids
USGS	US Geological Survey
VOC	volatile organic compounds
WAC	Washington Administrative Code
Windward	Windward Environmental LLC
WQC	water quality criteria

1 Introduction

This quality assurance project plan (QAPP) describes the quality assurance (QA) objectives, methods, and procedures for collecting surface water from the Lower Duwamish Waterway (LDW) for chemical analyses. As described in the *Pre-Design Studies Work Plan* (Windward and Integral 2017), hereafter referred to as the Work Plan, baseline surface water data will be collected and analyzed to address the third amendment to the Administrative Order on Consent (AOC) (EPA 2016c).

The Work Plan presents the data quality objectives (DQOs) and conceptual study design for surface water collection and associated chemical analyses (Windward and Integral 2017). This QAPP includes these DQOs and presents the detailed surface water study design, including details on project organization, field data collection, laboratory analyses, and data management.

US Environmental Protection Agency (EPA) guidance for QAPPs was followed in preparing this document (EPA 2002). The remainder of this QAPP is organized into the following sections:

- Section 2 – Project Objectives and Description
- Section 3 – Project Organization and Responsibilities
- Section 4 – Data Generation and Acquisition
- Section 5 – Assessment and Oversight
- Section 6 – Data Validation and Usability
- Section 7 – References

Appendix A to this QAPP is a health and safety plan (HSP) designed to protect on-site personnel from physical, chemical, and other hazards posed by the field sampling effort. Field collection forms are included as Appendix B. Laboratory methods and the associated reporting limits (RLs) are provided in Appendix C. Appendix D presents standard operating procedures (SOPs) for passive samplers.

2 Project Objectives and Description

EPA issued a Record of Decision (ROD) for the LDW Superfund site on November 21, 2014 (EPA 2014b). The ROD described the selected sediment remedy for the LDW, and identified monitoring activities, including baseline sampling of LDW media for comparison to post-remedial data. This QAPP focuses on baseline sampling of surface water.

2.1 DATA QUALITY OBJECTIVES

Per the third amendment to the AOC (EPA 2016c), the collection of baseline surface water quality data is required to assess progress toward applicable or relevant and appropriate requirement (ARAR) compliance and "to observe site-wide trends and changes in … surface water quality over time." Thus, as described in the Work Plan (Windward and Integral 2017), two DQOs were identified for the collection and analysis of baseline surface water samples. These DQOs are summarized in Table 2-1.

Table 2-1. Surface water DQOs

DQO Step	DQO 1	DQO 2
STEP 1: State the problem.	Assess progress toward water quality ARARs as sediment remediation and source control continue.	Establish baseline concentrations to be used to assess trends in PCB concentrations in surface water as sediment remediation and source control continue.
STEP 2: Identify the goals of the study.	The goal of DQO 1 is to establish current surface water concentrations for comparison to AWQC.	The goal of DQO 2 is to establish current baseline PCB concentrations for the evaluation of trends in surface water PCB concentrations.
STEP 3: Identify the information inputs.	Information inputs included the existing data and CSM.	
STEP 4: Define the boundaries of the study.	The boundary of the study has been defined by the ROD.	
STEP 5: Develop the analytical approach.	Composite grab samples will be analyzed for metals, PAHs, SVOCs, PCBs, dioxins/furans, select pesticides, and conventionals.	Passive samplers will be analyzed for PCB congeners.
STEP 6: Specify performance or acceptance criteria.	Performance or acceptance criteria are described in Section 4.6, including field quality control samples and laboratory quality control. Data quality indicators for laboratory analyses (i.e., precision, accuracy, representativeness, completeness, and comparability) will be met, as described in Section 4.5.	
STEP 7: Develop the detailed plan for obtaining data.	Composite grab samples will be collected from two locations within the LDW and one upstream reference location. At each location, composite samples will be collected one meter below the surface of the water and one meter above the sediment surface. Eight sampling events will be conducted over 2 years to characterize a range of baseline conditions described in detail in Table 4.3.	Passive samplers will be deployed 1 m above the sediment surface at two locations during the dry seasons of 2 consecutive years.

ARAR – applicable or relevant and appropriate requirement
AWQC – ambient water quality criteria
CSM – conceptual site model
DQO – data quality objective
PCB – polychlorinated biphenyl
QAPP – quality assurance project plan
ROD – Record of Decision

2.1.1 DQO 1 – ARAR compliance

The first DQO is:

- Assess progress toward water quality ARARs as sediment remediation and source control continue

Progress toward water quality ARAR compliance will be assessed by comparing chemical concentrations in composite-grab samples collected during baseline surface water sampling events (described in this QAPP) with water quality ARARs (as presented in Table C-5 of Appendix C). Samples collected during future long-term monitoring events following sediment remediation will also be compared with these values.

Using a Niskin bottle, baseline composite-grab samples will be collected from two LDW locations and one upstream reference location during eight events that will represent a range of conditions in the LDW (i.e., dry season baseflow,[1] wet season baseflow,[2] and storm events of various types). The sampling design considers the two-layer estuarine system of the LDW, as well as other factors that affect flow rates, in order to sample chemical concentrations in LDW surface water under various conditions.

2.1.2 DQO 2 – trends

The second DQO is:

- Establish baseline concentrations to be used to assess trends in polychlorinated biphenyl (PCB) concentrations in surface water as sediment remediation and source control continue

PCB concentration trends in surface water will be evaluated using passive samplers that uptake freely dissolved PCBs over time. Passive samplers will be deployed at two locations in the LDW for a 30-day period to target dry season baseflow conditions. As compared with composite-grab samples, the use of passive samplers is expected to improve the ability to characterize any long-term temporal trends in PCB concentrations because passive samplers have the advantage of integrating PCB concentrations over time and controlling for the influence of other factors (e.g., total suspended solids [TSS] and dissolved organic carbon [DOC]) on the data, thus

[1] Dry season baseflow is defined as flow conditions from July through September, when precipitation is low.
[2] Wet season baseflow is defined as flow conditions from December through March, when precipitation is generally high.

decreasing overall data variability and providing a more statistically powerful estimate of mean seasonal water concentrations.

PCBs were selected because 1) PCB concentrations in surface water are above water quality ARARs, 2) PCBs are a risk driver for multiple human health exposure scenarios and ecological receptors (river otters and benthic organisms), and 3) PCBs result in the largest sediment cleanup footprint in the LDW. Establishing baseline conditions for PCBs is of interest to better understand whether PCB concentrations in surface water are being reduced by sediment remediation in the LDW.[3] This QAPP describes the collection of baseline data for freely dissolved PCB concentrations, which will be compared with future long-term monitoring data using a parametric *t*-interval equation that estimates the difference between the means of two time periods.

2.2 PROJECT APPROACH AND SCHEDULE

As described in Section 2.1, two separate methods will be used to satisfy the two DQOs for baseline surface water sampling. The locations and anticipated timing of these sampling efforts are briefly described below, with more details presented in Section 4.

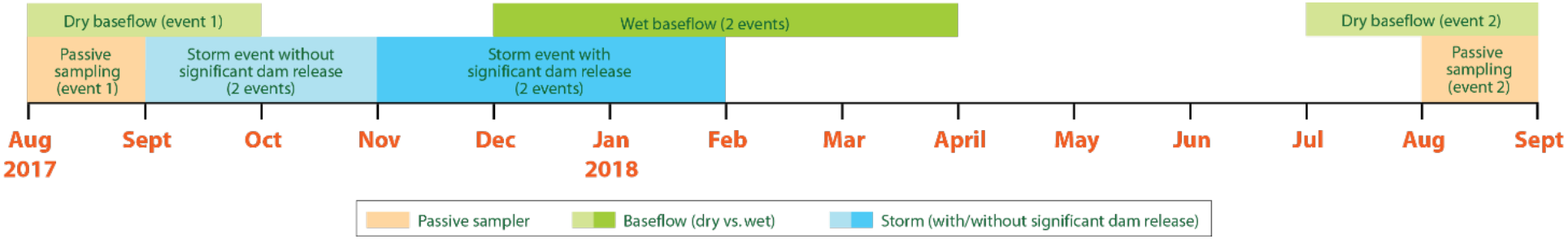
- **Composite-grab samples (DQO 1)** – Water samples and water quality data will be collected at two locations in the LDW (river mile [RM] 0.75 and RM 3.3), and at one reference location upstream of the LDW in the Green River (RM 10). Surface water sampling is anticipated to begin with dry-season baseflow in August 2017, and is anticipated to conclude in August 2018.[4]
- **Passive samplers (DQO 2)** – Passive samplers will be deployed 1 m above the sediment surface at two locations in the LDW (RM 2.1[5] and RM 3.3) during dry baseflow conditions (starting in August 2017 and again in August 2018).

Figure 2-1 presents the months targeted for the eight surface water sampling events and the passive sampler deployments. The exact sampling schedule will depend on QAPP approval as well as rainfall and flow conditions, as described in Section 4.1.

[3] Prior to baseline water sampling, significant sediment remediation in the LDW has been conducted through the cleanup of five early action areas (EAAs). The remainder of the sediment remediation will occur after baseline sampling is complete. The EAA cleanup, as well as the remaining sediment remediation (and ongoing source control), are expected to have an effect on PCB concentrations in surface water; however, the relative timing and extent of this effect is unknown (EPA 2014b).

[4] If any of the four storm events has not yet been sampled by August 2018, additional attempts will be made in the fall of 2018 (see Section 4.1.1.3).

[5] The 1st Avenue Bridge is the selected location. However, if consent for access cannot be obtained, one or more alternative locations will be proposed in a technical memorandum for EPA approval.



Note: Figure presents target schedule; actual dates and order of sampling events may differ depending on rainfall and flow conditions.

Figure 2-1. Timeline showing target schedule for surface water sampling events

Chemical analysis of the samples from each sampling event will require approximately four weeks. Data validation will be completed approximately three weeks after receipt of the chemistry data. EPA will be notified when the final data validation report has been received. Validated data will be submitted to EPA within 10 weeks of each sampling event. Final validated data will be submitted to the Washington State Department of Ecology's Environmental Information Management (EIM) system within 30 days of the approval of the final data report.

A draft surface water sampling data report (Work Plan Task 5) will be submitted to EPA 21 days after receipt of the final validated analytical results for the final round of sampling (i.e., in approximately November 2018). A draft final data report will be submitted to EPA 30 days after receipt of EPA's comments on the draft data report. Surface water data will be evaluated in an addendum to the data evaluation report in 2019 (Task 6).

3 Project Organization and Responsibilities

The overall project organization and the individuals responsible for the various tasks required for surface water sample collection and analysis are shown in Figure 3-1. Responsibilities of project team members, as well as laboratory project managers (PMs), are described in the following sections.

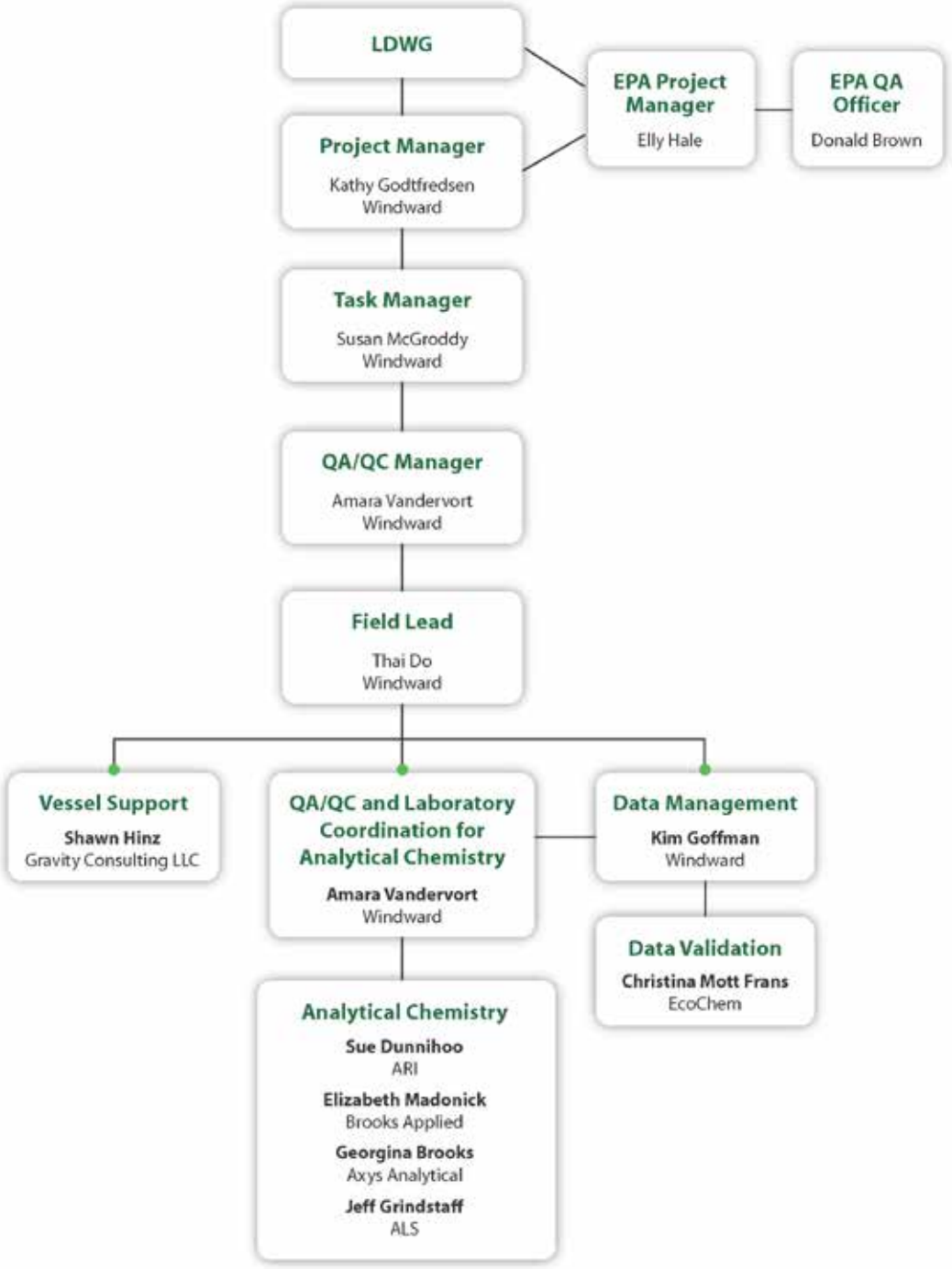


Figure 3-1.Project organization and team responsibilities

3.1 PROJECT MANAGEMENT

Both the Lower Duwamish Waterway Group (LDWG) and EPA are involved in all aspects of this project, including discussion, review, and approval of this QAPP, and interpretation of the results of the investigation. Elly Hale is the EPA PM for the pre-design studies (EPA 2016c).

Kathy Godtfredsen is the Windward Environmental LLC (Windward) PM. In this capacity, she will be responsible for overall project coordination, and for providing oversight for planning and coordination, work plans, all project deliverables, and performance of the administrative tasks needed to ensure timely and successful completion of the project. She will also be responsible for coordinating with LDWG and EPA on schedule, deliverables, and other administrative details. Dr. Godtfredsen can be reached as follows:

Dr. Kathy Godtfredsen
Windward Environmental LLC
200 West Mercer Street, Suite 401
Seattle, WA 98119
Telephone: 206.577.1283
E-mail: kathyg@windwardenv.com

Susan McGroddy is the Windward monitoring task manager (TM). As TM she will be responsible for communicating with the Windward PM on the progress of project tasks, conducting detailed planning and coordination, and monitoring and communicating any deviations from the QAPP. Significant deviations from the QAPP will be further reported to representatives of LDWG and EPA. Dr. McGroddy can be reached as follows:

Dr. Susan McGroddy
Windward Environmental LLC
200 West Mercer Street, Suite 401
Seattle, WA 98119
Telephone: 206.812.5421
E-mail: susanm@windwardenv.com

3.2 FIELD COORDINATION

Thai Do is the Windward field coordinator (FC). As FC, he will be responsible for managing field sampling activities and general field and QA / quality control (QC) oversight. He will ensure that appropriate protocols are observed for sample collection, preservation, and holding times, and will oversee delivery of environmental samples to the designated laboratories for chemical analyses. The FC will report deviations from this QAPP to the TM and PM for consultation. Significant deviations from the QAPP will be further reported to representatives of LDWG and EPA. Mr. Do can be reached as follows:

Mr. Thai Do
Windward Environmental LLC
200 West Mercer Street, Suite 401
Seattle, WA 98119
Telephone: 206.812.5407[6]
Email: thaid@windwardenv.com

Shawn Hinz is the boat captain. He will be responsible for operating the boat and will coordinate closely with the FC to ensure that samples are collected in keeping with the methods and procedures presented in this QAPP. Mr. Hinz can be reached as follows:

Mr. Shawn Hinz
Gravity Consulting LLC
32617 Southeast 44th Street
Fall City, WA 98024
Mobile: 425.281.1471
Email: shawn@gravity.com

3.3 QUALITY ASSURANCE/QUALITY CONTROL

Amara Vandervort is the Windward QA / QC coordinator. In this capacity, she will oversee coordination of the field sampling and laboratory programs, and will supervise data validation and project QA coordination, including coordination with the analytical laboratories and the EPA QA officer, Donald Brown. Ms. Vandervort will also maintain the official approved QAPP and ensure that the appropriate parties receive any updated versions of the QAPP. Ms. Vandervort can be reached as follows:

Ms. Amara Vandervort
Windward Environmental LLC
200 West Mercer Street, Suite 401
Seattle, WA 98119
Telephone: 206.812.5415
Email: amarav@windwardenv.com

Mr. Brown can be reached as follows:

Mr. Donald Brown
US Environmental Protection Agency, Region 10
1200 6th Avenue
Seattle, WA 98101
Telephone: 206.553.0717
Email: brown.donaldm@epa.gov

[6] A mobile phone number will be provided prior to field sampling.

Independent third-party chemical data review and validation will be provided by Ecochem. The PM at Ecochem can be reached as follows:

Ms. Christina Mott Frans
Ecochem
1011 Western Avenue, Suite 1006
Seattle, WA 98104
Telephone: 206.508.2110
Email: cmfrans@ecochem.net

3.4 LABORATORY RESPONSIBILITIES

Amara Vandervort of Windward is the laboratory coordinator for the analytical chemistry laboratories. Analytical Resources, Inc. (ARI) will perform all chemical analyses on the surface water samples, with the exception of analyses for PCB congeners, dioxins/furans, total and dissolved metals, inorganic arsenic, select organophosphorus pesticides, and carbaryl. Axys Analytical Services Ltd. (Axys) will perform analyses for PCB congeners and dioxins/furans, Brooks Applied Labs will perform analyses for total and dissolved metals, including inorganic arsenic, and ALS Environmental-Kelso (ALS) will perform analyses for select organophosphorus pesticides and carbaryl.

The laboratory PM at ARI can be reached as follows:

Ms. Susan Dunnihoo
Analytical Resources, Inc.
4611 South 134th Place
Tukwila, WA 98168-3240
Telephone: 206.695.6207
Email: limsadm@arilabs.com

The laboratory PM at Axys can be reached as follows:

Ms. Georgina Brooks
Axys Analytical Services Ltd.
2045 West Mills Road
Sidney, British Columbia V8L 5X2
Canada
Telephone: 250.655.5801
Email: gbrooks@axys.com

The laboratory PM at Brooks Applied Labs can be reached as follows:

Ms. Elizabeth Madonick
Brooks Applied Labs
18804 North Creek Parkway, Suite 100
Bothell, WA 98011

Telephone: 206.753.6141; ext. 129
Email: elizabeth@brooksapplied.com

The laboratory PM at ALS can be reached as follows:

Mr. Jeff Grindstaff
ALS Environmental-Kelso
1317 13th Avenue South
Kelso, WA 98626
Telephone: 360.577.7222
Email: Jeff.Grindstaff@alsglobal.com

The laboratories will meet the following requirements:

- Adhere to the methods outlined in this QAPP, including those methods referenced for each procedure.
- Adhere to documentation, custody, and sample logbook procedures.
- Implement QA/QC procedures defined in this QAPP.
- Meet all reporting requirements.
- Deliver electronic data files as specified in this QAPP.
- Meet turnaround times for deliverables as described in this QAPP.
- Allow EPA and the QA/QC manager, or a representative, to perform laboratory and data audits.

3.5 DATA MANAGEMENT

Kim Goffman of Windward will oversee data management, and will ensure that analytical data are incorporated into the LDW database with appropriate qualifiers following acceptance of the data validation. QA/QC of the database entries will ensure accuracy for use in the pre-design studies. Ms. Goffman can be reached as follows:

Ms. Kim Goffman
Windward Environmental LLC
200 West Mercer Street, Suite 401
Seattle, WA 98119
Telephone: 206.812.5414
Email: kimg@windwardenv.com

3.6 SPECIAL TRAINING/CERTIFICATION

The Superfund Amendments and Reauthorization Act of 1986 required the Secretary of Labor to issue regulations through the Occupational Safety and Health Administration (OSHA) providing health and safety standards and guidelines for workers engaged in hazardous waste operations. Accordingly, 29 Code of Federal Regulations (CFR) 1910.120 requires that employees be given the training necessary to provide them with

the knowledge and skills to enable them to perform their jobs safely and with minimum risk to their personal health. All sampling personnel will have completed the 40-hour HAZWOPER training and 8-hour refresher courses, as necessary, to meet OSHA regulations.

Also, ARI, Axys, Brooks Applied Labs, and ALS have current environmental laboratory accreditation for methods to be performed from the Washington State Department of Ecology (Ecology).

3.7 DOCUMENTATION AND RECORDS

All field activities and laboratory analyses will be documented following the protocols described in this section. In addition, data reduction rules and data report formats are provided herein.

3.7.1 Field observations

All field activities will be recorded in a field logbook maintained by the FC or designee. The field logbook will provide a description of all sampling activities, conferences between the FC and EPA oversight personnel associated with field sampling activities, sampling personnel, and weather conditions, as well as a record of all modifications to the procedures and plans identified in this QAPP and the HSP (Appendix A). The field logbook will consist of bound, numbered pages, and all entries will be made in indelible ink. Photographs, taken with a digital camera, will provide additional documentation of the surface water collection activities. The field logbook is intended to provide sufficient data and observations to enable participants to reconstruct events that occurred during the sampling period.

The following field data collection sheets, included as Appendix B, will also be used to record pertinent information after sample collection:

- Surface Water Collection Form
- Protocol Modification Form

Information regarding equipment calibration and other sampling activities will be documented in the field logbook. Water quality profile data will be recorded electronically.

3.7.2 Laboratory records

The chemistry laboratories will be responsible for internal checks on sample handling and analytical data reporting, and will correct errors identified during the QA review. The laboratory data packages will be submitted electronically and will include the following:

- **Project narrative**: This summary, in the form of a cover letter, will present any problems encountered during any aspect of sample analyses. The summary will include, but not be limited to, discussion of QC, sample shipment, sample

storage, and analytical difficulties. Any problems encountered by the laboratory will be documented, as will their resolutions. In addition, operating conditions for instruments used for the analysis of each suite of analytes and definitions of laboratory qualifiers will be provided.

- **Records**: Legible copies of the chain of custody (COC) forms will be provided as part of the data package. This documentation will include the time of receipt and the condition of each sample received by the laboratory. Additional internal tracking of sample custody by the laboratory will also be documented.
- **Sample results**: The data package will summarize the results for each sample analyzed. The summary will include the following information, as applicable:
  - Field sample identification (ID) code and the corresponding laboratory ID code
  - Sample matrix
  - Date of sample extraction / digestion
  - Date and time of analysis
  - Volume and / or weight[7] used for analysis
  - Final dilution volumes or concentration factor for the sample
  - Identification of the instruments used for analysis
  - MDLs and RLs[8]
  - All data qualifiers and their definitions
- **QA/QC summaries:** These summaries will contain the results of all QA / QC procedures. Each QA / QC sample analysis will be documented with the same information required for the sample results (see above). The laboratory will make no recovery or blank corrections except for isotope dilution method correction prescribed in EPA methods 1613b and 1668c. The required summaries are as follows:
  - The calibration data summary will contain the concentrations of the initial calibration and daily calibration standards and the date and time of analysis. The response factor, percent relative standard deviation (%RSD), relative percent differences (RPDs), and retention time for each analyte will be listed, as appropriate. Results for standards analyzed to indicate instrument sensitivity will be reported.

[7] Polyethylene (PE) strips are weighed during the passive sampler preparation process.

[8] The term MDL includes other types of detection limits (DLs) such as EDL values calculated for PCB congeners and dioxin / furan congeners.

- The internal standard area summary will report the internal standard areas, as appropriate.
- The method blank analysis summary will report the method blank analysis associated with each sample and the concentrations of all compounds of interest identified in these blanks.
- The surrogate spike recovery summary will report all surrogate spike recovery data for organic analyses. The names and concentrations of all compounds added, percent recoveries, and QC limits will be listed.
- The labeled compound recovery summary will report all labeled compound recovery data for EPA 1613b and 1668c analyses. The names and concentrations of all compounds added, percent recovery, and QC limits will be listed.
- The matrix spike (MS) recovery summary will report the MS or MS/matrix spike duplicate (MSD) recovery data for analyses, as appropriate. The names and concentrations of all compounds added, percent recoveries, and QC limits will be included. The RPD for all MS and MSD analyses will be reported.
- The matrix duplicate summary will report the RPD for all matrix duplicate analyses. The QC limits for each compound or analyte will be listed.
- The standard reference material (SRM) analysis[9] summary will report the results of the SRM analyses and compare these results with published concentration ranges for the SRMs.
- The LCS analysis summary will report the results of the analyses of LCSs. The QC limits for each compound or analyte will be included.
- The relative retention time summary will report the relative retention times for the primary and confirmational columns of each analyte detected in the samples, as appropriate.
- The ion abundance ratio summary for samples analyzed by EPA 1613b and 1668c will report computed ion abundance ratios compared to theoretical ratios listed in the applicable method.

- **Original data**: Legible copies of the original data generated by the laboratory will be provided, including the following:
  - Sample extraction/digestion, preparation, and cleanup logs
  - Instrument specifications and analysis logs for all instruments used on days of calibration and analysis

[9] SRMs will be analyzed for total and dissolved metals, mercury, and inorganic arsenic. All other analyses will include a laboratory control sample (LCS). Specific information is listed in Section 4.6.

- Reconstructed ion chromatograms for all samples, standards, blanks, calibrations, spikes, replicates, LCSs, and SRMs
- Enhanced and unenhanced spectra of target compounds detected in field samples and method blanks, with associated best-match spectra and background-subtracted spectra, for all gas chromatography / mass spectrometry (GC / MS) analyses
- Enhanced and unenhanced spectra of target performance reference compounds (PRCs) detected in field samples, day-zero blank, field blank, and method blanks, with associated best-match spectra and background-subtracted spectra, for all GC / MS analyses
- Quantitation reports for each instrument used, including reports for all samples, blanks, calibrations, MSs / MSDs, laboratory replicates, LCSs, and SRMs

The contract laboratories for this project will submit data electronically, in EarthSoft EQuIS® standard four-file or EZ_EDD format. Guidelines for electronic data deliverables for chemical data are provided on the EarthSoft website, http: / / www.earthsoft.com / en / index.html, and additional information will be communicated to the laboratories by the project QA / QC coordinator or data manager. All electronic data submittals must be tab-delimited text files with all results, MDLs (as applicable), and RLs reported to the appropriate number of significant figures. If laboratory replicate analyses are conducted on a single submitted field sample, the laboratory sample identifier must distinguish among the replicate analyses.

3.7.3 Data reduction

Data reduction is the process by which original data (analytical measurements) are converted or reduced to a specified format or unit to facilitate analysis of the data. Data reduction requires that all aspects of sample preparation that could affect the test result, such as sample volume analyzed or dilutions required, be taken into account in the final result. It is the laboratory analyst's responsibility to reduce the data, which are subjected to further review and reduction by the laboratory PM, the Windward TM, the QA / QC coordinator, and independent reviewers. The data will be generated in a format amenable to review and evaluation. Data reduction may be performed manually or electronically. If performed electronically, all software used must be demonstrated to be true and free from unacceptable error.

3.7.4 Data report

A data report will be prepared documenting all activities associated with the collection, handling, and analysis of samples, as specified in Task 5 of the third amendment to the AOC (EPA 2016c). At a minimum, the following information will be included in the data report:

- Summary of all field activities, including descriptions of any deviations from the approved QAPP
- Sampling locations reported in latitude and longitude to the nearest one-tenth of a second and in northing and easting to the nearest foot
- *In situ* water quality measurements
- Summary of the chemical data QA / QC review
- Results from the analyses of field samples, included as summary tables in the main body of the report, data forms submitted by the laboratories, and cross-tab tables produced from Windward's database
- Copies of field logs and photographs (appendix)
- Copies of COC forms (appendix)
- Data validation report (appendix)

Once the data report has been approved by EPA, a database export will be created from Windward's database. The data will be exported in two formats: one that is compatible with Ecology's Environmental Information Management System, and one that is compatible with EPA's Scribe database.

3.7.5 Data storage and backup

All electronic files related to the project will be stored on a secure server on Windward's network. The server contents are backed up on an hourly basis, and a copy of the backup is uploaded nightly to a secure off-site facility.

4 Data Generation and Acquisition

Surface water composite-grab samples and surface water passive samplers will be collected, processed, and analyzed according to the procedures described in this section. In addition, QA / QC, instrument maintenance and calibration, non-direct measurement, and data management requirements are provided.

4.1 SAMPLING DESIGN

Sampling design components—including sampling locations, sampling depths, flow conditions, and tidal cycles—for both types of surface water samples are detailed in the following sections for composite-grab samples (Section 4.1.1) and passive samplers (Section 4.1.2).

4.1.1 Surface water composite-grab sampling for DQO 1

This section presents the sampling design for the surface water composite grab samples that will be collected to evaluate DQO 1. An overview of this approach is presented in Table 4-1, and details are presented in the subsections that follow.

Table 4-1. Overview of composite grab sample approach

Design Component	Approach		Rationale
	LDW Locations	Upstream Reference Location	
Sample type	composite grab samples (each consisting of 4 grabs collected at least 1 hour apart)		Sections 4.1.1.1 and 4.1.1.4
Sampling locations	2 locations (RM 0.75 and 3.3)	1 location (RM 10)	Section 4.1.1.1
Sampling depth	near-surface and near-bottom	mid-depth	Section 4.1.1.2
Flow conditions	8 sampling events, including 4 storm events, 2 dry baseflow events, and 2 wet baseflow events		Section 4.1.1.3
Tidal cycles (baseflow only)	approximately centered around high= tide	outgoing tide	Section 4.1.1.4

LDW – Lower Duwamish Waterway
RM – river mile

4.1.1.1 Sampling locations

Composite-grab samples will be created by combining four grab samples from approximately four 1-hour periods at each of the three locations, including one upstream reference location and two LDW locations (Map 4-1). The following describes the criteria for location selection:

- **Location of the salt wedge** – The two LDW sampling locations were selected such that one near-bottom sample will be collected from a location that will be in the salt wedge (i.e., RM 0.75), and the other near-bottom sample will be collected

from a location that may be in the salt wedge, depending on flow and tidal conditions (i.e., RM 3.3).

- **Proximity to outfalls** – Sampling locations were selected to ensure that they are not adjacent to large outfalls that could impact sampling results.
- **Consistency with prior sampling** – When possible, prior surface water sampling locations were selected.

The LDW is a dynamic, well-mixed estuarine system due to the large tidal excursions that occur on a daily basis (two complete tidal cycles occur approximately every 24 hours), and thus localized effects from contamination levels in sediment are not expected to be discernable in the water column (see Section 4.1.2 for more detail). Thus, information related to pre- or post- cleanup sediment concentrations was not considered in the selection of sampling locations. Based on these criteria, Table 4-2 summarizes the selected sample locations and the rationale for their selection.

Table 4-2. Composite-grab sample locations and rationale

Sampling Location	Location Type	RM	Rationale
SW1	LDW	0.75	This location was selected to represent the area of the LDW where the salt wedge is always present (i.e., the near-bottom sample will be in the marine layer). This location is not located near large outfalls.
SW2	LDW	3.3	This location, near the South Park Bridge, was selected to represent the area of the LDW where the presence of the salt wedge varies depending on flow and tidal conditions. Additionally, this location is consistent with past surface water sampling of the LDW, and no large outfalls are located in this area.
SW3	upstream reference	10	This location on the Green River (upstream of the LDW) was selected for consistency with past surface water sampling conducted by the USGS and King County. It is accessed by Foster Golf Links course.

LDW – Lower Duwamish Waterway
RM – river mile
USGS – US Geological Survey

Because the available information (as described in Section 2 of the Work Plan) suggests that both marine and freshwater layers of surface water are well mixed laterally across the LDW (Windward and Integral 2017), samples will be collected only in the central portion of the waterway.

4.1.1.2 Sampling depth

To document differences in concentrations between the two-layer flow in the LDW (often referred to as freshwater or near-surface, and marine or near-bottom layers of the LDW), composite-grab samples will be collected at each LDW surface water sampling location at two depths. A near-surface sample will be collected 1 m below the surface of the water to represent the freshwater layer (or water with salinity generally < 5 ppt), and a near-bottom sample will be collected 1 m above the sediment

surface to represent the near-bottom layer.[10] A vertical profile of conductivity[11] and other relevant water quality information will be recorded during sample collection.

The upstream reference location will be sampled only at the midpoint of the water column; near-surface and near-bottom samples will not be needed because of the absence of the marine layer in this portion of the river and the comparatively shallow river depth (approximately 2 m[12]).

4.1.1.3 Flow conditions

The composite-grab sampling events will represent a range of flow conditions in order to characterize the chemical concentrations under a wide range of conditions. As described in the conceptual site model (CSM) in the Work Plan (Windward and Integral 2017), the targeted flow conditions are anticipated to include the conditions that result in the highest concentrations of chemicals such as PCBs.

Flow conditions in the LDW are dominated by the Howard Hanson Dam located in the upper Green River. Local storm events and seasonal conditions (dry vs. wet) also affect flow conditions. The following definitions will be used:

- **Storm events** – Precipitation forecasted to be greater than 0.25 in. within a 24-hour period (Storms 1 and 3, Table 4-3) and greater than 0.50 in. within a 24-hour period (Storms 2 and 4, Table 4-3).
- **Significant dam release**[13] – A flow rate greater than 2,000 cubic feet per second (cfs) at the US Geological Survey (USGS) gauge just below the Howard Hanson Dam (Gauge 12105900); the flow rate represents the rate of release from the dam.
- **Baseflow** – Average flow rates within wet and dry seasons, measured as rates of discharge at the USGS gauge just below the Howard Hanson Dam (i.e., daily averages of approximately 200–600 cfs during the dry summer months and approximately 800–1,200 cfs during the wet winter months).

To assess concentrations within the LDW system, eight sampling efforts will be conducted including: four storm events, both with and without significant dam release (targeting both ≥ 0.25 in. and ≥ 0.50 in. of precipitation); two sampling events to target dry baseflow conditions; and two sampling events to target wet baseflow conditions (Table 4-3 and Figure 2-1). If possible, composite samples will be collected from all

[10] Samples will be collected regardless of the salinity at the time of sampling. For example, the near-bottom sample at RM 3.3 may or may not represent the marine layer depending on the location of the salt wedge at the time of sampling.

[11] Salinity will be calculated based on conductivity and temperature recordings.

[12] Bathymetry data are not available for the Green River; however, a maximum depth of 2 m was reported for this location during sampling conducted in 2012 (King County 2014).

[13] Significant dam releases are not defined by USACE. Rather a significant dam release was defined as a rate greater than 2,000 cfs for consistency with rates used by King County and USGS water sampling programs (King County 2014; USGS 2016, 2017).

locations on the same day during all sampling events. Details regarding how sampling events will be scheduled are presented in Section 4.2.2.1.

Table 4-3. Composite-grab sampling events

Sampling Event	Event (ID)	Forecasted Precipitation[a]	Targeted Dam Release Conditions[b]	Target Schedule
Dry baseflow 1	DB1	3-day antecedent period without measurable rainfall	targeting dry season average dam releases (e.g., 200–600 cfs)	August/ September 2017
Storm 1[c]	ST1	≥ 0.25 in. in 24-hour period with 48-hour antecedent period without heavy rainfall[d]	without significant dam release (< 2,000 cfs)	September/ October 2017[f]
Storm 2[c]	ST2	≥ 0.50 in. in 24-hour period with 48-hour antecedent period without heavy rainfall[d,e]		
Storm 3[c]	ST3	≥ 0.25 in. in 24-hour period	with significant dam release (> 2,000 cfs)	November 2017 to January 2018
Storm 4[c]	ST4	≥ 0.50 in. in 24-hour period		
Wet baseflow 1	WB1	3-day antecedent period without measurable rainfall	targeting wet season average dam releases (e.g., 800–1,200 cfs)	December 2017 to March 2018
Wet baseflow 2	WB2			
Dry baseflow 2	DB2	3-day antecedent period without measurable rainfall	targeting dry season average dam releases (e.g., 200–600 cfs)	July/August 2018

[a] Forecasted precipitation will be based on local rainfall projections from the NOAA weather website. Rainfall prior to sampling (i.e., the antecedent period) will be based on measurements taken at the Hamm Creek gage (HAU2). See Section 4.2.2.1 for details.

[b] Dam releases are as measured at the USGS gage just below the Howard Hanson Dam (Gauge 12105900).

[c] Samples will generally be collected within 12 hours of the period during a storm that is predicted to have a greater amount of rainfall (see Section 4.2.2.1 for details).

[d] During the antecedent 48-hour period, up to approximately 0.2 in. of precipitation will be considered acceptable.

[e] Section 4.2.2.1 discusses the precipitation target when scheduling this event.

[f] If storm event samples without significant dam release cannot be collected in 2017, attempts will be made in September/October 2018.

cfs – cubic feet per second
ID – identification
NOAA – National Oceanic and Atmospheric Administration
USGS – US Geological Survey

4.1.1.4 Tidal cycles

Each composite-grab sample will consist of a composite of four grab samples collected at least one hour apart. This compositing approach will integrate short-term temporal variability to provide a better estimate of sample concentrations.

For dry and wet baseflow events, sampling during a consistent portion of the tidal cycle will increase the comparability of these events for long-term monitoring. Sampling periods for dry and wet baseflow will be as follows:

- **LDW locations (RM 0.75 and RM 3.3)** – The sampling period will be approximately centered around a daytime high tide for the LDW locations to maximize the residence time of the near-bottom layer and the likelihood of sampling the marine layer at the upper LDW location (RM 3.3).
- **Upstream location (RM 10)** – The upstream reference location will be sampled during an outgoing tide to ensure all flow is from Green River Watershed during sampling.

If possible, dry and wet baseflow sampling within the LDW will target spring and neap tides. Specifically, one dry and one wet baseflow event will be conducted during spring tides, while the other dry and wet baseflow events will be conducted during neap tides. A spring tide (which occurs just after a new or full moon) is when there is the largest difference between high and low tides, while a neap tide (which occurs halfway between a new and full moon) is when there is the smallest difference between high and low tides. The tidal cycle will be recorded during each sampling event.

For storm events, because of the need to capture specific precipitation levels and dam release conditions, specific tidal cycles will not be targeted. Tidal conditions at the time of sampling will be documented.

4.1.2 Surface water passive samplers for DQO 2

The sampling design for the passive samplers and its rationale are summarized in Table 4-4. As discussed in the draft Work Plan (Windward and Integral 2017), in order to provide a baseline dataset for PCBs that can be used to assess long-term trends, it is important to control for as many variables as possible. Thus, the CSM for the LDW was used to reduce the large number of sampling targets (e.g., location, depth, and season) to a reasonable subset that could effectively be measured during baseline sampling, and from which temporal inference could be made.

Table 4-4. Summary of passive sampler conceptual design and rationale

Design Component	Approach	Rationale
Passive sampler material	PE	PE is the recommended material to be used during passive sampler water column deployments for PCBs, as it allows for sufficient polymer mass to ensure reliable detection (EPA et al. 2017). The passive sampler consists of steel mesh envelopes containing PE strips that are suspended from a frame in the water column.
Deployment duration	1 month	The most-chlorinated PCB congeners can take several months to 1 year to fully equilibrate using a PE passive sampler (Tcaciuc et al. 2015). PRCs will therefore be used to correct for non-equilibrium conditions. One month is recommended as a balance between achieving sufficient equilibration within the sampler (to allow for reliable equilibrium corrections using PRC data), and minimizing the potential for sampler loss or biofouling. The one-month period also integrates and averages the actual short-term variability of PCB concentrations in the water, resulting in a measurement that allows for a more powerful assessment of long-term trends (Windward and Integral 2017; Appendix A).
Location	2 locations (RM 2.1 and RM 3.3 - South Park Bridge)	These locations have the permanence required to deploy a sampler so that it is less likely to be lost due to vessel traffic. The upstream location provides consistency with the composite-grab sample location (RM 3.3), where the near-bottom water is generally within the marine layer during the dry season.[a] The downstream location provides a second location to afford more data within the LDW.
Season	dry baseflow - summer (August)	Based on existing whole-water data and the CSM presented in the Work Plan (Windward and Integral 2017), the highest PCB concentrations are expected in the near-bottom water layer during the lower water flows encountered in the dry season. Within-season variability will be minimized by using month-long deployment.
Depth	1 m above sediment	The influence of the sediment remedy is of interest, and therefore the near-bottom layer of water was selected so that the passive sampler more directly represents the water influenced by PCBs flux from sediments than from other sources. This depth also ensures consistent exposure to the water column (i.e., tidal changes make higher elevation deployment more of a concern). Finally, this depth is consistent with the lower collection depth of the composite-grab samples being collected for DQO 1 (see Section 4.1.1.2).
Frequency	samplers deployed in August 2017 and August 2018	Samples will be collected over 2 years to assess 2 dry baseflow periods.
Number of replicates	9 replicates at bridge (attached to separate bridge supports)	Nine replicate samplers will be deployed at the same location and during the same sampling event in order to capture the variability of passive sampler analysis (see power analysis (Windward and Integral 2017; Appendix A)). Six additional samplers (for a total of 15) will be deployed in case any samplers are lost.

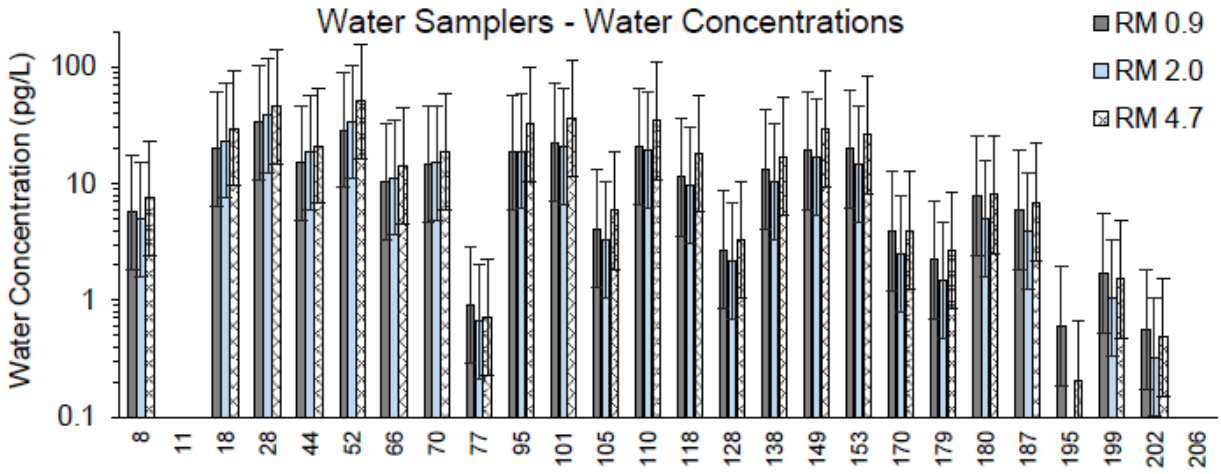
[a] The water in the near-bottom layer has longer residence time during low flows, because there is less entrainment into the outflowing surface layer, which reduces the net inflow from Elliott Bay.

ARAR – applicable or relevant and appropriate requirement
CSM – conceptual site model
DQO – data quality objective
EPA – US Environmental Protection Agency
LDW – Lower Duwamish Waterway
PCB – polychlorinated biphenyl
PE – polyethylene
PRC – performance reference compound
RM – river mile

As shown in Table 4-4, two locations (RM 2.1 and RM 3.3) were selected for deployment based on the results of a recent study (Apell and Gschwend 2017), which measured PCB congener concentrations in LDW surface water using passive samplers deployed at three locations (RM 0.9, RM 2.0, and RM 4.7). Three replicates samplers

were deployed 1 m below the water surface at each location for approximately eight weeks (June 2 to July 27, 2015), after which the samples (referred to as near-surface samples in that study) were analyzed for PCB congeners. Water concentrations of individual congeners were generally consistent for all the sampling locations. Five congeners (52, 95, 101, 110 and 118) had significantly higher concentrations at RM 4.7 than at the other locations. The sum of the PCB congeners ranged from 280 to 420 pg/L; the highest concentration was calculated for RM 4.7.

As shown in Figure 4-1, PCB congener concentrations were similar at the three sampling locations,[14] whereas variability among the concentrations across the three replicates was greater (variability was shown by error bars that represented 95th percentile confidence intervals).



Source: Apell and Gschwend (2017); Figure S4. Error bars represent the 95% confidence intervals for the mean by location.

Figure 4-1. Freely dissolved PCB congener concentrations derived from passive samplers deployed in the LDW 1 m below the water surface

Data collected as part of a 2014 MIT study in the LDW (Gschwend et al. 2016) were also reviewed to assess whether two locations for passive sampler deployment in the LDW are appropriate for monitoring PCB concentration trends in surface water. Total PCB concentrations in near-bottom water were compared with concentrations in both porewater and sediment to evaluate whether a relationship exists.

As part of the MIT study, 20 passive samplers were deployed in the LDW from RM 0.1 to RM 4.8 (Gschwend et al. 2016). The samplers were designed to measure *in situ* freely dissolved PCB concentrations in sediment porewater and the immediately

[14] The uncertainty analysis included an assessment of uncertainties associated with analytical measurements and partition coefficients.

overlying surface water (0–5 cm above the sediment surface), herein referred to as boundary layer water.[15] In this study, this boundary layer water was assessed to calculate flux from the sediment before being more broadly mixed into the water column.

While detailed data from this study are not yet available, total PCB concentrations have been presented graphically in a presentation by Gschwend et al. (2016). For this QAPP analysis, total PCB concentrations were estimated from data presented on Slide 17, which represent the sum of 18 PCB congeners in sediment porewater and boundary layer water. The estimated porewater concentrations ranged from approximately 350 to 1,850 pg/L; the associated boundary layer water concentrations had a smaller approximate range from 380 to 890 pg/L (Figure 4-2). As can be seen in Figure 4-2, there is no apparent relationship between the porewater and boundary layer water concentrations.

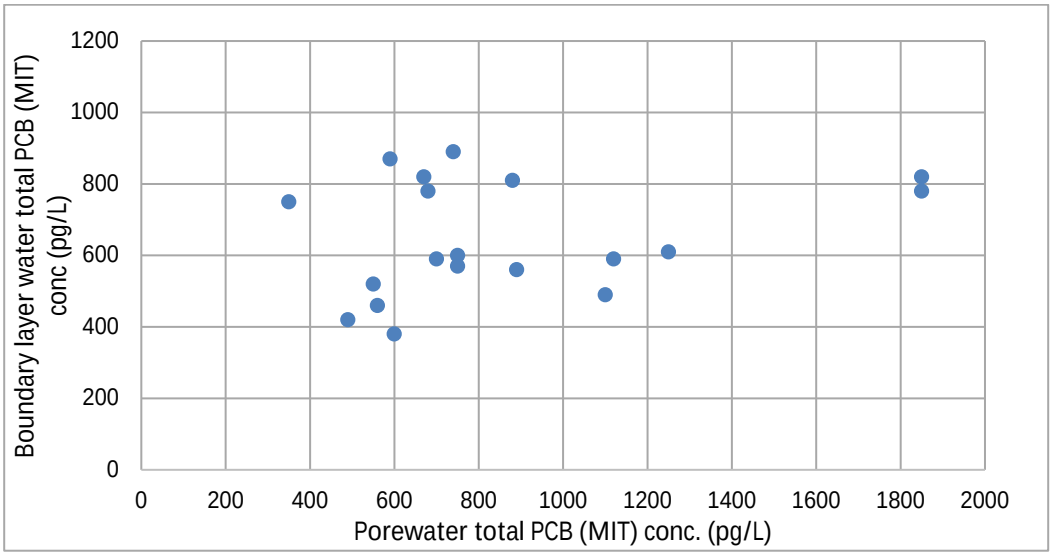


Figure 4-2. Approximate freely dissolved total PCB concentrations (sum of 18 congeners) in sediment porewater and boundary layer water (0–5 cm) samples from passive samplers deployed throughout the LDW

To further assess these data, approximate total PCB concentrations in surface sediment at each of the sampling locations were estimated using an interpolation of total PCB concentrations in surface sediment, as presented in the LDW feasibility study (AECOM 2012). Figure 4-3 presents these approximate sediment concentrations relative to the estimated boundary layer water concentrations. While there is considerable uncertainty in the estimation of sediment concentrations from

[15] In this study, surface water 0–5 cm above the sediment surface was referred to as bottom water. To distinguish the MIT samples from the near-bottom water samples, the former will be referred to as boundary layer water.

interpolated data, the approximate sediment concentrations ranged over three orders of magnitude from 15 to 3,900 µg/kg; the boundary layer water concentrations at these locations had a much tighter range from 380 to 890 pg/L (Figure 4-3). As with the comparison to sediment porewater, Figure 4-3 indicates that there is no apparent relationship between sediment and boundary layer water concentrations.

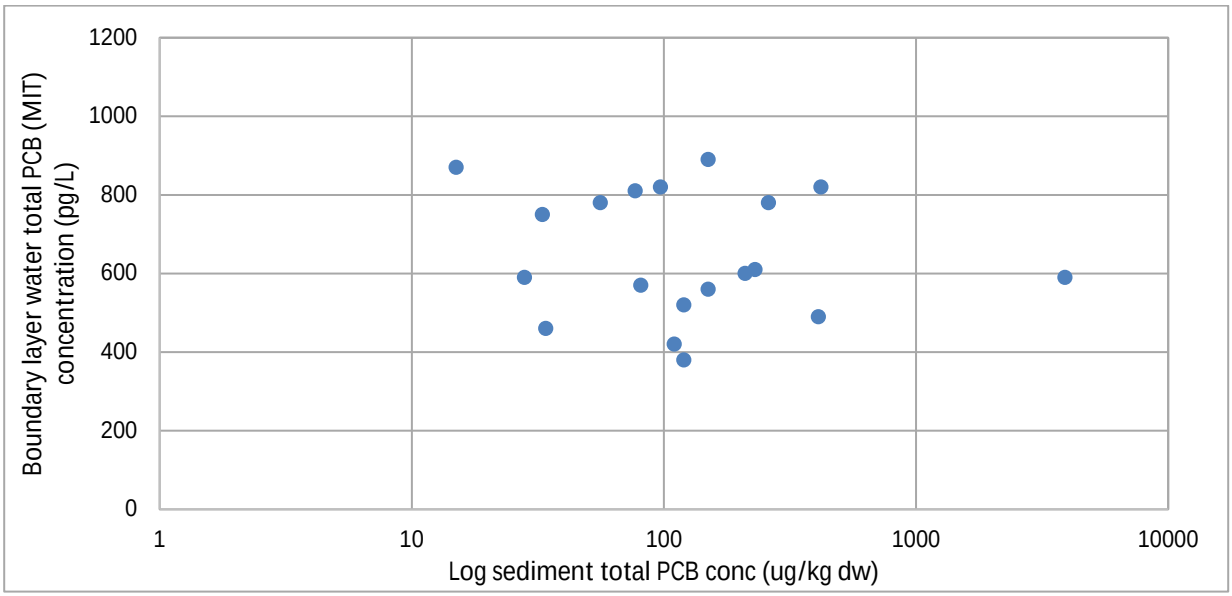


Figure 4-3. Approximate total PCB concentrations in surface sediment (based on FS interpolation) relative to approximate freely dissolved PCB concentrations (sum of 18 congeners) from passive samplers deployed in boundary layer water (0–5 cm)

Despite the uncertainty in the absolute individual values for boundary layer water, sediment, and porewater, it appears that the PCB concentrations in the boundary layer water (i.e., those that would be expected to be most closely associated with the sediment) are not directly proportional to the approximated sediment or porewater concentration at that location. These results are consistent with those presented for near-surface water collected in the upper portion of the water column (Figure 4-1), as well as the CSM presented in the Work Plan (Windward and Integral 2017), indicating that the marine near-bottom layer is not strongly influenced by localized sediment influences. Therefore, using passive samplers in two locations of the waterway is sufficient to evaluate PCB trends over time.

4.2 SAMPLING METHODS

Sample identification and field sampling will be performed following the protocols described in this section. Contingencies may arise during field activities that require modification of the general procedures outlined below. Such modifications will be at the discretion of the FC after consultation with the Windward TM and PM, the boat captain, and the EPA representative in the field, if applicable. LDWG and EPA will be

consulted if significant deviations from the sampling design are required. All modifications will be recorded in the protocol modification form (Appendix B).

4.2.1 Sample identification

Unique alphanumeric ID numbers will be assigned to each surface water sample and recorded on the surface water collection form (Appendix B).

For the composite-grab samples, the sample ID will include the following:

- Project area ID (i.e., LDW or Green River) and two-digit year
- Sample location ID (Table 4-2)
- Sampling event ID (Table 4-3)
- Depth horizon identifier (i.e., S [near-surface], M [mid-depth], or B [near-bottom])

For example, the near-surface composite-grab sample collected from RM 0.75 during the first dry baseflow sampling event will be identified as LDW17-SW1-DB1-S.

For the passive samplers, the sample ID will include the following:

- Project area ID (i.e., LDW) and two-digit year
- Passive sampler location ID (i.e., PS1 or PS2)
- Sampling event ID (i.e., DB1 or DB2)
- Two-digit sequential replicate number

For example, the ninth passive sampler replicate collected in 2017 during dry baseflow will be identified as LDW17-PS1-DB1-09.

All relevant information for each sample—including sample ID, sample date, sample time, and sample depth and location—will be recorded on the surface water collection form (Appendix B) and included as an appendix in the data report.

4.2.2 Surface water sampling methods

Composite-grab samples will be collected using a Teflon-coated 5-L Niskin bottle sampler. Freely dissolved PCB concentrations will be determined using polyethylene (PE) passive samplers. Details for each method are presented below. The sampling locations for each type of sample are summarized in Table 4-5.

Table 4-5. Sampling locations

Sampling Location	Sample Type	RM	Coordinates[a]				Sample Depth(s)[b]
			Latitude (DD)	Longitude (DD)	Easting (X)	Northing (Y)	
SW1	composite grabs	0.75	-122.344762	47.559049	1267254	207589	near-surface, near-bottom
SW2	composite grabs	3.3	-122.314172	47.529387	1274597	196624	near-surface, near-bottom
PS1	passive sampler	3.3[c]	-122.314454	47.529462	1274528	196653	near-bottom
SW3	Composite grabs	10	-122.258585	47.478666	1287985	177867	mid-depth

[a] North American Datum 1983. Easting/Northing in US Survey feet.

[b] Near-surface samples will be collected at 1 m below water surface; near-bottom samples will be collected at 1 m above sediment surface.

[c] Passive samplers will be deployed along the wing wall at the base of South Park Bridge.

DD – decimal degrees

RM – river mile

4.2.2.1 Composite-grab samples

Scheduling of Sampling Events

As described in Table 4-3, the eight surface water sampling events will focus on specific criteria regarding the targeted precipitation and dam release conditions. In addition, as described in Section 4.1.1.4, tidal conditions will be important in determining the schedule of baseflow sampling events. To target these conditions, various websites will be used to track the precipitation, dam discharge, and tidal considerations in order to schedule the sampling events (Table 4-6).

Table 4-6. Websites for tracking sampling criteria

Criteria	Details	Website
Precipitation	**Forecast**: Local 24-hour precipitation predictions will be monitored by checking NOAA's National Weather Forecast website, which provides hourly weather forecasts.	http://www.weather.gov/
	Real-time data: Real-time data from King County's rain gauge at Hamm Creek (HAU2) will be tracked. The Hamm Creek gauge was selected because it provides real-time data that are helpful for field logistics.	http://green2.kingcounty.gov/hydrology/
Dam discharge rates	Pre-sampling dam discharge conditions will be monitored by checking USGS's discharge data for the Green River below the Howard Hanson Dam (Gauge 12105900). Flow conditions at the gauge for the Green River location in Auburn, Washington (Gauge 12113000), and at Foster Links Golf Course (Gauge 12113390)[a] will also be recorded to document the hydrograph and estimate flows at the downstream sampling locations corresponding to the sampling period.	https://waterdata.usgs.gov/nwis or http://www.nwd-wc.usace.army.mil/nws/hh/www/index.html#
Tidal conditions (baseflow only)	If the target flow conditions are met, NOAA's tidal conditions at the Eighth Avenue South Duwamish Waterway station (Gauge 9447029) will be checked in order to time the collection of the baseflow water samples to be approximately centered around the daytime high tide. These tidal conditions will not be targeted for storm events.	https://tidesandcurrents.noaa.gov/tide_predictions.html?gid=1415

Criteria	Details	Website
Spring and neap tides (baseflow only)	If possible, dry and wet baseflow sampling within the LDW will target spring and neap tides. Specifically, one dry and one wet baseflow event will be conducted during spring tides, while the other dry and wet baseflow events will be conducted during neap tides. A spring tide (which occurs just after a new or full moon) is when there is the largest difference between high and low tides, while a neap tide (which occurs halfway between a new and full moon) is when there is the smallest difference between high and low tides.	https://www.timeanddate.com/moon/phases/usa/seattle

[a] USGS Gauge 12113390 will be used as long as it remains active.

NOAA – National Oceanic and Atmospheric Administration

USGS – US Geological Survey

The procedures to be used to schedule baseflow sampling events will be as follows:

- **Identify target date** – Because baseflow sampling is intended to capture more common dry and wet season conditions, a target date will be selected based on a review of the upcoming daytime high tides and targeting spring or neap tides. The target sampling date will also be based on expected dam release conditions and long-range forecasts.
- **Track conditions** – Starting two weeks prior to the target sampling date, the FC will track the current dam release conditions and forecasted precipitation to assess the likelihood that target requirements for baseflow sampling will be met (i.e., a three-day antecedent period without measurable rainfall). Detailed records of the precipitation and dam release conditions will be recorded for the week prior to sampling.
- **Mobilize for sampling** – The day before sampling is schedule, the FC will determine whether target conditions are met. If conditions are met, (e.g., no measurable precipitation has fallen during the previous two days and none is forecast for the current day [i.e., there will be a three-day antecedent period without measurable rainfall], and dam release rates are similar to those specified in Table 4-3), the FC will determine that sampling can proceed as scheduled, and the sampling team will mobilize for baseflow sampling and coordinate with the laboratory to ensure day-of filtration of samples. If target conditions are not met (e.g., measurable rainfall is forecast as "likely" in the day prior to sampling), the FC will re-schedule the baseflow sampling date.

Scheduling the storm events will be more difficult than scheduling baseflow events. Rapid mobilization will be required to ensure that the sampling team collects samples generally within 12 hours of the majority of the rainfall (i.e., period of maximum intensity) during a qualifying storm event. Storm sampling events will be scheduled as follows:

- **Track precipitation forecast** – The FC will use the National Oceanic and Atmospheric Administration (NOAA) website (Table 4-6) to track the forecast for storm events predicted as > 0.25 in. and > 0.5 in. of rainfall. Rainfall classified on the NOAA website as having a "likely" (or higher) chance of occurring will

be used as the threshold for targeting storm events. It is important to recognize that storm events will be targeted for sampling based on forecasted precipitation, and that actual rainfall may be more or less than predicted. For example, a storm with a "likely" chance of 0.3 in. of rain may only result in 0.23 in. of rain at the Hamm Creek gauge, but the storm will still be classified as meeting the 0.25 in. forecasted precipitation threshold for the storm event.

- **Track precipitation forecast for antecedent period –** In addition, when attempting to target storm events without significant dam release (Storms 1 and 2; see Table 4-2), the FC will use the NOAA website (as well as actual rainfall data from the Hamm Creek gauge) to evaluate whether the storm event will be preceded by a two-day period with relatively little precipitation (< 0.2 in. within a 48-hour period).
- **Track dam release conditions** – When a qualifying storm event is forecasted, the FC will track current dam release conditions and consider seasonal dam release patterns to determine whether a significant dam release (> 2,000 cfs) is likely.
- **Mobilize for sampling** – When a storm event is forecasted that meets the precipitation and dam release conditions for one of the four storm events, the sampling team will plan to mobilize for sampling within 12 hours of the time period during which the majority of the rainfall is predicted (i.e., period of maximum intensity) during the storm event. Because of the need for rapid mobilization, it is important to recognize that some flexibility will be required regarding the timing of sampling. In addition, for safety reasons, the field team will only conduct sampling during daylight hours.[16]

As noted above, sampling storm events is expected to be challenging because of the limited number of qualifying storms in a given year that also meet the dam release conditions. This will be particularly true for the storm event targeting > 0.5 in. of rainfall without significant dam release and without precipitation in the two-day period prior to the storm. If the targeted precipitation and dam release conditions do not occur from fall 2017 through spring 2018 because the conditions do not occur in a predictable manner, additional attempts will be made during fall 2018.

Collection of Composite-Grab Samples

For the two LDW sample locations, composite-grab sampling will be conducted from a boat. During sampling, the boat will be positioned on-station such that the motor / exhaust is downstream of the sample collection point to minimize the likelihood of sample contamination. The upstream reference location will be sampled from the bridge at the Foster Golf Links course (at approximately RM 10).

[16] The field team will not mobilize before dawn or within four hours of sunset. Sampling may be conducted on weekends if necessary.

Composite grab samples will be collected using a 5-L Teflon-lined Niskin bottle sampler, which will be manually lowered on a line to the targeted depth and triggered to close via a messenger. After the end caps of the sampler have been triggered shut, the sampler will be retrieved. Four grab samples will be collected, each approximately one hour apart, and combined to create a composite sample, according to the methods described below. One near-surface and one near-bottom composite sample will be collected at each LDW location during each sampling event. The upstream reference location will be sampled only at the midpoint of the water column.

When collecting each composite-grab sample, *in situ* conventional water quality parameters will be measured throughout the water column at each location (measurements will be taken at short intervals as the meter is slowly lowered through the water column). Accordingly, four profiles will be completed per composite-grab sample. Water quality parameters will be measured using a multi-parameter water quality meter to record a profile of the entire water column for conductivity, temperature, dissolved oxygen, pH, and turbidity. Salinity of the composite-grab samples will also be analyzed in the laboratory.

Compositing Methodology

Four surface water grab samples from each sampling location and depth will be combined during each sampling event (i.e., both baseflow and storm events) to create composite samples.

Compositing will be conducted as follows:

- Sample containers will be pre-cleaned and labeled to the extent possible. Preservative will be added to sample bottles for inorganic arsenic prior to field sampling. All other samples will be preserved at the laboratories.
- Upon collection, each of the four surface water grab samples will be distributed from the Niskin bottles in equal aliquots to pre-labelled sample bottles to create a composite sample for each sampling location and depth.
- The aliquots will be measured using a graduated cylinder to represent one-fourth of the total sample volume for each sample bottle. For example, a 4-L bottle would receive a 1-L aliquot from each of the four grabs collected at a sampling location. Similarly, a 2-L bottle would receive a 500-mL aliquot, a 500-mL bottle would receive a 125-mL aliquot and a 125-mL bottle would receive a 31-mL aliquot from each of the four grab samples (Figure 4-4).
- The Niskin bottle sampler will be hand agitated in the field prior to dispensing each individual aliquot; the agitation will re-suspend any particulate in the sample to create a representative composite.
- Water from each of the three additional grab samples will be dispensed into the sample containers in the same manner. The order in which the sample

containers are filled will be reversed for each grab sample. Sample labels will be completed prior to the end of the sampling day.

- After the first aliquot has been measured into sample containers, containers will be capped and held on ice in coolers during the collection of the additional aliquots and until delivery to the laboratory.

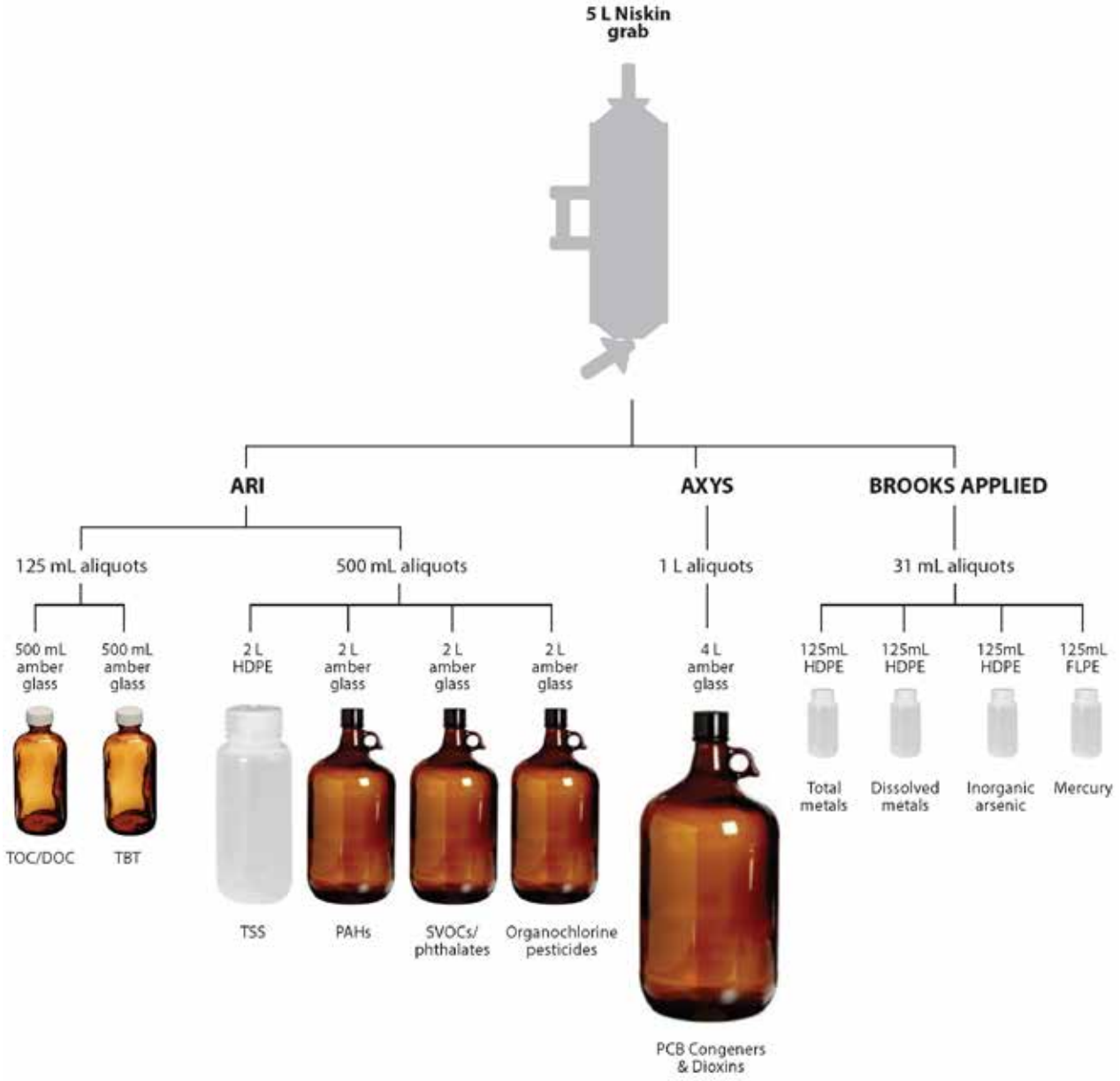


Figure 4-4. Distribution scheme for each individual surface water grab

4.2.2.2 Passive samplers

Sampler Preparation

Passive samplers consist of a stainless steel mesh envelope containing a low-density PE strip attached to a polyvinyl chloride (PVC) frame. The PE strips will be 25 µm thick and cut into 5- × 6-in. strips. The stainless steel mesh envelope will protect the PE strips from loss and damage, and will be customized to fit the PE strips (Figure 4-5) (Appendix D).

Figure 4-5. Polyethylene sampler and holder for surface water deployment

Using methods based on those outlined by (Gschwend et al. 2012), Axys will prepare the passive samplers by cleaning a known mass of PE sheeting using sequential extractions with solvent (e.g., dichloromethane [DCM], methanol). The mesh envelopes will be cleaned with DCM, methanol, and reagent water. Axys will cut the clean PE into 5- × 6-in. strips.

Clean PE strips will be loaded with PRC standards by equilibrating the strips with methanol:water PRC solutions in a glass container for at least seven days. Prior to deployment, the PE strips will be submerged in ultra-clean water for three days to remove the methanol. The PE strips will then be placed in stainless steel mesh envelopes to create the passive samplers. Each sampler will be wrapped in aluminum foil and placed in a resealable plastic bag at < 4ºC for shipment to Windward for deployment. A day-zero PE strip will be stored, wrapped in foil, frozen at Axys, and analyzed with the sampler replicates.

PRCs are used to allow non-equilibrium conditions between the PE and the water column to be quantified. Using PRCs, passive samplers can be deployed for shorter time periods, which has been found to decrease the risk of loss, damage, and

biological fouling. The carbon-13-labelled PCBs to be used for PRCs will include ^{13}C-PCB8, ^{13}C-PCB28, ^{13}C-PCB95, ^{13}C-PCB111, ^{13}C-PCB153 and ^{13}C-PCB178. The PRC loading details will be recorded on a worksheet by the analyst. The worksheet will document the date, the list of PRCs used, and the concentrations in the soaking solution.

Field Deployment and Retrieval of Passive Samplers

Within 7 to 10 days of receipt, Windward will deploy the passive samplers. They will be transported to the field on ice in a cooler. Individual passive samplers will be unwrapped and attached to the passive sampling frame for deployment.

Passive samplers will be deployed at both locations, in groups of five (approximately 1 ft apart) attached to one sampling frame (Figure 4-6). At each location, three sampling frames will be deployed for a total of 15 passive samplers. The deployment frames will be constructed from PVC pipe and used as the primary structure to suspend the passive samplers in the near-bottom layer of the water column. Three anchor weights will be attached across the bottom of the frames to secure the samplers and minimize the agitation of nearby sediment. The loaded frames will then be deployed from a boat by lowering the frames to the sediment surface; they will be secured to the bridge's fender boards when the anchor weights reach the bottom.

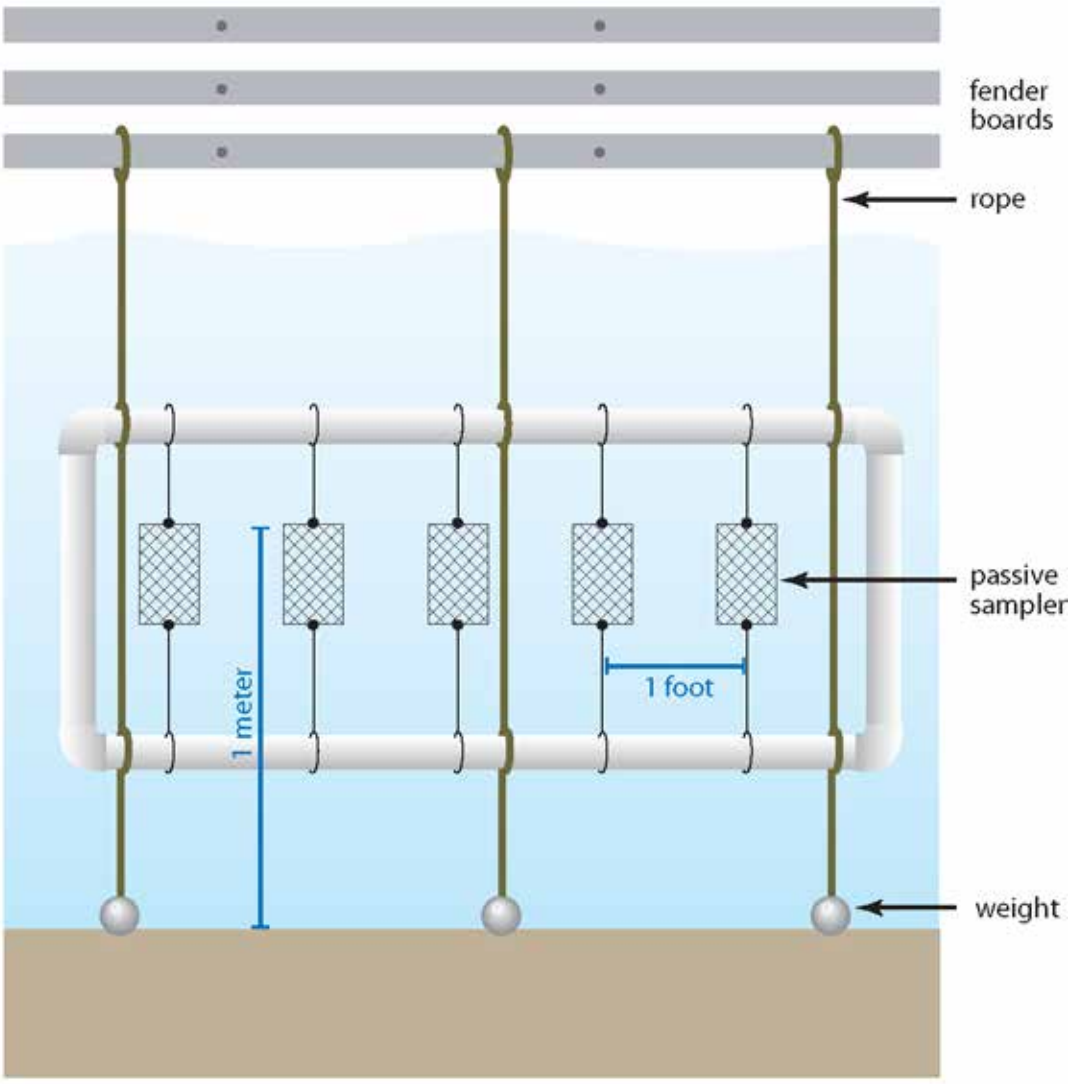


Figure 4-6. Conceptual design of passive sampler deployment frame

Multi-parameter data loggers will be deployed with the frames at the same depth as the passive samplers at each location. The data logger will collect *in situ* water quality data (e.g., conductivity, temperature, dissolved oxygen, and pH) for the duration of the sampling period.

After approximately 30 days, the passive sampler frames will be retrieved from the site. Each passive sampler will be detached from the frame but will be kept in its mesh envelope. The passive samplers will then be wrapped in aluminum foil, double-bagged in resealable plastic bags, and labelled with appropriate sample ID. Passive samplers will be placed on ice in a cooler for shipment to Axys. The multi-parameter data loggers will also be detached from the frame, and water quality data will be downloaded off-site.

Calculation of Freely Dissolved PCB Congener Concentrations in Surface Water from PE Concentrations

Following PCB congener analysis of the PE strips by Axys (see Section 4.4.2), PCB congener concentrations in the PE strips will be used to calculate the concentrations of freely dissolved PCB congeners present in the water column during the *in situ* exposure, as summarized in Figure 4-7.

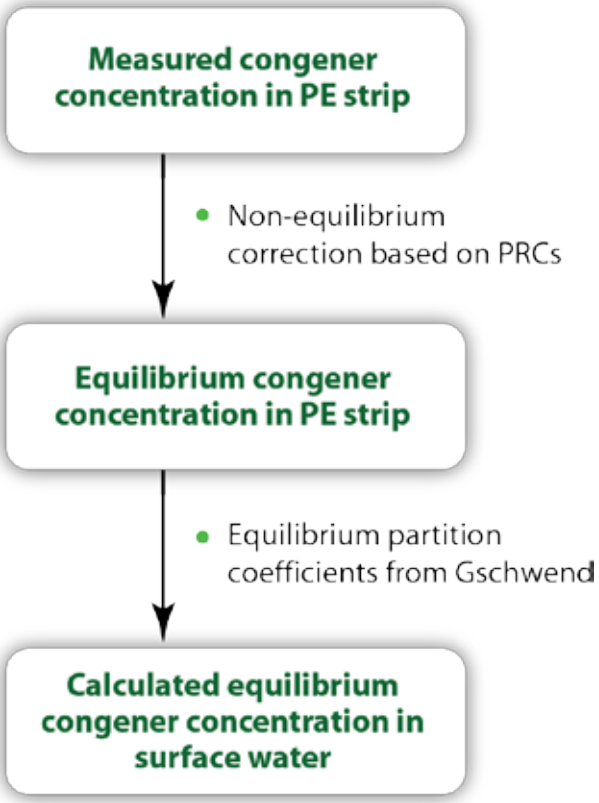


Figure 4-7. Calculation method for freely dissolved PCB congeners in water column from passive sampler

The first step will be to convert the measured PE concentrations to equilibrium PE concentrations based on the PRC concentrations in the samplers. PRC concentrations remaining in the PE sampler after deployment will be used to estimate the degree of equilibrium between the sampler and the surface water.

PRCs of varying hydrophobicities have been selected, because the rates of mass transfer in and out of the sampler will depend on the hydrophobic properties of each congener. Measured fractions of PRCs lost after deployment will be used to calculate a regression line between the model-estimated partitioning constant (K_D) and the octanol-water partitioning constant (K_{OW}) (Apell and Gschwend 2014). This K_{OW}/K_D fit will be used to calculate the fractional equilibration for each PCB congener using a PRC correction calculator accessed via a graphical user interface, as described by EPA et al. (2017).

Appendix C presents the physical and chemical properties that will be used to correct for nonequilibrium conditions. PRC calculator default values will be used for the properties of the PCB congeners. If more than 90% 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 surface water in that sampler (Gschwend et al. 2014). The equilibrium PE congener concentrations (C_{PE}) calculated using PRC data as described above, and the default PE-to-water partition constants (K_{PEW}) provided in Gschwend et al. (2014) (Appendix C), will then be used to calculate the freely dissolved PCB concentrations in surface water (C_{SW}) using the following equation:

$$C_{SW} = C_{PE} / K_{PEW} \qquad \textbf{Equation 1}$$

4.3 SAMPLE HANDLING AND CUSTODY REQUIREMENTS

Sample custody is a critical aspect of environmental investigations. Sample possession and handling must be traceable from the time of sample collection, through laboratory and data analyses, to delivery of the sample results to the recipient. Procedures to be followed for sample handling, custody, and shipping are detailed in this section. In addition, procedures for decontamination of equipment and disposal of field-generated waste are described.

4.3.1 Sample handling procedures

At each laboratory, a unique sample identifier will be assigned to each sample (termed either project ID or laboratory ID). The laboratory will ensure that a sample tracking record follows each sample through all stages of laboratory processing. The sample tracking record must contain, at a minimum, the name/initials of responsible individuals performing the analyses, dates of sample extraction/preparation and analysis, and type of analyses being performed.

4.3.1.1 Composite-grab samples

The FC will be responsible for reviewing water sample information recorded on field collection forms (Appendix B), and will correct any improperly recorded information. Composite-grab samples will be double bagged and immediately stored in coolers with wet ice. Sample labels will contain the project number, sampling personnel, date, time, and sample ID. Pertinent information about the sample, including its location and depth, will be traceable through the sample label. A complete sample label will be affixed to each individual sample bottle. Labels will be filled out as completely as possible prior to each sampling event.

Samples will be placed on ice after collection and for transport to the laboratories. Sample packaging and transport information is summarized in Section 4.3.3.

4.3.1.2 Passive samplers

Upon collection of the passive samplers, each PE strip replicate will remain in its stainless steel mesh envelope, which will be wrapped in aluminum foil and placed in a

resealable, waterproof plastic bag with appropriate labels. Samples will be placed on ice after collection and for transport to Axys.

4.3.2 Sample custody procedures

Samples are considered to be in custody if they are: 1) in the custodian's possession or view; 2) in a secured place (under lock) with restricted access; or 3) in a container and secured with an official seal(s) such that the sample cannot be reached without breaking the seal(s). Custody procedures, described below, will be used for all samples throughout the collection, transportation, and analytical processes, and for all data and data documentation whether in hard copy or electronic format. Custody procedures will be initiated during sample collection.

A COC form will accompany all samples to the analytical laboratory. Each person who has custody of the samples will sign the COC form and ensure that the samples are not left unattended unless properly secured. Minimum documentation of sample handling and custody will include:

- Sample location, project name, and unique sample ID number
- Sample collection date and time
- Any special notations on sample characteristics or problems
- Name of the person who initially collected the sample
- Date sample was sent to the laboratory
- Shipping company name and waybill number

In the field, the FC will be responsible for all sample tracking and custody procedures. The FC will also be responsible for final sample inventory, and will maintain sample custody documentation. The FC or a designee will complete COC forms prior to removing samples from the sampling area. At the end of each day, and prior to sample transfer, COC entries will be made for all samples. Information on the sample labels will be checked against sample log entries, and sample tracking forms and samples will be recounted. COC forms, which will accompany all samples, will be signed at each point of transfer. Copies of all COC forms will be retained and included as appendices to QA / QC reports and data reports. Samples will be shipped in sealed coolers.

The laboratories will ensure that COC forms are properly signed upon receipt of the samples, and will note questions or observations concerning sample integrity on the COC forms. The laboratories will contact the FC and project QA / QC coordinator immediately if discrepancies are discovered between the COC forms and the sample shipment upon receipt.

4.3.3 Shipping requirements

As shown in Figure 4-1, sample collection was designed to enable splits to be sent to the appropriate analytical laboratories. Samples will be transported directly to ARI (i.e., by field staff), and samples will be transported to Axys, Brooks Applied Labs, and ALS via courier. Prior to shipping, containers with composite-grab samples will be wrapped in bubble wrap and securely packed inside a cooler with ice packs. Passive sampler replicates will be wrapped in foil, placed in resealable plastic bags, and securely packed inside a cooler with ice packs. The original signed COC forms will be placed in a sealed plastic bag and taped to the inside lid of the cooler. Fiber tape will be wrapped completely around the cooler. On each side of the cooler, a *This Side Up* arrow label will be attached; a *Handle with Care* label will be attached to the top of the cooler, and the cooler will be sealed with a custody seal in two locations.

The temperature inside the cooler(s) containing the composite-grab samples and passive sampler replicates will be checked by the laboratory upon receipt of the samples. The laboratory will specifically note any coolers that do not contain ice packs, or that are not sufficiently cold (≤ 6°C) upon receipt. All samples will be handled so as to prevent contamination or sample loss. Any remaining composite-grab samples will be disposed upon receipt of written notification by the Windward PM. Water sample holding times vary by analysis and are summarized in Section 4.4.2. Passive sampler replicates will be held until the laboratory is notified by the Windward PM.

4.3.4 Decontamination procedures

Water sampling requires strict measures to prevent contamination. Sources of extraneous contamination can include sampling gear, grease from ship winches or cables, spilled engine fuel (gasoline or diesel), engine exhaust, dust, ice chests, and ice used for cooling. All potential sources of contamination in the field will be identified by the FC, and appropriate steps will be taken to minimize or eliminate contamination. For example, during retrieval of sampling gear, the boat will be positioned, when feasible, so that engine exhaust does not fall on the deck. Ice chests will be scrubbed clean with Alconox® detergent and rinsed with distilled water after use at each sampling location to prevent potential cross contamination. To avoid contamination from melting ice, the wet ice will be placed in separate plastic bags. Prior to each sampling event, the Niskin bottle sampler will be cleaned with Alconox® phosphate-free detergent, rinsed with nitric acid, and rinsed with methanol. Between each subsample and sampling location, the field team will clean the Niskin bottle sampler with Alconox® phosphate-free detergent, rinse it with deionized water, and rinse it with site water.

4.3.5 Field-generated waste disposal

Excess grab sample water, generated equipment rinsates, and decontamination water[17] will be returned to each sampling location after sampling has been completed for that location. All disposable sampling materials and personal protective equipment (PPE) used in sample processing, such as disposable coveralls, gloves, and paper towels, will be placed in heavyweight garbage bags or other appropriate containers. Disposable supplies will be removed from the site by sampling personnel and placed in a normal refuse container for disposal as solid waste.

4.4 LABORATORY METHODS

Laboratories will meet the sample handling requirements and follow the procedures described in this section. In addition, analytical methods and data quality indicator (DQI) criteria are provided herein.

4.4.1 Laboratory sample handling

Samples will be packed in coolers and held at ≤ 4°C (± 2°C). Samples for ARI will be directly delivered to the laboratory by field staff. Samples for Axys, Brooks Applied Labs, and ALS will be delivered via courier service. Laboratories will filter, preserve, and store samples as described in Section 4.4.2.

4.4.2 Analytical methods

Chemical analysis of the composite-grab samples will be conducted at three different laboratories (Table 4-7). Chemical analyses of passive sampler replicates will be performed by Axys. Analytical methods and laboratory sample handling requirements for all measurement parameters are presented in Tables 4-8 and 4-9. High salinity interferes with metals analyses (except mercury), so dilution of samples may be necessary to remove such interference.

Table 4-7. Procedures to be conducted at each analytical laboratory

Laboratory	Analyses to be Conducted	Individual Analytes
Axys	PCB congeners	all 209 congeners (refer to Appendix C)
	dioxin/furan congeners	2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF, and OCDF
ARI	conventionals	DOC, salinity, TOC, TSS
	TBT	TBT

[17] Because decontamination water is an Alconox®-water solution (that is phosphate-free), it can be returned to the sampling location for disposal.

Laboratory	Analyses to be Conducted	Individual Analytes
	PAHs	acenaphthene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, and pyrene
	phthalates	bis(2-ethylhexyl)phthalate, butyl benzyl phthalate, diethyl phthalate, dimethyl phthalate, and di-n-butyl phthalate
	SVOCs	1,2,4,5-tetrachloro-benzene, 1,2-diphenylhydrazine, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, 2,4-dichlorophenol, 2,4-dimethylphenol, 2,4-dinitrophenol, 2,4-dinitrotoluene, 2-chloronaphthalene, 2-chlorophenol, 3,3'-dichlorobenzidine, 4,6-dinitro-o-cresol, 4-chloro-3-methylphenol, benzidine, bis(2-chloroethyl)ether, bis(2-chloroisopropyl)ether, bis(chloromethyl) ether, hexachlorobenzene, hexachloroethane, hexachlorocyclopentadiene, isophorone, n-Nitrosodiethylamine, n-Nitrosodimethylamine, n-Nitroso-di-n-butylamine, n-Nitroso-di-n-propylamine, n-Nitrosodiphenylamine, n-Nitrosopyrrolidine, nitrobenzene, nonylphenol (mixed isomers), pentachlorobenzene, pentachlorophenol, phenol, total dinitrophenols, and total nitrosamines
	organochlorine pesticides	4,4'-DDD, 4,4'-DDE, 4,4'-DDT, aldrin, dieldrin, alpha-BHC, beta-BHC, gamma-BHC, total chlordane, alpha-endosulfan, beta-endosulfan, endosulfan sulfate, endrin, endrin aldehyde, heptachlor, heptachlor epoxide, hexachlorocyclohexane-G, methoxychlor, mirex, and toxaphene
Brooks Applied Labs	total metals	antimony, mercury, and thallium
	dissolved metals	arsenic, cadmium, chromium, copper, lead, nickel, selenium, silver, and zinc
	inorganic arsenic	inorganic arsenic
ALS	organophosphate pesticides	chlorpyrifos, diazinon, and malathion
	carbamate pesticides	carbaryl

ALS – ALS Environmental-Kelso
ARI – Analytical Resources, Inc.
Axys – Axys Analytical Services Ltd.
BHC – benzene hexachloride
DDD – dichlorodiphenyldichloroethane
DDE – dichlorodiphenyldichloroethylene
DDT – dichlorodiphenyltrichloroethane
DOC – dissolved organic carbon
HpCDD – heptachlorodibenzo-*p*-dioxin
HpCDF – heptachlorodibenzofuran
HxCDD – hexachlorodibenzo-*p*-dioxin
HxCDF – hexachlorodibenzofuran
OCDD – octachlorodibenzo-*p*-dioxin
OCDF – octachlorodibenzofuran
PAH –polycyclic aromatic hydrocarbon
PCB – polychlorinated biphenyl
PeCDD – pentachlorodibenzo-*p*-dioxin
PeCDF – pentachlorodibenzofuran
SVOC – semivolatile organic compound
TBT – tributyltin
TCDD – tetrachlorodibenzo-p-dioxin
TCDF – tetrachlorodibenzofuran
TOC – total organic carbon
TSS – total suspended solids

Table 4-8. Analytical methods and sample handling requirements for composite-grab samples

Parameter[a]	Method	Reference	Extraction Solvent	Cleanup	Laboratory	Container	Preservative	Sample Holding Time
TSS	gravimetric	SM 2540 D-97	na	na	ARI	2-L HDPE	cool to ≤ 6°C	7 days
TOC	high-temperature combustion	SM 5310 B-00	na	na	ARI	250-mL amber glass	cool to ≤ 6°C; sulfuric acid to pH < 2	28 days
DOC	high-temperature combustion	SM 5310 B-00	na	na	ARI	250-mL amber glass	cool to ≤ 6°C; 0.45 µm filter within 48 hours; sulfuric acid to pH < 2	28 days
Salinity	ion-selective electrode	SM 2520 B-00	na	na	ARI	250-mL amber glass	cool to ≤ 6°C	28 days
Total and dissolved metals	ICP-MS	EPA 1638	na	na	Brooks Applied Labs	125-mL HDPE	nitric acid to pH < 2; dissolved samples filtered with 0.45-µm filter[b]	6 months
Inorganic arsenic	HG-AFS	EPA 1632	na	na	Brooks Applied Labs	125-mL HDPE	hydrochloric acid to pH < 2 at collection; 0–4°C in the dark	28 days
Mercury	CV-AFS	EPA 1631E	na	na	Brooks Applied Labs	125-mL FLPE or glass bottle with FLPE lined lid	5 mL/L bromine monochloride	90 days
TBT	GC/MS	EPA 3510C/ EPA 8270-SIM	0.10% tropolone/ DCM (EPA 3660B) hexyl magnesium bromide in diethyl ether derivitization (Krone)	alumina (EPA 3610B) or silica gel (EPA 3630C)	ARI	500-mL amber glass	cool to ≤ 6°C	7 days until extraction, 40 days after extraction; store extracts at ≤ 6°C and in the dark
PAHs	GC/MS	EPA 3510C/ EPA 8270D-SIM	DCM	silica gel (EPA 3630C)	ARI	4-L amber glass	cool to ≤ 6°C	7 days until extraction, 40 days after extraction; store extracts at ≤ 6°C and in the dark

Parameter[a]	Method	Reference	Extraction Solvent	Cleanup	Laboratory	Container	Preservative	Sample Holding Time
Phthalates	GC/MS	EPA 3510C/ EPA 8270D	DCM	none	ARI	2-L amber glass	cool to ≤ 6°C	7 days until extraction, 40 days after extraction; store extracts at ≤ 6°C and in the dark
Other SVOCs	GC/MS	EPA 3510C/ EPA 8270D	DCM	none	ARI	2-L amber glass	cool to ≤ 6°C	7 days until extraction, 40 days after extraction; store extracts at ≤ 6°C and in the dark
PCB congeners	HRGC/ HRMS	EPA 1668c	DCM	biobead multi-layered acid/base silica, alumina, florisil	Axys	4-L amber glass	cool to ≤ 6°C	1 year until extraction, 1 year after extraction (if in the dark at ≤ -10°C)
Dioxins/ furans	HRGC/ HRMS	EPA 1613B	DCM/ hexane	biobead multi-layered acid/base silica, florisil, alumina, carbon/celite	Axys	4-L amber glass	cool to ≤ 4°C	store in the dark at 0–4°C; store extracts for up to 1 year at ≤ 10°C
Organochlorine pesticides	GC/ECD dual column	EPA3510C/ EPA 8081B	DCM	sulfur cleanup (EPA 3660B), silica gel (EPA 3630C)	ARI	2-L amber glass	cool, ≤ 6°C	7 days until extraction, analyze within 40 days after extraction; store extracts at ≤ 6°C and in the dark
Organophosphate pesticides	GC/NPD	EPA3510C/ EPA 8141B	DCM	none	ARI	4-L amber glass	cool, ≤ 6°C, adjust pH to 5–9	7 days until extraction, analyze within 40 days after extraction; store extracts at ≤ 6°C and in the dark

Parameter[a]	Method	Reference	Extraction Solvent	Cleanup	Laboratory	Container	Preservative	Sample Holding Time
Carbamate pesticides (Carbaryl)	HPLC/ TS/MS	EPA 3535/ EPA 8321	methanol	none	ALS	4-L amber glass	cool, ≤6 °C	7 days until extraction, 40 days after extraction; store extracts at ≤ 6°C and in the dark

[a] Individual analytes are listed in Table 4-7.

[b] Samples will be filtered in the laboratory as soon as possible following collection. The method specifies field filtration within 15 minutes of sample collection. However, laboratory filtration under clean, controlled conditions greatly reduces the risk of sample contamination during filtration. The resulting data will be qualified as estimated (J-flagged).

ARI – Analytical Resources, Inc.

Axys – Axys Analytical Services Ltd.

CV-AFS – cold vapor-atomic fluorescence spectrometry

DCM – dichloromethane

DOC – dissolved organic carbon

EPA – US Environmental Protection Agency

FLPE – fluorinated high-density polyethylene

GC/ECD – gas chromatography/electron capture detection

GC/MS – gas chromatography/mass spectrometry

GC/NPD – gas chromatography/nitrogen-phosphorus detector

HDPE – high-density polyethylene

HG-AFS – hydride generation-atomic fluorescence spectrometry

HPLC/TS/MS – high-performance liquid chromatography/thermospray/mass spectrometry

HRGC/HRMS – high-resolution gas chromatography/high-resolution mass spectrometry

ICP-MS – inductively coupled plasma-mass spectrometry

na – not applicable or not available

PAH – polycyclic aromatic hydrocarbon

PCB – polychlorinated biphenyl

SIM – selected ion monitoring

SM – Standard Methods

SVOC – semivolatile organic compound

TBT – tributyltin

TOC – total organic carbon

TSS – total suspended solids

Table 4-9. Analytical methods and sample handling requirements for the passive samplers

Parameter	Method	Reference	Extraction Solvent	Cleanup	Labor-atory	Container	Preserv-ative	Sample Holding Time
PCB congeners	HRGC/ HRMS	EPA 1668c	DCM	biobead multi-layered acid/base silica, alumina, florisil	Axys	PE strip/ aluminum foil	cool to ≤ -4°C	NA

Axys – Axys Analytical Services Ltd.
DCM – dichloromethane
EPA – US Environmental Protection Agency
HRGC/HRMS – high-resolution gas chromatography/ high-resolution mass spectrometry
PCB – polychlorinated biphenyl
PE – polyethylene

4.4.2.1 Composite Grab Samples

The composite-grab samples will be analyzed for analytes included in Washington's water quality standards (Washington Administrative Code [WAC] 173-201A-240), national recommended ambient water quality criteria (AWQC)[18] (Clean Water Act [CWA] Section 304[a]), and the Washington Toxics Rule (40 CFR 131.45 as applied to Washington[19]), with a few exceptions.[20]

RL goals for all of the individual analytes are listed in Appendix C. All of the RL goals for metals, except thallium, are below the corresponding WQC. The RL goals for tributyltin (TBT), some semivolatile organic compounds (SVOCs), and pesticides are higher than the lowest WQC for these compounds. The RL values represent the lowest concentrations at which the laboratory can quantitatively measure and report results analyzed by the methods listed. The analytes for which the RL goals are above the

[18] For the LDW, the relevant and appropriate AWQC for the protection of human health are only those established for the consumption of organisms, because LDW surface water is not a source of potable water and those analytes that could come from sediments or lateral sources entering the site. The relevant and appropriate AWQC for the protection of aquatic life are the acute and chronic marine water quality criteria (WQC).

[19] Washington State criteria include standards promulgated in WAC 173-201A and human health criteria consistent with the Washington Toxics Rule (40 CFR 131.45, as applied to Washington) and 40 CFR 131.36 (d)(14), including the 40 CFR 131 criteria updated on November 28, 2016. These criteria were updated after publication of the ROD.

[20] As discussed in the draft Work Plan, volatile organic compounds (VOCs) will not be analyzed in the water samples because these compounds are volatile and rarely detected in LDW surface water samples. VOCs are neither LDW contaminants of concern nor contaminants of potential concern for human health. In addition, two organophosphorus compounds and one carbamate pesticide (carbaryl) that have AWQC marine values will not analyzed because they are exclusively agricultural compounds that are rarely detected at concentrations above AWQC in water monitoring in agricultural areas (Tuttle et al. 2017).

lowest WQC are highlighted in Appendix C. The selected analytical methods are the most sensitive methods available for these analytes.

After the completion of sampling events in 2017 (e.g., the first three sampling events, including the first dry baseflow and the first two storm events [without significant dam releases]), the analyte list will be re-evaluated based on data from these events as well as historical water data from the LDW and East Waterway (Windward 2010; Windward and Anchor QEA 2014). If any analyte concentrations are below water quality ARARs[21] or are not detected (regardless of whether the method detection limit [MDL] for a non-detected contaminant is greater than the applicable criteria), a memorandum will be submitted to EPA proposing that these analytes be deleted from the analyte list for the remaining baseline sampling events and future long-term monitoring events associated with the ROD.[22]

4.4.2.2 Passive Samplers

The PE strips will be extracted and analyzed for PCB congeners following EPA method 1668c (Table 4-9). The sample handling and extraction protocols are provided in Appendix D. Prior to extraction, the PE strips will be cleaned with laboratory water or wipes to remove biofilm and weighed.

The lowest possible DLs for PCB congeners in surface water based on the results from the PE passive samplers will be calculated based on the laboratory analytical DLs for the PE strips, the partition coefficients between surface water and PE (from Gschwend et al. 2014), and equilibrium assumptions. Preliminary DLs calculated for each congener (assuming 100% equilibrium) are provided in Appendix C; however, these estimated DLs are likely too low and may be modified based on further analysis. Specifically, the more chlorinated PCB congeners will likely not achieve equilibrium. The actual DLs will be greater than those calculated for any PCB congener that does not reach equilibrium within the deployment period.

4.5 ANALYTICAL DATA QUALITY OBJECTIVE AND CRITERIA

The analytical DQO for composite-grab samples and passive sampler replicates is to develop and implement procedures that will ensure the collection of representative data of known, acceptable, and defensible quality. Parameters used to assess data quality are precision, accuracy, representativeness, comparability, completeness, and sensitivity. These parameters are discussed below, and specific DQIs for water and passive sampler replicates are presented in Section 4.5.6.

[21] Water quality ARARs are presented in Table C-5 of Appendix C.

[22] This approach is consistent with Section 13.2.3 of the ROD (EPA 2014b), which states that "following the first few sampling rounds, the surface water analyte list will be reduced to the contaminants that exceeded AWQC, NTR, or Washington WQS values."

4.5.1 Precision

Precision is the measure of reproducibility among individual measurements of the same property, usually under similar conditions, such as multiple measurements of the same sample. Precision is assessed by performing multiple analyses on a sample; it is expressed as a RPD when duplicate analyses are performed, and as a %RSD when more than two analyses are performed on the same sample (e.g., triplicates). Precision is assessed by laboratory duplicate analyses (e.g., duplicate samples, MSDs, and LCS duplicates) for all parameters. Precision measurements can be affected by the nearness of a chemical concentration to the DL, whereby the percent error (expressed as either %RSD or RPD) increases. The DQI for precision varies depending on the analyte (Section 4.5.6). The equations used to express precision are as follows:

$$RPD = \frac{(\text{measured conc} - \text{measured duplicate conc})}{(\text{measured conc} + \text{measured duplicate conc}) / 2} \times 100$$ **Equation 2a**

$$\%RSD = (SD/D_{ave}) \times 100$$

Where:

$$SD = \sqrt{\frac{\sum (D_n - D_{ave})^2}{(n-1)}}$$ **Equation 2b**

D = sample concentration
D_{ave} = average sample concentration
n = number of samples
SD = standard deviation

4.5.2 Accuracy

Accuracy is an expression of the degree to which a measured or computed value represents the true value. Accuracy may be expressed as a percentage recovery for MS and LCS analyses. The DQI for accuracy varies depending on the analyte (Section 4.5.6). The equation used to express accuracy for spiked samples is as follows:

$$\text{Percent recovery} = \frac{\text{spike sample result} - \text{unspiked sample result}}{\text{amount of spike added}} \times 100$$ **Equation 3**

4.5.3 Representativeness

Representativeness is an expression of the degree to which data accurately and precisely represent an environmental condition. The sampling approach was designed to address the specific objectives described in Section 2.1. Assuming those objectives are met, the samples collected should be considered adequately representative of the environmental conditions they are intended to characterize.

4.5.4 Comparability

Comparability is an expression of the confidence with which one dataset can be evaluated in relation to another dataset. Therefore, the sample collection and chemical and physical testing will adhere to the most recent Puget Sound Estuary Program (PSEP) QA / QC procedures (PSEP 1997) and EPA and Standard Methods (SM) analysis protocols.

4.5.5 Completeness

Completeness is a measure of the amount of data that is determined to be valid in proportion to the amount of data collected. The equation used to calculate completeness is as follows:

$$\text{Completeness} = \frac{\text{number of valid measurements}}{\text{total number of data points planned}} \times 100 \qquad \textbf{Equation 4}$$

The DQI for completeness for all components of this project is 90%. Data that have been qualified as estimated because the QC criteria were not met will be considered valid for the purpose of assessing completeness. Data that have been qualified as rejected will not be considered valid for the purpose of assessing completeness.

4.5.6 Sensitivity

Analytical sensitivity is the minimum concentration of an analyte above which a data user can be reasonably confident that the analyte was reliably detected and quantified. For this study, the MDL[23] will be used as the measure of sensitivity for each measurement process.

Tables 4-10 and 4-11 list specific DQIs for water quality measurements, laboratory analyses of composite-grab samples, and laboratory analyses of passive samplers.

[23] The term MDL includes other types of DLs such as estimated detection limit (EDL) values calculated for PCB congeners and dioxin / furan congeners. Recent revisions to EPA SW846 methods no longer require the calculation of MDLs.

Table 4-10. Data quality indicators for water quality measurements

Parameter	Precision[a]	Accuracy[b]	Completeness
Dissolved oxygen	± 20%	± 0.1 mg/L or 1% of reading	90%
pH	± 20%	± 0.2 pH unit	90%
Specific conductance	± 20%	± 0.5% of reading or 0.001 mS/cm	90%
Temperature	± 20%	± 0.05 °C	90%
Turbidity	± 20%	0 to 999 FNU: 0.3 FNU or ±2% of reading, (whichever is greater); 1000 to 4000 FNU: ±5% of reading	90%

Note: Water quality measurements will be made using a YSI© EXO1 or similar water quality meter.

[a] Precision is assessed by duplicate field measurements.

[b] Accuracy is as reported for YSI© EXO1 instrument specifications.

FNU – Formazin Nephelometric Unit

Table 4-11. Data quality indicators for laboratory analyses

Parameter[a]	Unit	Precision[b]	Accuracy[b]		Completeness
			SRM/LCS[c]	Spiked Samples	
TOC	mg/L	± 20%	80–120%	80–120%	90%
DOC	mg/L	± 20%	80–120%	80–120%	90%
TSS	mg/L	± 20%	90–110%	na	90%
Salinity	ppt	± 20%	90–110%	na	90%
Total and dissolved metals	µg/L	± 20%	75–125%	75–125%	90%
Inorganic arsenic	µg/L	± 35%	65–135%	65–135%	90%
Mercury	µg/L	± 25%	80–120%	71–125%	90%
TBT	µg/L	± 30%	30–160%	30–160%	90%
PAHs	µg/L	± 30%	30–160%	30–160%	90%
Phthalates	µg/L	± 30%	50–120%	50–120%	90%
Other SVOCs	µg/L	± 30%	10–160%	10–160%	90%
PCB congeners	µg/L	± 20%	60–135%	15–145%	90%
Dioxins/ furans	pg/L	± 20%	70–130%	17–130%	90%
Organochlorine pesticides	µg/L	± 30%	30–160%	30–160%	90%
Organophosphate pesticides	µg/L	± 30%	43–127%	43–127%	90%
Carbamate pesticides (Carbaryl)	µg/L	± 30%	70–130%	70–130%	90%

[a] Individual analytes are listed in Table 4-7.

[b] Values listed are performance-based limits provided by the laboratories.

[c] An LCS may be used to assess accuracy when SRM is unavailable. SRM will be analyzed for total and dissolved metals, mercury, and inorganic arsenic only.

DOC – dissolved organic carbon
LCS – laboratory control sample
na – not applicable
SRM – standard reference material
SVOC – semivolatile organic compound
TBT – tributyltin

PAH - polycyclic aromatic hydrocarbon
PCB – polychlorinated biphenyl
ppt – parts per thousand
TOC – total organic carbon
TSS – total suspended solids

Standard surface water volume requirements are specified to meet RLs for each particular analytical method. Table 4-9 summarizes the sample volume needed for each sample type.

Table 4-12. Sample volume required by analyte and laboratory

Analyte[a]	Sample Volume (L)	Sample Container
ARI		
TOC/DOC/salinity	0.5	500-mL amber glass
TBT	0.5	500- mL amber glass
TSS	2	2-L HDPE
PAHs	2	2-L amber glass
Organochlorine pesticides	2	4-L amber glass
Other SVOCs and phthalates	2	2-L amber glass
Brooks Applied Labs		2-L amber glass
Total and dissolved metals	0.25	two 125-mL HDPE (one total and one dissolved)
Inorganic arsenic	0.125	125-mL HDPE
Mercury	0.125	125-mL FLPE
Axys		
PCB congeners	2	4-L amber glass
Dioxins/furan congeners	2	
ALS[b]		
Organophosphate pesticides	4	4-L amber glass
Carbamate pesticides (Carbaryl)	0.040	
Total volume	**17.54 L**	**13 containers**

[a] Individual analytes are listed in Table 4-7.
[b] Samples for organophosphate pesticides and carbaryl will be collected only during the first storm event.

ALS – ALS Environmental-Kelso
ARI – Analytical Resources, Inc.
Axys – Axys Analytical Services, Ltd.
DOC – dissolved organic carbon
HDPE – high-density polyethylene
PAH – polycyclic aromatic hydrocarbon
PCB – polychlorinated biphenyl
SVOC – semivolatile organic compound
TBT – tributyltin
TOC – total organic carbon
TSS – total suspended solids

4.6 QUALITY ASSURANCE/QUALITY CONTROL

The types of samples analyzed and the procedures conducted for QA / QC in the field and laboratory are described in this section.

4.6.1 Field quality control samples

Field QA / QC samples, such as field duplicates and rinsate blanks, are generally used to evaluate the efficiency of field decontamination procedures and the variability attributable to sample handling. One equipment blank will be generated for each whole-water composite-grab sampling event. An additional Niskin bottle sampler will be used to collect a field duplicate composite sample at one sampling location and depth per sampling event.

A passive sampler field blank will be used to assess possible field contamination due to the high sorption capacity of the passive samplers. A field blank will be prepared at the same time and following the same methods as the passive samplers deployed in the LDW. It will be taken to the field and exposed to the atmosphere there for the duration of both the deployment and retrieval of the passive sampler replicates.

4.6.2 Laboratory quality control

Before analyzing the samples, the laboratory must provide written protocols for the analytical methods to be used, calculate RLs for each analyte in each matrix of interest as applicable, and establish an initial calibration curve for all analytes. The laboratory must also demonstrate its continued proficiency by participation in inter-laboratory comparison studies, and by repeated analysis of certified reference materials, calibration checks, laboratory reagent and rinsate blanks, and spiked samples.

4.6.2.1 Sample delivery group

Project- and / or method-specific QC measures, such as MSs and MSDs or laboratory duplicates, will be analyzed per sample delivery group (SDG) preparatory batch, or per analytical batch as specified in Table 4-13. A SDG is defined as no more than 20 samples or a group of samples received at the laboratory within a 2-week period. Although a SDG may span two weeks, all holding times specific to each analytical method will be met for each sample in the SDG.

Table 4-13. Laboratory quality control sample analysis summary

Analysis Type	Initial Calibration	Initial Calibration Verification (second source)	Continuing Calibration Verification	SRM or LCS[a]	Laboratory Replicates	MSs	MSDs	Method Blanks	Surrogate Spikes
TOC/DOC	prior to analysis	after initial calibration	every 10 samples	1 per prep batch[b]	1 per batch or SDG	1 per batch or SDG	na	1 per prep batch	na
TSS	na	na	na	1 per prep batch[b]	1 per batch or SDG	na	na	1 per prep batch	na
Salinity	prior to analysis	na	na	1 per prep batch[b]	1 per batch or SDG	na	na	1 per prep batch	na
Total and dissolved metals	prior to analysis	after initial calibration	every 10 samples	1 per prep batch[c]	1 per batch or SDG	1 per batch or SDG	1 per batch or SDG	1 per prep batch	na
Inorganic arsenic	prior to analysis	after initial calibration	every 10 samples	1 per prep batch[d]	1 per batch or SDG	1 per batch or SDG	1 per batch or SDG	1 per prep batch	na
Mercury	prior to analysis	after initial calibration	beginning and end of each batch	1 per prep batch[e]	na	1 per batch or SDG	1 per batch or SDG	3 per batch	na
TBT	prior to analysis	after initial calibration	every 10 samples	1 per prep batch[b]	na	1 per batch or SDG	1 per batch or SDG	1 per prep batch	each sample
PAHs	prior to analysis	after initial calibration	every 10–20 analyses or 12 hours	1 per prep batch[b]	na	1 per batch or SDG	1 per batch or SDG	1 per prep batch	each sample
Phthalates	prior to analysis	after initial calibration	every 10–20 analyses or 12 hours	1 per prep batch[b]	na	1 per batch or SDG	1 per batch or SDG	1 per prep batch	each sample
Other SVOCs	prior to analysis	after initial calibration	every 10–20 analyses or 12 hours	1 per prep batch[b]	na	1 per batch or SDG	1 per batch or SDG	1 per prep batch	each sample
PCB congeners	prior to analysis	after initial calibration	every 12 hours	1 per prep batch[b]	na	na	na	1 per prep batch	each sample
Dioxins/furans	prior to analysis	after initial calibration	every 12 hours	1 per prep batch[b]	na	na	na	1 per prep batch	each sample

Analysis Type	Initial Calibration	Initial Calibration Verification (second source)	Continuing Calibration Verification	SRM or LCS[a]	Laboratory Replicates	MSs	MSDs	Method Blanks	Surrogate Spikes
Pesticides (organochlorine and organophosphate)	prior to analysis	after initial calibration	every 10–20 analyses or 12 hours	1 per prep batch[b]	na	1 per batch or SDG	1 per batch or SDG	1 per prep batch	each sample
Carbamate pesticides (carbaryl)	prior to analysis	after initial calibration	every 10–20 analyses or 12 hours	1 per prep batch	na	1 per batch or SDG	1 per batch or SDG	1 per prep batch	each sample

Note: A batch is a group of samples of the same matrix analyzed or prepared at the same time, not exceeding 20 samples.

[a] An LCS may be used to assess accuracy when SRM is unavailable.

[b] An LCS will be used to assess accuracy.

[c] NIST 1640a or NIST 1643f will be used to assess accuracy for total and dissolved metals.

[d] TMDA 70.2 will be used to assess accuracy for inorganic arsenic.

[e] NIST 1641d will be used to assess accuracy for mercury.

DOC – dissolved organic carbon
LCS – laboratory control sample
MS – matrix spike
MSD – matrix spike duplicate
na – not applicable or not available
NIST – National Institute of Standards and Technology
PAH – polycyclic aromatic hydrocarbon
PCB – polychlorinated biphenyl
SDG – sample delivery group
SRM – standard reference material
SVOC – semivolatile organic compound
TBT – tributyltin
TOC – total organic carbon
TSS – total suspended solids

4.6.2.2 Laboratory quality control samples

The analyst will review the results of QC analyses from each sample group immediately after a sample group has been analyzed. The QC sample results will then be evaluated to determine whether control limits have been exceeded.

If control limits have been exceeded, then appropriate corrective action, such as recalibration followed by reprocessing of the affected samples, must be initiated before a subsequent group of samples is processed. The project QA / QC coordinator must be contacted immediately by the laboratory PM if satisfactory corrective action to achieve the DQIs outlined in this QAPP is not possible. All laboratory corrective action reports relevant to the analysis of project samples must be included in the data deliverable packages.

All primary chemical standards and standard solutions used in this project will be traceable to the National Institute of Standards and Technology (NIST), Environmental Resource Associates, National Research Council of Canada, or other documented, reliable, commercial sources. Standards will be validated to determine their accuracy by comparing them to independent standards. Laboratory QC standards are verified in a multitude of ways: second-source calibration verifications (i.e., same standard, two different vendors) are analyzed to verify initial calibrations; new working standard mixes (e.g., calibrations, spikes, etc.) are verified against the results of the original solution and must be within 10% of the true value; or newly purchased standards are verified against current data. Any impurities found in the standard will be documented.

The following sections summarize the procedures that will be used to assess data quality throughout sample analysis. Table 4-13 summarizes the QC procedures to be performed by the laboratory, as well as the associated control limits for precision and accuracy.

Method Blanks

Method blanks are analyzed to assess possible laboratory contamination at all stages of sample preparation and analysis. A minimum of 1 method blank will be analyzed for each SDG or for every 20 samples, whichever is more frequent.

Axys has reported increased concentrations of PCB 11 in its method blank samples for the past year. The laboratory is actively working to resolve this issue and is monitoring the situation closely. In order to ensure the accuracy of the data, blank correction will be employed for PCB 11 on all samples.[24] The blank correction will be based on the mean PCB 11 concentrations in water laboratory method blanks for the three months preceding the analysis of the samples.

[24] If the increased concentrations of PCB 11 are resolved, then the blank correction will not be required. EPA will be consulted before any changes are made.

Standard Reference Material

SRMs are samples of similar matrices and known analyte concentrations, processed through the entire analytical procedure and used as an indicator of method accuracy. A minimum of 1 SRM will be analyzed for each SDG or for every 20 samples, whichever is more frequent. SRMs will be analyzed for total and dissolved metals, mercury, and inorganic arsenic. An LCS sample can be used to assess accuracy if appropriate SRM is not available. An LCS will be analyzed for conventional and organic analyses.

Laboratory Control Samples

LCSs are prepared from a clean matrix using the same process as the project samples that are spiked with known amounts of the target compounds. The recoveries of the compounds are used as a measure of the accuracy of the test methods.

Laboratory Replicate Samples

Laboratory replicate samples provide information on the precision of the analysis, and are useful in assessing potential sample heterogeneity and matrix effects. Laboratory replicates are subsamples of the original sample that are prepared and analyzed as a separate sample, assuming sufficient sample matrix is available. A minimum of 1 laboratory replicate sample will be analyzed for each SDG or for every 20 samples, whichever is more frequent, for inorganic and conventional parameters.

Matrix Spikes and Matrix Spike Duplicates

The analysis of MS samples provides information on the extraction efficiency of the method on the sample matrix. By performing MSD analyses, information on the precision of the method is also provided for organic analyses. For organic analyses, a minimum of 1 MS/MSD pair will be analyzed for each SDG or for every 20 samples, whichever is more frequent, when sufficient sample volume is available, with the exception of PCB congeners and dioxins/furans. For inorganic analyses (i.e., metals), a minimum of one MS sample will be analyzed for each SDG, when sufficient sample volume is available.

Surrogate Spikes

All project samples analyzed for organic compounds will be spiked with appropriate surrogate compounds as defined in the analytical methods. Surrogate recoveries will be reported by the laboratories; however, no sample results will be corrected for recovery using these values.

Isotope Dilution Quantitation

All project samples analyzed for PCB and dioxin/furan congeners will be spiked with a known amount of surrogate compounds, as defined in the analytical methods. The labeled surrogate compounds will respond similarly to the effects of extraction, concentration, and gas chromatography. Data will be corrected for the recovery of the surrogates used for quantification.

Internal Standard Spikes

Internal standards may be used for calibrating and quantifying organic compounds and metals using MSs. If internal standards are required by the method, all calibration, QC, and project samples will be spiked with the same concentration of the selected internal standard(s). Internal standard recoveries and retention times must be within method and/or laboratory criteria.

Performance Reference Compounds

PRCs are used to determine the degree to which passive samplers have come to equilibrium during the period of deployment. The PE strips will be loaded with carbon-13 (C^{13})-labelled PCBs prior to deployment. The carbon-13-labelled PCBs to be used for PRCs will include ^{13}C-PCB8, ^{13}C-PCB28, ^{13}C-PCB95, ^{13}C-PCB111, ^{13}C-PCB153 and ^{13}C-PCB178. The change in PRC concentration during deployment will be used to help quantify the non-equilibrium conditions between the surface water and the PE for various PCB congeners.

PRC Day-zero Blank

Day-zero test samples will be set aside and analyzed to confirm PRC concentrations. These samples will be stored, frozen, at the laboratory and analyzed with the passive sampler replicates to measure PRC concentrations. PRC concentrations in the day-zero blanks will be used to establish pre-deployment PRC concentrations, which will be necessary to determine the fraction of PRC lost from each sampler during deployment. The change in PRC concentration during deployment will be used to quantify non-equilibrium conditions, as described in Section 3.4.

4.7 INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

Prior to each field event, measures will be taken to test, inspect, and maintain all field equipment. All equipment used, including the multi-parameter water quality meter, differential global positioning system (GPS) unit, and digital camera, will be tested for accuracy before leaving for the field event.

The FC will be responsible for overseeing the testing, inspection, and maintenance of all field equipment. The laboratory PM will be responsible for ensuring laboratory equipment testing, inspection, and maintenance requirements are met. The methods used in calibrating the analytical instrumentation are described in the following section.

4.8 INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY

Multipoint initial calibration will be performed on each analytical instrument at the start of the project, after each major interruption to the instrument, and when any continuing calibration does not meet the specified criteria. The number of points used in the initial calibration is defined in each analytical method. Continuing calibrations will be performed daily for organic analyses, every 10 samples for inorganic analyses, and

with every sample batch for conventional parameters to ensure proper instrument performance.

Gel permeation chromatography (GPC) calibration verifications will be performed at least once every seven days, and corresponding raw data will be submitted by the laboratory with the data package. In addition, florisil performance checks will be performed for every florisil lot, and the resulting raw data will be submitted with the data package.

Calibration of analytical equipment used for chemical analyses includes the use of instrument blanks or continuing calibration blanks, which provide information on the stability of the baseline established. Continuing calibration blanks will be analyzed immediately after the continuing calibration verification, at a frequency of 1 blank for every 10 samples analyzed for inorganic analyses and 1 blank every 12 hours for organic analyses. If the continuing calibration does not meet the specified criteria, the analysis must stop. Analysis may resume after corrective actions have been taken to meet the method specifications. All project samples analyzed by an instrument found to be out of compliance must be reanalyzed.

The multi-parameter water quality meter will be used to collect *in situ* water quality data (e.g., conductivity, temperature, dissolved oxygen, pH), and turbidity at each sampling location and associated with each composite sample, as outlined in this QAPP. All sensors, except temperature, require calibration to ensure high performance. The meter will be calibrated daily to ensure that the sensors meet the manufacturer's accuracy specifications for conductivity, dissolved oxygen, pH, and turbidity.

A Trimble© SPS461 or similar GPS receiver unit will be employed for the various sampling methods outlined in this QAPP. The GPS receiver will be calibrated daily to ensure that it is accurately recording positions from known benchmarks and functioning within the individual unit's factory specifications.

4.9 INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

The FC will gather and check field supplies daily for satisfactory conditions before each field event. Batteries used in the digital camera will be checked daily and recharged as necessary. Supplies and consumables for the field sampling effort will be inspected upon delivery and accepted if the condition of the supplies is satisfactory.

4.10 DATA MANAGEMENT

All field data will be recorded on field forms, which the FC will check for missing information at the end of each field day and amend as necessary. A QC check will be done to ensure that all data have been transferred accurately from the field forms to the database. Field forms will be archived in the Windward library.

The analytical laboratories are required to submit data in an electronic format, as described in Section 3.7.2. The laboratory PM will contact the project QA / QC coordinator prior to data delivery to discuss specific format requirements.

A library of routines will be used to translate typical electronic output from laboratory analytical systems and to generate data analysis reports. The use of automated routines will ensure that all data are consistently converted to the desired data structures, and that operator time is kept to a minimum. In addition, routines and methods for quality checks will be used to ensure such translations are correctly applied.

Written documentation will be used to clarify how field and analytical laboratory duplicates and QA/QC samples were recorded in the data tables, and to provide explanations of other issues that may arise. The data management task will include keeping accurate records of field and laboratory QA/QC samples so that project team members who use the data will have appropriate documentation. All data management files will be secured on the Windward network. Data management procedures outlined in Appendix C of the Work Plan will be followed (Windward and Integral 2017).

5 Assessment and Oversight

5.1 Compliance Assessments and Response Actions

EPA or its designees may observe field activities during each sampling event, as needed. If situations arise wherein there is a significant inability to follow the QAPP methods precisely, the Windward PM will determine the appropriate actions and consult EPA (or its designee).

5.1.1 Compliance assessments

Laboratory and field performance assessments will consist of on-site reviews conducted by EPA of QA systems and equipment for sampling, calibration, and measurement. EPA personnel may conduct a laboratory audit prior to sample analysis. Any pertinent laboratory audit reports will be made available to the project QA/QC coordinator upon request. Analytical laboratories will be required to have written procedures addressing internal QA/QC. All laboratories and QA/QC coordinators will be required to ensure that all personnel engaged in sampling and analysis tasks have appropriate training.

5.1.2 Response actions for field sampling

The FC, or a designee, will be responsible for correcting equipment malfunctions throughout field sampling, and for resolving situations in the field that may result in nonconformance or noncompliance with this QAPP. All corrective measures will be immediately documented in the field logbook, and protocol modification forms will be completed.

5.1.3 Corrective action for laboratory analyses

Analytical laboratories will be required to comply with their current written SOPs, laboratory QA plan, and analytical methods. All laboratory personnel will be responsible for reporting problems that may compromise the quality of the data. The analysts will identify and correct any anomalies before continuing with sample analysis. The laboratory PMs will be responsible for ensuring that appropriate corrective actions are initiated as required for conformance with this QAPP.

The project QA/QC coordinator will be notified immediately if any QC sample exceeds the DQIs outlined in this QAPP (Table 4-11) and the exceedance cannot be resolved through standard corrective action procedures. A description of the anomaly, the steps taken to identify and correct the anomaly, and the treatment of the relevant sample batch (i.e., recalculation, reanalysis, and re-extraction) will be submitted with the data package using the case narrative or corrective action form.

5.2 REPORTS TO MANAGEMENT

The FC will prepare a summary email for submittal to LDWG and EPA following each sampling day. The project QA / QC coordinator will also prepare progress reports for submittal by email to LDWG and EPA on the following occasions: 1) after sampling has been completed and samples have been submitted for analysis, 2) when information is received from the laboratory, and 3) when analyses are complete. The status of the samples and analyses will be indicated, with emphasis on any deviations from this QAPP. A data report will be written after validated data are available, as described in Section 2.2.

6 Data Validation and Usability

6.1 DATA VALIDATION

The data validation process will begin in the laboratory with the review and evaluation of data by supervisory personnel or QA specialists. The laboratory analyst will be responsible for ensuring that the analytical data are correct and complete, that appropriate procedures have been followed, and that QC results are within acceptable limits. The project QA / QC coordinator will be responsible for ensuring that all analyses performed by the laboratories are correct, properly documented, and complete, and that they satisfy the project DQOs specified in this QAPP.

Data will not be considered final until validated. Data validation will be conducted following EPA guidance (EPA 2016a, b, 2014a).

Independent third-party data review and summary validation of the analytical chemistry data will be conducted by Ecochem or a suitable alternative. All data will undergo validation and a minimum of 10% or one SDG will undergo full data validation. Full data validation parameters will include:

- QC analysis frequencies
- Analysis holding times
- Laboratory blank contamination
- Instrument calibration
- Surrogate recoveries
- LCS recoveries
- MS recoveries
- MS / MSD RPDs
- Compound identifications—verification of raw data with the reported results (10% of analytes)
- Compound quantitations—verification of calculations and RLs (10% of analytes)
- Instrument performance check (tune) ion abundances
- Internal standard areas and retention time shifts

If no discrepancies are found between reported results and raw data in the dataset that undergoes full data validation, then a summary validation of the rest of the data can proceed using all of the QC forms submitted in the laboratory data package. QA review of the surface water chemistry data will be performed in accordance with the QA requirements of the project, the technical specifications of the analytical methods indicated in Table 4-11, and EPA guidance for organic and inorganic data review (EPA

2016a, b). The EPA PM may have EPA peer review the third-party validation or perform data assessment / validation on a percentage of the data.

All discrepancies and requests for additional, corrected data will be discussed with the laboratories prior to issuance of the formal data validation report. The project QA / QC coordinator should be informed of all contacts with the laboratories during data validation. Review procedures used and findings made during data validation will be documented on worksheets. The data validator will prepare a data validation report that will summarize QC results, qualifiers, and possible data limitations. This data validation report will be appended to the surface water data report. Only validated data with appropriate qualifiers will be released for general use.

6.2 RECONCILIATION WITH DATA QUALITY OBJECTIVES

Data QA will be conducted by the project QA / QC coordinator in accordance with EPA guidelines (EPA 2016a, b). The results of the third-party independent review and validation will be reviewed, and cases wherein the project DQOs were not met will be identified. The usability of the data will be determined in terms of the magnitude of the DQO exceedance.

7 References

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Harbor I.

Harbor I.

L. Washington

LDW-SW1

Slip 1

LDW-PS2

Slip 2

Slip 3

Slip 4

LDW-PS1

LDW-SW2

Slip 6

Upper Turning Basin

1st Ave S Bridge

16th Ave Bridge

0 1 2 Miles

0 1 2 Kilometers

GR-SW1

- Baseline surface water sampling location
- Baseline upstream reference location
- Baseline passive sampler location
- Early Action Area
- LDW Superfund Boundary
- Road
- Navigation Channel
- River mile

Note: If consent for access to LDW-PS2 location cannot be obtained, one or more alternate locations will be proposed in a technical memorandum for EPA approval.

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N

0 0.25 0.5 Miles

0 0.5 1 Kilometers

Map 4-1. Baseline surface water sampling locations

Prepared by mikey, 8/3/2017; W:\Projects\Duwamish AOC3\GIS\Maps and Analyses\Task 03 QAPPs\Surface Water\Map 4-1 6522 Surface water sampling plan.mxd

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BASELINE SURFACE WATER COLLECTION AND CHEMICAL ANALYSES - QUALITY ASSURANCE PROJECT PLAN: APPENDIX A: HEALTH AND SAFETY PLAN

FINAL

Prepared for

Lower Duwamish Waterway Group

For submittal to

US Environmental Protection Agency

Prepared by:

Windward environmental LLC

200 West Mercer Street, Suite 401 s Seattle, Washington s 98119

HEALTH AND SAFETY PLAN

Title and Approval Page: LDW Surface Water Sampling Health and Safety Plan

By their signature, the undersigned certify that this health and safety plan is approved and that it will be used to govern health and safety aspects of fieldwork described in the quality assurance project plan to which it is attached.

Name Project Manager	Date
Name Corporate Health and Safety Manager	Date
Name Field Coordinator/Health and Safety Officer	Date

Table of Contents

Tables

Maps

Acronyms

CFR	Code of Federal Regulations
CPR	cardiopulmonary resuscitation
FC	field coordinator
HSM	health and safety manager
HSO	health and safety officer
HSP	health and safety plan
LDW	Lower Duwamish Waterway
MSDS	material safety data sheets
OSHA	Occupational Safety and Health Administration
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PFD	personal flotation device
PM	project manager
PPE	personal protective equipment
QAPP	quality assurance project plan
TBT	tributyltin
TCDD	tetrachlorodibenzo-*p*-dioxin
USCG	US Coast Guard
Windward	Windward Environmental LLC

1 Introduction

This site-specific health and safety plan (HSP) describes safe working practices for conducting field activities at potentially hazardous sites and for handling potentially hazardous materials / waste products. This HSP covers elements specified in 29 Code of Federal Regulations (CFR) 1910§120. The procedures and guidelines contained herein are based on generally recognized health and safety practices. Any changes or revisions to this HSP will be made by a written amendment that will become a permanent part of this document. The goal of this HSP is to establish procedures for safe working practices for all field personnel and visitors.

This HSP addresses all activities associated with the collection and handling of surface water samples from the Lower Duwamish Waterway (LDW) for chemical analyses. During site work, this HSP is to be implemented by the field coordinator (FC), who is also the designated site health and safety officer (HSO), in cooperation with the Windward Environmental LLC (Windward) health and safety manager (HSM) and the Windward project manager (PM).

All personnel involved in fieldwork on this project are required to comply with this HSP. The contents of this HSP reflect anticipation of the types of activities to be performed, knowledge of the physical characteristics of the site, and consideration of preliminary chemical data from previous investigations at the site. This HSP may be revised based on new information and / or changed conditions during site activities. Revisions will be documented in the project records.

2 Site Description and Project Scope

2.1 SITE DESCRIPTION

The sampling area is in the LDW (see Map 4-1 in the quality assurance project plan [QAPP]). The QAPP to which this HSP is appended provides complete details of the sampling program. This section summarizes the types of work that will be performed during field activities.

2.2 SCOPE OF WORK

Specific tasks to be performed are as follows:

- Collection of surface water samples from a boat and from a bridge using a 5 L Niskin bottle sampler
- Deployment and retrieval of passive samplers
- Sample handling, processing, and shipping

Additional details on sampling design and methods are provided in Section 4 of the QAPP.

3 Health and Safety Personnel

Key health and safety personnel and their responsibilities are described below. These individuals are responsible for the implementation of this HSP; they will be responsible for informing all individuals who are assigned to work on the site, or who visit the site, of the contents of this plan, and for ensuring that each person signs the Health and Safety Plan Acknowledgment Form (Attachment 1). By signing the Health and Safety Plan Acknowledgment Form, individuals recognize the site health and safety hazards, known or suspected, and agree to adhere to the protocols required to minimize exposure to such hazards.

Project Manager: The PM will have overall responsibility for the successful outcome of the project. The PM will ensure that adequate resources and budget are provided for the health and safety staff to carry out their responsibilities during fieldwork. In consultation with the HSM, the PM will make final decisions concerning implementation of the HSP.

Field Coordinator/Health and Safety Officer: Because of the limited scope and duration of fieldwork for this project, the FC and HSO will be the same person. The FC / HSO will direct field sampling activities, coordinate the technical components of the field program with health and safety components, and ensure that work is performed according to the QAPP.

The FC / HSO will implement this HSP at the work location, and will be responsible for all health and safety activities and the delegation of duties to a health and safety technician in the field, if appropriate. The FC / HSO will also have stop-work authority, to be used if there is an imminent safety hazard or potentially dangerous situation. The FC / HSO or his designee will be present during sampling and operations.

Corporate Health and Safety Manager: The HSM will have overall responsibility for preparation, approval, and revisions of this HSP. The HSM will not necessarily be present during fieldwork, but will be readily available, if required, for consultation regarding health and safety issues during fieldwork.

Field Crew: All field crew members must be familiar and comply with the information in this HSP. They will also have the responsibility to report any potentially unsafe or hazardous conditions to the FC / HSO immediately.

4 Hazard Evaluation and Control Measures

This section covers potential physical and chemical hazards that may be associated with the proposed project activities, and presents control measures for addressing these hazards. The activity hazard analysis, Section 4.3, lists the potential hazards associated with each site activity and the recommended site control to be used to minimize each potential hazard.

Confined space entry will not be necessary for this project. Therefore, hazards associated with this activity are not discussed in this HSP.

4.1 PHYSICAL HAZARDS

For this project, it is anticipated that physical hazards will present a greater risk of injury than chemical hazards. Physical hazards are identified and discussed below.

4.1.1 Slips, trips, and falls

As with all field work, caution should be exercised to prevent slips on slick surfaces. In particular, sampling from a boat or other floating platform requires careful attention to minimize the risk of falling down or overboard. The same care should be used in rainy conditions or on the shoreline where slick rocks are found. Slips can be minimized by wearing boots with good tread, made of material that does not become overly slippery when wet.

Trips are always a hazard on the uneven deck of a boat, in a cluttered work area, or in the intertidal zone where uneven substrate is common. Personnel will keep work areas as free as possible from items that interfere with walking.

Falls may be avoided by working as far from exposed edges as possible, by erecting railings, and by using fall protection when working on elevated platforms. For this project, open hatches may present a fall hazard, so hatches will remain closed when not being accessed for storage. Personnel should be aware of the area around any open hatches and use extra caution when accessing them.

4.1.2 Sampling equipment deployment

A Niskin sampler will be used to collect surface water samples and passive samplers will be deployed, as described in Section 4.2.2 of the QAPP. Before sampling activities begin, there will be a training session for all field personnel for the equipment that will be onboard the sampling vessel.

4.1.3 Falling overboard

Sampling activities will be conducted from a boat or a bridge. As with any work from a floating platform, there is a chance of falling overboard. US Coast Guard-approved Type II or III personal flotation devices (PFDs) will be worn while working on the deck of the boat.

4.1.4 Manual lifting

Equipment and samples must be lifted and carried. Back strain can result if lifting is done improperly. During any manual handling tasks, personnel should lift with the load supported by their legs and not their backs. For heavy loads, an adequate number of people will be used, or if possible, a mechanical lifting / handling device will be used.

4.1.5 Heat stress

Heat stress could be an issue during summer. Heat-related problems include heat rash, heat cramps, heat exhaustion, and heat stroke if the person does not ingest sufficient fluids. Heat rash can occur when sweat is not allowed to evaporate, leaving the skin wet most of the time and making it subject to irritation. Heat cramps are painful spasms of the muscles from excessive salt loss associated with sweating. Excessive sweating can also lead to heat exhaustion, resulting in moist, clammy skin. Physical signs and symptoms of heat exhaustion include headache, nausea, vertigo, weakness, thirst, and giddiness. Heat exhaustion may progress to heat stroke if a worker is unable to cool and re-hydrate his or her body. The primary signs and symptoms of heat stroke are confusion, irrational behavior, loss of consciousness, convulsions, a lack of sweating, hot dry skin, and an abnormally high body temperature. Workers should be aware of the key differences between the signs and symptoms of heat stroke and those of heat exhaustion, such as the lack of sweating, the color of the skin (red), and the rise in body temperature associated with the former. Heat stroke is a medical emergency that requires immediate medical attention.

A person exhibiting any of the signs of heat stress should be removed from the work area to a shaded area. Immediate steps that can be taken to reduce the symptoms include using a fan or soaking with water to increase cooling and promote evaporation, rehydrating with electrolyte replacement fluids, and removing outer layers of clothing.

4.1.6 Hypothermia or frostbite

Hypothermia occurs when the body's core temperature falls below 95°F. The sampling may occur during the time of year when cold and wet weather conditions prevail, making hypothermia a concern. Hypothermia is also a risk when someone becomes wet from falling overboard. The FC / HSO will monitor all crew members for early symptoms of hypothermia (e.g., shivering, muscle incoordination, mild confusion). If such symptoms are observed, the FC / HSO will take immediate steps to reduce heat loss by providing extra layers of clothing, or by temporarily moving the affected crew member to a warmer environment.

All personnel will wear protective clothing appropriate for the weather conditions and physical activity. A person exhibiting any of the signs of hypothermia should be removed from the work area to a warmer environment. Immediate steps that can be taken to reduce the symptoms of hypothermia include minimizing exposure to cold and wet conditions, limiting sitting or standing still for long periods, rehydration with

warm fluids, and the removal of any wet outer layers of clothing to permit sweat evaporation during rest periods in a warm environment.

Sampling operations and conditions that might result in the occurrence of frostbite are not anticipated. The sampling will take place when extreme cold weather conditions are not expected to occur.

4.1.7 Weather

In general, field team members will be equipped for the normal range of weather conditions. The FC / HSO will be aware of current weather conditions, and of the potential for those conditions to pose a hazard to the field crew. Some conditions that might force work stoppage are electrical storms, high winds, or high waves resulting from winds.

4.1.8 Vessel traffic

Because of the high volume of vessel traffic on the LDW, precautions and safe boating practices will be implemented to ensure that the field boat does not interrupt such traffic. As practical, the field boat will stay out of the navigation channel.

4.2 CHEMICAL HAZARDS

Previous investigations have shown that some chemicals are present at higher-than-background concentrations in the sampling area. For the purposes of discussing the potential exposure of individuals to chemicals in sediments, the chemicals of concern are metals, tributyltin, petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs). Care will also be exercised with adding chemical preservatives used for some analytes.

4.2.1 Exposure routes

Potential routes of chemical exposure include inhalation, dermal contact, and ingestion. Exposure will be minimized by using safe work practices and by wearing the appropriate personal protective equipment (PPE). Further discussion of PPE requirements is presented in Section 7.

4.2.1.1 Inhalation

Inhalation is a route of exposure primarily for chemicals used to decontaminate sampling equipment; such chemicals are only to be used in open, well-ventilated areas.

4.2.1.2 Dermal exposure

Dermal exposure to hazardous substances associated with sediments, surface water, or equipment decontamination will be controlled by the use of PPE, and by adherence to detailed sampling and decontamination procedures.

4.2.1.3 Ingestion

Incidental ingestion of sediment or surface water is not considered a major route of exposure for this project. Accidental ingestion of surface water is possible. However, careful handling of equipment and containers while onboard the boat should prevent water from splashing or spilling during sample collection and handling activities.

4.2.2 Description of chemical hazards

4.2.2.1 Metals and tributyltin

Exposure to metals may occur via ingestion or skin contact. As mentioned above, neither is a likely exposure route. Metal fumes or metal-contaminated dust will not be encountered during field and sample handling activities. Momentary skin contact allows little, if any, opportunity for metals to pass into the body. Field procedures require immediate washing of water or sediments from exposed skin.

4.2.2.2 Petroleum hydrocarbons and polycyclic aromatic hydrocarbons

Exposure to petroleum hydrocarbons and PAHs may occur via ingestion or skin contact. Inhalation, the most important human health exposure pathway for this group of chemicals, is not expected to occur at this site. Animal studies have also shown that PAHs can have harmful effects on the skin, body fluids, and the ability to fight disease after both short- and long-term exposure, but these effects have not been observed in humans. Some PAHs may reasonably be expected to be carcinogens. However, large amounts of water would need to be ingested for any detrimental effects to occur. Momentary skin contact allows little, if any, opportunity for compounds to pass into the body. Field procedures require immediate washing of sediments from exposed skin.

4.2.2.3 Polychlorinated biphenyls

Prolonged skin contact with PCBs may cause acne-like symptoms known as chloracne. Irritation to eyes, nose, and throat may also occur. Acute and chronic exposure can damage the liver and cause symptoms of edema, jaundice, anorexia, nausea, abdominal pains, and fatigue. PCBs are a suspected human carcinogen. Skin absorption may contribute substantially to the uptake of PCBs. Large amounts of water would need to be ingested for any detrimental effects to occur. Momentary skin contact allows little, if any, opportunity for compounds to pass into the body. Field procedures require immediate washing of water or sediments from exposed skin.

4.2.2.4 Dioxins/furans

Prolonged skin contact with dioxins/furans may cause acne-like symptoms known as chloracne. Other effects on the skin, such as red skin rashes, have been reported to occur in people following exposure to high concentrations of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). Acute and chronic exposure can damage the liver, increase the risk of diabetes and abnormal glucose tolerance, and possibly increase the risk for reproductive and developmental effects. 2,3,7,8-TCDD is a possible

human carcinogen, and a mixture of dioxins/furans with six chlorine atoms (four of the six chlorine atoms at the 2-, 3-, 7-, and 8-positions) is a probable human carcinogen. Skin absorption may substantially contribute to the uptake of dioxins/furans. Large amounts of water would need to be ingested for any detrimental effects to occur. Momentary skin contact allows little, if any, opportunity for the passage of any of the compounds into the body. Field procedures require the immediate washing of water or sediments from exposed skin.

4.2.2.5 Chemicals used for sampling equipment decontamination

As described in Section 4.3.4 of the QAPP, nitric acid and methanol will be used for sampling equipment decontamination prior to each sampling event. Personnel are required to wear protective gloves and eye protection whenever handling these decontamination agents. These chemicals are to be used in open, well-ventilated areas only, away from any source of ignition (e.g., power generator). Material safety data sheets (MSDS) describing the toxicological effects of these chemicals will be available for reference during field decontamination activities. In addition, all containers of hazardous materials will be clearly labeled, ideally using the original manufacturer's label. Such labels will also need to be applied to any transfer bottles that are used.

4.3 ACTIVITY HAZARD ANALYSIS

The activity hazard analysis summarizes the field activities to be performed during the project, outlines the hazards associated with each activity, and presents controls that can reduce or eliminate the risk of the hazard occurring.

Table A-1 presents the activity hazard analysis for surface water sampling from a boat.

Table A-1. Activity hazard analysis

Activity	Hazard	Control
Sampling from a boat	falling overboard	Use care in boarding/departing from the vessel. Deploy and recover the sampling equipment from the back deck of the boat. Wear a PFD.
	skin contact with contaminated sediments or liquids	Wear modified Level D PPE.
	back strain	Use appropriate lifting technique when deploying and retrieving sampling devices, or seek help.
	overhead hazards	Use caution and be aware of overhead and gear hazards such as frames and doors. Wear a hard hat and modified Level D PPE when working on deck if overhead hazards are present.
	open hatches	Keep hatches closed when not being accessed. Be aware around hatch area and use caution when entering/exiting hatch.
	heat stress	Monitor crew members for signs/symptoms of heat stress. Remove person to cool area and remove extra layers of clothing. Promote evaporative cooling and rehydrate with electrolytic fluids.

Activity	Hazard	Control
	hypothermia	Monitor crew members for signs/symptoms of hypothermia. Minimize prolonged exposure to wet and cold conditions. Remove person to warm area and remove wet clothing. Rehydrate with warm fluids.
Sampling from a bridge	falling over	Use care when deploying and retrieving equipment from the bridge.
	back strain	Use appropriate lifting technique when deploying and retrieving sampling devices, or seek help.
	golf balls	Wear a hard hat for head protection, and a bright, reflective safety vest to increase visibility.
	vehicle traffic	Use caution and be aware of vehicle activity when crossing the maintenance yard or parking area at Foster Golf Links.
	heat stress	Monitor crew members for signs/symptoms of heat stress. Remove person to cool area and remove extra layers of clothing. Promote evaporative cooling and rehydrate with electrolytic fluids.
	hypothermia	Monitor crew members for signs/symptoms of hypothermia. Minimize prolonged exposure to cold and wet conditions. Remove person to warm area and remove wet clothing. Rehydrate with warm fluids.
Passive sampler deployment and retrieval[a]	sharp edges of mesh envelopes	Take care when handing passive samplers to avoid sharp edges of mesh envelopes.

[a] Hazards related to sampling from a boat are also applicable.

PFD – personal flotation device

PPE – personal protective equipment

5 Work Zones and Shipboard Access Control

During sampling and sample handling activities, work zones will be established to identify where sample collection and processing are actively occurring. The intent of the zones is to limit the migration of sample material out of its zone, and to restrict unauthorized access to active work areas by defining work zone boundaries.

5.1 WORK ZONE

A work zone will encompass the area where sample collection and handling activities are being performed. The FC / HSO will delineate the work zone as a particular area onboard the collection vessel. Only persons with appropriate training, PPE, and authorization from the FC / HSO will be allowed to enter the work zone while work is in progress.

5.2 DECONTAMINATION STATION

A decontamination station where personnel will clean soiled boots and / or PPE prior to leaving the work zone will be set up for LDW locations. The station will have the buckets, brushes, soapy water, rinse water, or wipes necessary to clean boots, PPE, or other equipment leaving the work zone. Plastic bags will be provided for expendable and disposable materials. If the sampling location does not allow for the establishment of a decontamination station, the FC / HSO will provide alternatives to prevent the spread of contamination.

Decontamination of the boat will be completed at the end of each work day. Cockpit and crew areas will be rinsed down with water to minimize the accumulation of sediment.

5.3 ACCESS CONTROL

Security and control of access to the boat will be the responsibility of the FC / HSO and boat captain. Boat access will be granted to necessary project personnel and authorized visitors only. Any security or access control problems will be reported to the client or appropriate authorities.

6 Safe Work Practices

Following common sense will minimize the risk of exposure or accidents at a work site. The following general safety rules will be adhered to on-site:

- Do not climb over or under obstacles of questionable stability.
- Do not eat, drink, smoke, or perform other hand-to-mouth transfers in the work zone.
- Work only in well-lighted spaces.
- Never enter a confined space without the proper training, permits, and equipment.
- Make eye contact with equipment operators when moving within the range of their equipment.
- Be aware of the movements of shipboard equipment when not in the operator's range of vision.
- Get immediate first aid for all cuts, scratches, abrasions, or other minor injuries.
- Use the established sampling and decontamination procedures.
- Always use the buddy system.
- Be alert to your own and other workers' physical conditions.
- Report all accidents, no matter how minor, to the FC / HSO.
- Do not do anything dangerous or unwise even if ordered by a supervisor.

7 Personal Protective Equipment and Safety Equipment

Appropriate PPE will be worn as protection against potential hazards. In addition, a PFD will be required when working onboard the boat. Prior to donning PPE, the field crew will inspect their PPE for any defects that might render the equipment ineffective.

Fieldwork will be conducted in Level D or modified Level D PPE, as discussed in Sections 7.1 and 7.2. Situations requiring PPE beyond modified Level D are not anticipated. Should the FC / HSO determine that PPE beyond modified Level D is necessary, the HSM will be notified and an alternative selected.

New personnel or visitors will be informed of PPE requirements during their initial site briefing (see Section 3).

7.1 Level D Personal Protective Equipment

Workers performing general activities during which skin contact with contaminated materials is unlikely will wear Level D PPE. Level D PPE includes the following:

- Cotton overalls or lab coats
- Chemical-resistant steel-toed boots
- Chemical-resistant gloves
- Safety glasses

7.2 Modified Level D Personal Protective Equipment

Workers performing activities during which skin contact with contaminated materials is possible, and during which inhalation risks are not expected, will be required to wear an impermeable outer suit. The type of outerwear will be chosen according to the types of chemical contaminants that might be encountered. Modified Level D PPE includes the following:

- Impermeable outer garb such as rain gear
- Waterproof and chemical-resistant steel-toed boots
- Chemical-resistant outer gloves
- Hard hats
- Bright, reflective safety vest

7.3 Safety Equipment

In addition to PPE that will be worn by shipboard personnel, basic emergency and first aid equipment will be provided. Equipment for the field team will include:

- A copy of this HSP

- A first aid kit adequate for the number of personnel
- Emergency eyewash
- Sunscreen

The FC / HSO will ensure that the safety equipment is onboard. Equipment will be checked daily to ensure its readiness for use.

8 Monitoring Procedures for Site Activities

A monitoring program that addresses the potential site hazards will be maintained. For this project, air, dust, and noise monitoring will not be necessary. No volatile organic compounds have been identified among the expected contaminants, the sampled media will be wet and will not pose a dust hazard, and none of the equipment will emit high-amplitude (> 85 dBA) sound. For this project, the monitoring program will consist of all workers monitoring themselves and their co-workers for signs that might indicate physical stress or illness.

All personnel will be instructed to look for and inform each other of any deleterious changes in their physical or mental condition during the performance of all field activities. Examples of such changes are as follows:

- Headaches
- Dizziness
- Nausea
- Symptoms of heat stress
- Blurred vision
- Cramps
- Irritation of eyes, skin, or respiratory system
- Changes in complexion or skin color
- Changes in apparent motor coordination
- Increased frequency of minor mistakes
- Excessive salivation or changes in papillary response
- Changes in speech ability or speech pattern
- Shivering
- Blue lips or fingernails

If personnel develop any of these conditions, work will be halted immediately and the affected person(s) evaluated. If further assistance is needed, personnel at the local hospital will be notified, and an ambulance will be summoned if the condition is thought to be serious. If the condition is the direct result of sample collection or handling activities, procedures will be modified to address the problem.

9 Decontamination

Decontamination is necessary to prevent the migration of contaminants from the work zone(s) into the surrounding environment, and to minimize the risk of exposure of personnel to contaminated materials that might adhere to PPE. The following sections discuss personnel and equipment decontamination. The following supplies will be available to perform decontamination activities:

- Wash buckets
- Rinse buckets
- Long-handled scrub brushes
- Clean water sprayers
- Paper towels
- Plastic garbage bags
- Alconox® or similar decontamination solution

9.1 MINIMIZATION OF CONTAMINATION

The first step in addressing contamination is to prevent or minimize exposure to existing contaminated materials and the spread of those materials. During field activities, the FC / HSO will enforce the following measures:

Personnel:

- Do not walk through areas of obvious or known contamination.
- Do not handle, touch, or smell contaminated materials directly.
- Make sure PPE has no cuts or tears prior to use.
- Fasten all closures on outer clothing, covering with tape if necessary.
- Protect and cover any skin injuries.
- Stay upwind of airborne dusts and vapors.
- Do not eat, drink, chew tobacco, or smoke in the work zones.

Sampling equipment and boat:

- Place clean equipment on a plastic sheet or aluminum foil to avoid direct contact with contaminated media.
- Keep contaminated equipment and tools separate from clean equipment and tools.
- Clean boots before entering the boat.

9.2 PERSONNEL DECONTAMINATION

The FC / HSO will ensure that all site personnel are familiar with personnel decontamination procedures. Personnel will perform the following decontamination procedures, as appropriate, before eating lunch, taking a break, or leaving the work location:

1. If outer suit is heavily soiled, rinse it off.
2. Wash and rinse outer gloves and boots with water.
3. Remove outer gloves; inspect and discard if damaged.
4. Wash hands.

Before returning to work, personnel will re-don all necessary PPE. If leaving for the day, personnel will dispose of soiled, expendable PPE.

9.3 SAMPLING EQUIPMENT DECONTAMINATION

Sampling equipment will be decontaminated, as described in Section 4.3.4 of the QAPP, to minimize sample contamination and worker exposure to contamination from samples. The following practices will be followed:

- All sampling equipment used directly in collecting surface water samples (e.g., Niskin bottle sampler) will be scrubbed with Alconox® detergent, rinsed with nitric acid, rinsed with methanol, and rinsed with deionized water before use.
- Ice chests will be scrubbed with Alconox® detergent and rinsed with deionized water prior to any sampling activities.
- Wet ice used for sample storage during field activities will be contained in separate plastic bags, and samples will be placed in resealable, waterproof plastic bags to avoid contamination from melting ice.
- Sampling equipment will be free from contaminants such as oils, grease, and fuels.

10 Disposal of Contaminated Materials

Contaminated materials that may be generated during field activities include PPE and excess sample material. These contaminated materials will be disposed of as an integral part of the project.

10.1 Personal Protective Equipment

Gross surface contamination will be removed from PPE. All disposable sampling materials and PPE—such as disposable coveralls, gloves, and paper towels used in sample processing—will be placed in heavyweight garbage bags. Filled garbage bags will be placed in a normal refuse container for disposal as solid waste.

10.2 Excess Sample Materials

At each sampling location, excess surface water collected for the composite-grab samples will be returned to the river.

11 Training Requirements

Individuals performing work at locations where potentially hazardous materials and conditions may be encountered must meet specific training requirements. It is not anticipated that hazardous concentrations of contaminants will be encountered in sampled material, so training will consist of site-specific instruction for all personnel and oversight of inexperienced personnel by an experienced person for one working day. The following sections describe the training requirements for this fieldwork.

11.1 PROJECT-SPECIFIC TRAINING

In addition to HAZWOPER training, as described in Section 3.6 of the QAPP, field personnel will undergo training specifically for this project. All personnel and visitors must read this HSP and be familiar with its contents before beginning work or providing oversight. They must acknowledge reading the HSP by signing the HSP review form in Attachment 1. The signed form will be kept in the project files.

The boat captain and FC / HSO will also be required to have the US Coast Guard (USCG) Auxiliary Boating Safety certification. The boat captain or a designee will provide project-specific training prior to the first day of fieldwork and whenever new workers arrive. Field personnel will not be allowed to begin work until project-specific training has been completed and documented by the FC / HSO. Training will address the HSP and all health and safety issues and procedures pertinent to field operations. Training will include, but not be limited to, the following topics:

- Activities with the potential for exposure to chemicals
- Activities that pose physical hazards, and actions to control the hazards
- Ship access control and procedures
- Use and limitations of PPE
- Decontamination procedures
- Emergency procedures
- Use and hazards of sampling equipment
- Location of emergency equipment on the vessel
- Vessel safety practices
- Vessel evacuation and emergency procedures

11.2 DAILY SAFETY BRIEFINGS

The FC / HSO or a designee and the boat captain will present safety briefings before the start of each day's activities. These safety briefings will outline the activities expected for the day, update work practices and hazards, address any specific concerns

associated with the work location, and review emergency procedures and routes. The FC / HSO or designee will document all safety briefings in the logbook.

11.3 FIRST AID AND CPR

At least two members of the field team must have first aid and cardiopulmonary resuscitation (CPR) training. Documentation of which individuals possess first aid and CPR training will be kept in the project health and safety files.

12 Medical Surveillance

A medical surveillance program conforming to the provisions of 29 CFR 1910§120(f) is not necessary for field team members on this project, because they do not meet any of the following four criteria outlined in the regulations for implementation of a medical surveillance program:

- Employees who are or may be exposed to hazardous substances or health hazards at or above permissible exposure levels for 30 days or more per year (1910.120(f)(2)(I).
- Employees who must wear a respirator for 30 days or more per year (1910.120(f)(2)(ii)).
- Employees who are injured or become ill as a result of possible overexposures involving hazardous substances or health hazards from an emergency response or hazardous waste operation (1910.120(f)(2)(iii)).
- Employees who are members of HAZMAT teams (1910.120(f)(2)(iv)).

As described in Section 8, employees will monitor themselves and each other for any deleterious changes in their physical or mental conditions during the performance of all field activities.

13 Reporting and Record Keeping

Each member of the field crew will sign the HSP review form (Attachment 1). If necessary, accident/incident report forms and Occupational Safety and Health Administration (OSHA) Form 200s will be completed by the FC/HSO.

The FC/HSO or a designee will maintain a health and safety field logbook with records of health- and safety-related details for the project. Alternatively, entries may be made in the field logbook, in which case a separate health and safety logbook will not be required. The logbook must be bound and the pages must be numbered consecutively. Entries will be made with indelible blue ink. At a minimum, each day's entries must include the following information:

- Project name or location
- Names of all personnel onboard
- Weather conditions
- Type of fieldwork being performed

The person maintaining the entries will initial and date the bottom of each completed page. Blank space at the bottom of an incompletely filled page will be lined out. Each day's entries will begin on the first blank page after the previous workday's entries.

14 Emergency Response Plan

As a result of the hazards onboard the sampling vessels and the conditions under which operations will be conducted, the potential exists for an emergency situation to occur. Emergencies may include personal injury, exposure to hazardous substances, fire, explosion, or release of toxic or non-toxic substances (spills). OSHA regulations require that an emergency response plan be available for use onboard to guide actions in emergency situations.

Onshore organizations will be relied upon to respond to emergency situations. Given the location of the site, the local fire department and ambulance service can provide timely response. Field personnel will be responsible for identifying an emergency situation, providing first aid if applicable, notifying the appropriate personnel or agency, and evacuating any hazardous area. Shipboard personnel will attempt to control only very minor hazards that could present an emergency situation, such as a small fire; otherwise, all personnel will rely on outside emergency response resources.

The following sections identify the onboard individual(s) who should be notified in case of emergency, provide a list of emergency telephone numbers, offer guidance for particular types of emergencies, and provide directions and a map for getting from any sampling location to a hospital.

14.1 Pre-emergency Preparation

Before the start of field activities, the FC / HSO will ensure that preparation has been made in anticipation of emergencies. Preparatory actions include the following:

- Meeting between the FC / HSO and equipment handlers concerning emergency procedures in the event that a person is injured
- A training session given by the FC / HSO informing all field personnel of emergency procedures, locations of emergency equipment and its uses, and proper evacuation procedures
- A training session given by senior staff on operating field equipment to apprise field personnel of operating procedures and specific risks associated with that equipment
- Ensuring that field personnel are aware of the existence of the emergency response plan in the HSP, and ensuring that a copy of the HSP accompanies the field team

14.2 Project Emergency Coordinator

The FC / HSO will serve as the project emergency coordinator in the event of an emergency. He will designate his replacement during those times when he is not onboard or is not serving as the project emergency coordinator; the designation will be

noted in the logbook. The project emergency coordinator will be notified immediately when an emergency is recognized. The project emergency coordinator will be responsible for evaluating the emergency situation, notifying the appropriate emergency response units, coordinating access with those units, and directing interim actions onboard before the arrival of emergency response units. The project emergency coordinator will notify the HSM and the Windward PM as soon as possible after initiating an emergency response action. The Windward PM will have responsibility for notifying the client.

14.3 EMERGENCY RESPONSE CONTACTS

All onboard personnel must know whom to notify in the event of an emergency situation, even though the FC / HSO has primary responsibility for notification. Table A-2 lists the names and phone numbers for emergency response services and individuals.

Table A-2. Emergency response contacts

Contact	Telephone Number
Emergency Numbers	
Ambulance	911
Police	911
Fire	911
Harborview Medical Center	206.323.3074
Emergency Responders	
US Coast Guard Emergency General information	206.286.5400 206.442.5295 UHF Channel 16
National Response Center	800.424.8802
US Environmental Protection Agency	800.424.8802
Washington State Department of Ecology – Northwest Region Spill Response (24-hour emergency line)	206.649.7000
Emergency Contacts	
Windward Project Manager	
Kathy Godtfredsen	206.812.5413
Windward Corporate Health and Safety Manager	
Susan McGroddy	206.812.5421
Field Coordinator/ Field Health and Safety Officer	
Thai Do	206.812.5407

14.4 RECOGNITION OF EMERGENCY SITUATIONS

Emergency situations will generally be recognizable by observation. An injury or illness will be considered an emergency if it requires treatment by a medical professional and cannot be treated with simple first aid techniques.

14.5 DECONTAMINATION

In the case of evacuation, decontamination procedures will be performed only if doing so does not further jeopardize the welfare of site workers. If an injured individual is also heavily contaminated and must be transported by emergency vehicle, the emergency response team will be informed of the type of contamination. To the extent possible, contaminated PPE will be removed from the injured individual, but only if doing so does not exacerbate the injury. Plastic sheeting will be used to reduce the potential for spreading contamination to the inside of the emergency vehicle.

14.6 FIRE

Field personnel will attempt to control only small fires, should they occur. If an explosion appears likely, personnel will follow evacuation procedures specified during the training session. If a fire cannot be controlled with the onboard fire extinguisher that is part of the required safety equipment, personnel will either withdraw from the vicinity of the fire or evacuate the boat as specified in the training session.

14.7 PERSONAL INJURY

In the event of serious personal injury, including unconsciousness, possibility of broken bones, severe bleeding or blood loss, burns, shock, or trauma, the first responder will immediately do the following:

- Designate an individual to call 911 and administer first aid, if qualified.
- If not qualified, seek out an individual who is qualified to administer first aid, if time and conditions permit.
- Notify the project emergency coordinator of the incident, the name of the injured individual(s), the location of the individual, and the nature of the injury.

The project emergency coordinator will immediately do the following:

- Notify the boat captain and the appropriate emergency response organization.
- Assist the injured individual(s).
- Follow the emergency procedures for retrieving or disposing of equipment reviewed in the training session, and leave the site en route to the predetermined land-based emergency pickup.
- Designate someone to accompany the injured individual to the hospital.
- If a life-threatening emergency occurs (i.e., injury where death is imminent without immediate treatment), the FC / HSO or boat captain will call 911 and arrange to meet the ambulance unit at the nearest accessible dock.

- If a non-life-threatening emergency occurs (i.e., broken bones, minor lacerations, etc.), the project emergency coordinator will follow the procedures outlined above and proceed to the Harbor Island Marina, or to an alternative location of his choice if that would be more expedient.
- Notify the HSM and the PM.

If the project emergency coordinator determines that an emergency response is not necessary, he may direct someone to decontaminate and transport the individual by vehicle to the nearest hospital. Directions showing the route to the hospital are in Section 14.11.

If a worker leaves the boat to seek medical attention, another worker should accompany him to the hospital. When in doubt about the severity of an injury or exposure, always seek medical attention as a conservative approach, and notify the project emergency coordinator.

The project emergency coordinator will be responsible for completing all accident/incident field reports, OSHA Form 200s, and other required follow-up forms.

14.8 Overt Personal Exposure or Injury

If an overt exposure to toxic materials occurs, the first responder to the victim will initiate actions to address the situation. The following actions should be taken, depending on the type of exposure.

14.8.1 Skin contact

- Wash/rinse the affected area thoroughly with copious amounts of soap and water.
- If eye contact has occurred, rinse the eyes for at least 15 minutes using the eyewash that is part of the onboard emergency equipment.
- After initial response actions have been taken, seek appropriate medical attention.

14.8.2 Inhalation

- Move victim to fresh air.
- Seek appropriate medical attention.

14.8.3 Ingestion

- Seek appropriate medical attention.

14.8.4 Puncture wound or laceration

- Seek appropriate medical attention.

14.9 SPILLS AND SPILL CONTAINMENT

No bulk chemicals or other materials subject to spillage are expected to be used during this project. Accordingly, no spill containment procedure is required for this project.

14.10 BOATING HAZARDS

Emergency responses to boating hazards are described in Table A-3.

Table A-3. Potential boat emergency hazards and responses

Potential Emergency Hazard	Response
Fire or explosion	If manageable, attempt to put out a small fire with a fire extinguisher. Otherwise, call the USCG or 911, evacuate the area (by life rafts, rescue boat, or swimming), and meet at a designated location. The HSO will take roll call to make sure everyone has evacuated safely. Emergency meeting locations will be determined in the field during the daily safety briefings.
Medical emergency/ personal injury	At least two people with current first aid and CPR training will be onboard the vessel at all times. This person will attempt to assess the nature and critical path of the injury, call 911 immediately, and apply first aid/CPR if necessary. Stop work and wait for medical personnel to arrive. Fill out a site accident report.
Falling into an open hatch	Stop work and rescue the person, if safe and necessary. Assess the nature of the injury, and follow the response for medical emergency/personal injury.
Person overboard	Immediately throw a life ring to the person in the water. Have one onboard person keep an eye on the victim and shout the distance (boat lengths) and direction (o'clock) of the victim from the vessel. Stop work and use the vessel to retrieve the person in the water.
Sinking vessel	Call the USCG immediately. If possible, wait for a rescue boat to arrive to evacuate vessel personnel. See fire/explosion section (above) for emergency evacuation procedures. The HSO will take roll call to make sure everyone has evacuated safely.
Hydraulic oil spill or leak	If the leak/spill is small, immediately apply absorbent pads to control the leak and continue work. If the leak/spill is uncontainable, stop work, call 911 immediately, and wait for assistance. The vessel operator will assess the personal safety hazard associated with the leak/spill and begin evacuation procedures if necessary.
Lack of visibility	If navigation visibility or personal safety is compromised because of smoke, fog, or other unanticipated hazards, stop work immediately. The vessel operator and HSO will assess the hazard and, if necessary, send out periodic horn blasts to notify other vessels potentially in the area of the sampling vessel's location. Move to a secure location (i.e., berth) and wait for visibility to clear.
Loss of power	Stop work and call the USCG for assistance. Vessel personnel should watch for potential collision hazards and notify vessel operator if hazards exist. Secure vessel to a berth, dock, or mooring as soon as possible.
Collision	Stop work and call the USCG for assistance. HSO and vessel operator will assess damage and potential hazards. If necessary, vessel will be evacuated and secured until repairs can be made.

CPR – cardiopulmonary resuscitation
HSO – health and safety officer
USCG – US Coast Guard

14.11 EMERGENCY ROUTES TO THE HOSPITAL

The name, address, and telephone number of the hospital that will be used to provide medical care is as follows:

Harborview Medical Center
325 - 9th Avenue
Seattle, WA
206.323.3074

Directions from the vicinity of the LDW to Harborview Medical Center are as follows (Map 1):

From the 1st Avenue South boat launch:

- Drive east on South River Street.
- Turn left on Occidental Avenue South.
- Turn left on East Marginal Way South.
- Turn right on South Michigan Street.
- Look for entrance ramps to I-5 Northbound.
- Drive north on I-5.
- Take the James Street exit.
- Drive east on James Street to 9th Avenue.
- Turn right on 9th Avenue.
- Emergency entrance will be two blocks south on the right.

From Harbor Island Marina:

- From marina parking lot, turn sharp right onto Klickitat Way Southwest.
- Turn slight right onto Southwest Spokane Street
- Turn slight left to take the ramp toward WA-99 N/I-5/Columbian Way.
- Keep left at the fork in the ramp.
- Stay straight to go onto West Seattle Bridge.
- Merge onto I-5 North via the ramp on the left.
- Take the James Street exit.
- Head east on James Street to 9th Avenue.
- Turn right on 9th Avenue.
- Emergency entrance will be two blocks south on the right.

From South Park Marina:

- From marina parking lot, turn right onto Dallas Avenue South.
- Turn right onto 16th Avenue South.
- Turn left on East Marginal Way South.
- Look for entrance ramps to I-5 Northbound.
- Drive north on I-5.
- Take the James Street exit.
- Drive east on James Street to 9th Avenue.
- Turn right on 9th Avenue.
- Emergency entrance will be two blocks south on the right.

From Foster Golf Links:

- From parking lot, turn right onto Interurban Avenue South.
- Turn right onto I-5 Northbound ramp.
- Drive north on I-5.
- Take the James Street exit.
- Drive east on James Street to 9th Avenue.
- Turn right on 9th Avenue.
- Emergency entrance will be two blocks south on the right.

Map 1. Emergency routes to Harborview Medical Center

Attachment 1. Health and Safety Plan Acknowledgment Form

I have read a copy of the Health and Safety Plan (HSP), which covers field activities that will be conducted to investigate potentially contaminated areas in the Lower Duwamish Waterway (LDW). I understand the health and safety requirements of the project, which are detailed in this HSP.

Signature	Date
Signature	Date
Signature	Date
Signature	Date
Signature	Date
Signature	Date
Signature	Date
Signature	Date
Signature	Date
Signature	Date
Signature	Date
Signature	Date
Signature	Date

APPENDIX B. FIELD FORMS

- Surface Water Collection Form
- Protocol Modification Form

SURFACE WATER COLLECTION FORM

Project Name: ______________________________ **Task no.:** ____________________

Date: __________ **Time:** __________ **WW crew:** ____________________

Weather: ______________________________ **Other crew:** ____________________

Latitude (y): __________ **Longitude (x):** __________ **Tide:** ____flood ____ebb ___slack

Location ID: ______________________________ **Bottom depth:** ________m

Sample ID:		**Sample time:**
***In situ* measurements**		**Sample collection depth**
Temp: _____________˚C	DO: _______________mg/L	___ U: Upper (1m below surface)
Conductivity: ________µS/cm	pH: _______________	___ M: Mid-depth (_______m)
		___ L: Lower (1m above bottom)
Notes (i.e., other water quality characteristics, presence of sheen, odor, field duplicate)**:**		

Sample ID:		**Sample time:**
***In situ* measurements**		**Sample collection depth**
Temp: _____________˚C	DO: _______________mg/L	___ U: Upper (1m below surface)
Conductivity: ________µS/cm	pH: _______________	___ M: Mid-depth (_______m)
		___ L: Lower (1m above bottom)
Notes (i.e., other water quality characteristics, presence of sheen, odor, field duplicate)**:**		

Sample ID:		**Sample time:**
***In situ* measurements**		**Sample collection depth**
Temp: _____________˚C	DO: _______________mg/L	___ U: Upper (1m below surface)
Conductivity: ________µS/cm	pH: _______________	___ M: Mid-depth (_______m)
		___ L: Lower (1m above bottom)
Notes (i.e., other water quality characteristics, presence of sheen, odor, field duplicate)**:**		

Sample ID:		**Sample time:**
***In situ* measurements**		**Sample collection depth**
Temp: _____________˚C	DO: _______________mg/L	___ U: Upper (1m below surface)
Conductivity: ________µS/cm	pH: _______________	___ M: Mid-depth (_______m)
		___ L: Lower (1m above bottom)
Notes (i.e., other water quality characteristics, presence of sheen, odor, field duplicate)**:**		

PROTOCOL MODIFICATION FORM

Project Name/Task Number: _____

Material to be Sampled: _____

Measurement Parameter: _____

Standard Procedure for Field Collection & Laboratory Analysis (cite reference):

Reason for Change in Field Procedure or Analysis Variation: _____

Variation from Field or Analytical Procedure: _____

Special Equipment, Materials or Personnel Required: _____

Initiator's Name: _____ Date: _____

Project Manager: _____ Date: _____

QA Manager: _____ Date: _____

APPENDIX C. ANALYTICAL METHODS AND REPORTING LIMITS

Tables

Table C-1. Methods and RL goals for conventional analyses

Analyte	Matrix	Method	Unit	RL
Salinity	surface water	SM 2520 B-00	ppt	0.1
TSS	surface water	SM 2540 D-97	mg/L	1.0
TOC	surface water	SM 5310 B-00	mg/L	0.500
DOC	surface water	SM 5310 B-00	mg/L	0.500

DOC – dissolved organic carbon
ppt – parts per thousand
RL – reporting limit
SM – Standard Methods
TOC – total organic carbon
TSS – total suspended solids

Table C-2. Methods and RL goals for water analytes that are components of sums

Analyte	Method	Units	MDL[a]	RL[b]
Chlordanes				
alpha-Chlordane	EPA 8081B	µg/L	0.00820	0.025
cis-Nonachlor	EPA 8081B	µg/L	0.0950	0.050
gamma-Chlordane	EPA 8081B	µg/L	0.00820	0.02
Oxychlordane	EPA 8081B	µg/L	0.0356	0.050
trans-Nonachlor	EPA 8081B	µg/L	0.00860	0.050

[a] SW846 no longer requires MDL values. The laboratories have the option to use these values to assess sensitivity for EPA 8000 series methods. ARI has continued to maintain MDL studies for these analytes.

[b] RL values are consistent with the LLOQ values required under EPA SW846

ARI – Analytical Resources, Inc.

EPA – US Environmental Protection Agency

LLOQ – lower limit of quantification

MDL – method detection limit

RL – reporting limit

Table C-3. RL goals for PCB congeners

Analyte	EPA Method 1668C			
	Water (pg/L) Based on a 1-L sample		Passive Sampling (pg/sample) Based on 1 PE strip	
	EDL[a]	LMCL[b]	EDL[a]	LMCL[b]
PCB-1	1.0	4.0	1.0	4.0
PCB-2	1.0	4.0	1.0	4.0
PCB-3	1.0	4.0	1.0	4.0
PCB-4	2.0	4.0	2.0	4.0
PCB-5	2.0	4.0	2.0	4.0
PCB-6	2.0	4.0	2.0	4.0
PCB-7	2.0	4.0	2.0	4.0
PCB-8	2.0	4.0	2.0	4.0
PCB-9	2.0	4.0	2.0	4.0
PCB-10	2.0	4.0	2.0	4.0
PCB-11	2.0	4.0	2.0	4.0
PCB-12/13	2.0	4.0	2.0	4.0
PCB-14	2.0	4.0	2.0	4.0
PCB-15	2.0	4.0	2.0	4.0
PCB-16	1.0	4.0	1.0	4.0
PCB-17	1.0	4.0	1.0	4.0
PCB-19	1.0	4.0	1.0	4.0
PCB-21/33	1.0	4.0	1.0	4.0
PCB-22	1.0	4.0	1.0	4.0
PCB-23	1.0	4.0	1.0	4.0
PCB-24	1.0	4.0	1.0	4.0
PCB-25	1.0	4.0	1.0	4.0
PCB-26/29	1.0	4.0	1.0	4.0
PCB-27	1.0	4.0	1.0	4.0
PCB-28/20	1.0	4.0	1.0	4.0
PCB-30/18	1.0	4.0	1.0	4.0
PCB-31	1.0	4.0	1.0	4.0
PCB-32	1.0	4.0	1.0	4.0
PCB-34	1.0	4.0	1.0	4.0
PCB-35	1.0	4.0	1.0	4.0
PCB-36	1.0	4.0	1.0	4.0
PCB-37	1.0	4.0	1.0	4.0

Table C-3. RL goals for PCB congeners

Analyte	EPA Method 1668C			
	Water (pg/L) Based on a 1-L sample		Passive Sampling (pg/sample) Based on 1 PE strip	
	EDL[a]	LMCL[b]	EDL[a]	LMCL[b]
PCB-38	1.0	4.0	1.0	4.0
PCB-39	1.0	4.0	1.0	4.0
PCB-41/40/71	1.0	4.0	1.0	4.0
PCB-42	1.0	4.0	1.0	4.0
PCB-43	1.0	4.0	1.0	4.0
PCB-44/47/65	1.0	4.0	1.0	4.0
PCB-45/51	1.0	4.0	1.0	4.0
PCB-46	1.0	4.0	1.0	4.0
PCB-48	1.0	4.0	1.0	4.0
PCB-50/53	1.0	4.0	1.0	4.0
PCB-52	1.0	4.0	1.0	4.0
PCB-54	1.0	4.0	1.0	4.0
PCB-55	1.0	4.0	1.0	4.0
PCB-56	1.0	4.0	1.0	4.0
PCB-57	1.0	4.0	1.0	4.0
PCB-58	1.0	4.0	1.0	4.0
PCB-59/62/75	1.0	4.0	1.0	4.0
PCB-60	1.0	4.0	1.0	4.0
PCB-61/70/74/76	1.0	4.0	1.0	4.0
PCB-63	1.0	4.0	1.0	4.0
PCB-64	1.0	4.0	1.0	4.0
PCB-66	1.0	4.0	1.0	4.0
PCB-67	1.0	4.0	1.0	4.0
PCB-68	1.0	4.0	1.0	4.0
PCB-69/49	1.0	4.0	1.0	4.0
PCB-72	1.0	4.0	1.0	4.0
PCB-73	1.0	4.0	1.0	4.0
PCB-77	1.0	4.0	1.0	4.0
PCB-78	1.0	4.0	1.0	4.0
PCB-79	1.0	4.0	1.0	4.0
PCB-80	1.0	4.0	1.0	4.0
PCB-81	1.0	4.0	1.0	4.0
PCB-82	1.0	4.0	1.0	4.0

Table C-3. RL goals for PCB congeners

Analyte	EPA Method 1668C			
	Water (pg/L) Based on a 1-L sample		Passive Sampling (pg/sample) Based on 1 PE strip	
	EDL[a]	LMCL[b]	EDL[a]	LMCL[b]
PCB-83/99	1.0	4.0	1.0	4.0
PCB-84	1.0	4.0	1.0	4.0
PCB-88/91	1.0	4.0	1.0	4.0
PCB-89	1.0	4.0	1.0	4.0
PCB-92	1.0	4.0	1.0	4.0
PCB-94	1.0	4.0	1.0	4.0
PCB-95/100/93/102/98	1.0	4.0	1.0	4.0
PCB-96	1.0	4.0	1.0	4.0
PCB-103	1.0	4.0	1.0	4.0
PCB-104	1.0	4.0	1.0	4.0
PCB-105	1.0	4.0	1.0	4.0
PCB-106	1.0	4.0	1.0	4.0
PCB-108/124	1.0	4.0	1.0	4.0
PCB-109/119/86/97/125/87	1.0	4.0	1.0	4.0
PCB-107	1.0	4.0	1.0	4.0
PCB-110/115	1.0	4.0	1.0	4.0
PCB-111	1.0	4.0	1.0	4.0
PCB-112	1.0	4.0	1.0	4.0
PCB-113/90/101	1.0	4.0	1.0	4.0
PCB-114	1.0	4.0	1.0	4.0
PCB-117/116/85	1.0	4.0	1.0	4.0
PCB-118	1.0	4.0	1.0	4.0
PCB-120	1.0	4.0	1.0	4.0
PCB-121	1.0	4.0	1.0	4.0
PCB-122	1.0	4.0	1.0	4.0
PCB-123	1.0	4.0	1.0	4.0
PCB-126	1.0	4.0	1.0	4.0
PCB-127	1.0	4.0	1.0	4.0
PCB-128/166	1.0	4.0	1.0	4.0
PCB-130	1.0	4.0	1.0	4.0
PCB-131	1.0	4.0	1.0	4.0
PCB-132	1.0	4.0	1.0	4.0
PCB-133	1.0	4.0	1.0	4.0

Table C-3. RL goals for PCB congeners

Analyte	EPA Method 1668C			
	Water (pg/L) Based on a 1-L sample		Passive Sampling (pg/sample) Based on 1 PE strip	
	EDL[a]	LMCL[b]	EDL[a]	LMCL[b]
PCB-134/143	1.0	4.0	1.0	4.0
PCB-136	1.0	4.0	1.0	4.0
PCB-137	1.0	4.0	1.0	4.0
PCB-138/163/129/160	1.0	4.0	1.0	4.0
PCB-139/140	1.0	4.0	1.0	4.0
PCB-141	1.0	4.0	1.0	4.0
PCB-142	1.0	4.0	1.0	4.0
PCB-144	1.0	4.0	1.0	4.0
PCB-145	1.0	4.0	1.0	4.0
PCB-146	1.0	4.0	1.0	4.0
PCB-147/149	1.0	4.0	1.0	4.0
PCB-148	1.0	4.0	1.0	4.0
PCB-150	1.0	4.0	1.0	4.0
PCB-151/135/154	1.0	4.0	1.0	4.0
PCB-152	1.0	4.0	1.0	4.0
PCB-153/168	1.0	4.0	1.0	4.0
PCB-155	1.0	4.0	1.0	4.0
PCB-156/157	1.0	4.0	1.0	8.0
PCB-158	1.0	4.0	1.0	4.0
PCB-159	1.0	4.0	1.0	4.0
PCB-161	1.0	4.0	1.0	4.0
PCB-162	1.0	4.0	1.0	4.0
PCB-164	1.0	4.0	1.0	4.0
PCB-165	1.0	4.0	1.0	4.0
PCB-167	1.0	4.0	1.0	4.0
PCB-169	1.0	4.0	1.0	4.0
PCB-170	1.0	4.0	1.0	4.0
PCB-171/173	1.0	4.0	1.0	4.0
PCB-172	1.0	4.0	1.0	4.0
PCB-174	1.0	4.0	1.0	4.0
PCB-175	1.0	4.0	1.0	4.0
PCB-176	1.0	4.0	1.0	4.0
PCB-177	1.0	4.0	1.0	4.0

Table C-3. RL goals for PCB congeners

Analyte	EPA Method 1668C			
	Water (pg/L) Based on a 1-L sample		Passive Sampling (pg/sample) Based on 1 PE strip	
	EDL[a]	LMCL[b]	EDL[a]	LMCL[b]
PCB-178	1.0	4.0	1.0	4.0
PCB-179	1.0	4.0	1.0	4.0
PCB-180/193	1.0	4.0	1.0	4.0
PCB-181	1.0	4.0	1.0	4.0
PCB-182	1.0	4.0	1.0	4.0
PCB-183/185	1.0	4.0	1.0	4.0
PCB-184	1.0	4.0	1.0	4.0
PCB-186	1.0	4.0	1.0	4.0
PCB-187	1.0	4.0	1.0	4.0
PCB-188	1.0	4.0	1.0	4.0
PCB-189	1.0	4.0	1.0	4.0
PCB-190	1.0	4.0	1.0	4.0
PCB-191	1.0	4.0	1.0	4.0
PCB-192	1.0	4.0	1.0	4.0
PCB-194	1.0	4.0	1.0	4.0
PCB-195	1.0	4.0	1.0	4.0
PCB-196	1.0	4.0	1.0	4.0
PCB-197/200	1.0	4.0	1.0	4.0
PCB-198/199	1.0	4.0	1.0	4.0
PCB-201	1.0	4.0	1.0	4.0
PCB-202	1.0	4.0	1.0	4.0
PCB-203	1.0	4.0	1.0	4.0
PCB-204	1.0	4.0	1.0	4.0
PCB-205	1.0	4.0	1.0	4.0
PCB-206	1.0	4.0	1.0	4.0
PCB-207	1.0	4.0	1.0	4.0
PCB-208	1.0	4.0	1.0	4.0
PCB-209	1.0	4.0	1.0	4.0

[a] EDL is a sample-specific DL. The value provided here is an estimate, and the sample-specific values will vary based on sample mass and the analytical conditions at the time of analysis.

[b] LMCL is Axys's lowest calibration limit. Detected values below the LMCL are J-qualified. The reported LMCL will be adjusted based on the volume or mass of each sample.

Axys – Axys Analytical Services Ltd.
DL – detection limit
EDL – estimated detection limit
EPA – US Environmental Protection Agency
J – estimated concentration
LMCL – lower method calibration limit
PCB – polychlorinated biphenyl
PE - polyethylene
RL – reporting limit

Table C-4. RL goals for dioxin/furan congeners

Analyte	EPA Method 1613B Water (pg/L) Based on a 1-L sample	
	EDL[a]	LMCL[b]
2,3,7,8-TCDD	0.50	2.0
1,2,3,7,8-PeCDD	0.50	10.0
1,2,3,4,7,8-HxCDD	0.50	10.0
1,2,3,6,7,8-HxCDD	0.50	10.0
1,2,3,7,8,9-HxCDD	0.50	10.0
1,2,3,4,6,7,8-HpCDD	0.50	10.0
OCDD	0.50	20.0
2,3,7,8-TCDF	0.50	2.0
1,2,3,7,8-PeCDF	0.50	10.0
2,3,4,7,8-PeCDF	0.50	10.0
1,2,3,4,7,8-HxCDF	0.50	10.0
1,2,3,6,7,8-HxCDF	0.50	10.0
1,2,3,7,8,9-HxCDF	0.50	10.0
2,3,4,6,7,8-HxCDF	0.50	10.0
1,2,3,4,6,7,8-HpCDF	0.50	10.0
1,2,3,4,7,8,9-HpCDF	0.50	10.0
OCDF	0.50	20.0

[a] EDL is a sample-specific DL. The value provided here is an estimate, and the sample-specific values will vary based on sample mass and the analytical conditions at the time of analysis

[b] LMCL is Axys's lowest calibration limit. Detected values below the LMCL are J-qualified. The reported LMCL will be adjusted based on the volume of each sample.

Axys – Axys Analytical Services Ltd.
DL – detection limit
EPA – US Environmental Protection Agency
EDL – estimated method detection limit
HpCDD – heptachlorodibenzo-p-dioxin
HpCDF – heptachlorodibenzofuran
HxCDD – hexachlorodibenzo-p-dioxin
HxCDF – hexachlorodibenzofuran
LMCL – lower method calibration limit
OCDD – octachlorodibenzo-p-dioxin
OCDF – octachlorodibenzofuran
PeCDD – pentachlorodibenzo-p-dioxin
PeCDF – pentachlorodibenzofuran
RL – reporting limit
TCDD – tetrachlorodibenzo-p-dioxin
TCDF – tetrachlorodibenzofuran

Table C-5. Surface water analytes, analytical methods, MDLs, RL goals, and WQC

Analyte	Method	Unit	MDL	RL	National Recommended AWQC			Washington State Criteria[a]		
					Aquatic Life		Human Health	Aquatic Life		Human Health
					Marine		Consumption of Organism Only	Marine		Consumption of Organism Only
					CMC (Acute)	CCC (Chronic)		Acute	Chronic	
Metals and organometals										
Antimony	EPA 1638	µg/L	0.1	0.3	–	–	640	–	–	90
Arsenic	EPA 1638	µg/L	0.07	0.4	69[b]	36[b]		69[b]	36[b]	
Inorganic arsenic	EPA 1632	µg/L	0.008	0.025			0.14			0.14
Cadmium	EPA 1638	µg/L	0.04	0.12	33[b]	7.9[b]	–	42[b]	9.3[b]	–
Chromium	EPA 1638	µg/L	0.25	0.75	–	–	–	–	–	–
Chromium III[c]	na	µg/L	–	–	–	–	–	–	–	–
Chromium VI[c]	na	µg/L	–	–	1,100[b]	50[b]	–	1,100[b]	50[b]	–
Copper	EPA 1638	µg/L	0.22	0.66	4.8[b]	3.1[b]	–	4.8[b]	3.1[b]	–
Lead	EPA 1638	µg/L	0.05	0.15	210[b]	8.1[b]	–	210.0[b]	8.1[b]	–
Mercury[d]	EPA 1631E	µg/L	0.0001	0.0004	1.8[b]	0.94[b]	–	1.8[b]	0.025	–
Methylmercury[c, d]	na	µg/L	0.000020	0.00005	1.8[b]	0.94[b]	0.3[d]	–	–	–
Nickel	EPA 1638	µg/L	0.23	0.69	74[b]	8.2[b]	4,600	74.0[b]	8.2[b]	100
Selenium	EPA 1638	µg/L	0.11	0.4	290[b]	71[b]	4,200	290[b]	71.0[b]	200
Silver	EPA 1638	µg/L	0.06	0.18	1.9[b]	–	–	1.9[b]	–	–
Thallium	EPA 1638	µg/L	0.13	**0.4**	–	–	0.47	–	–	0.27
Zinc	EPA 1638	µg/L	1.2	4	90[b]	81[b]	26,000	90[b]	81[b]	1000
TBT	EPA 8270D-SIM	µg/L	TBD[e]	**0.052**	0.42	0.0074	–	–	–	–
PAHs										
Acenaphthene	EPA 8270D-SIM	µg/L	0.00289	0.0100	–	–	90	–	–	30
Anthracene	EPA 8270D-SIM	µg/L	0.00116	0.0100	–	–	400	–	–	100
Benzo(a)anthracene	EPA 8270D-SIM	µg/L	**0.000750**	**0.0100**	–	–	0.0013	–	–	0.00016
Benzo(a)pyrene	EPA 8270D-SIM	µg/L	**0.00248**	**0.0100**	–	–	0.00013	–	–	0.000016
Benzo(b)fluoranthene	EPA 8270D-SIM	µg/L	**0.000460**	**0.0100**	–	–	0.0013	–	–	0.00016
Benzo(k)fluoranthene	EPA 8270D-SIM	µg/L	**0.00321**	**0.0100**	–	–	0.013	–	–	0.0016
Chrysene	EPA 8270D-SIM	µg/L	0.000900	0.0100	–	–	0.13	–	–	0.016
Dibenzo(a,h)anthracene	EPA 8270D-SIM	µg/L	**0.00134**	**0.0100**	–	–	0.00013	–	–	0.000016
Fluoranthene	EPA 8270D-SIM	µg/L	0.00171	0.0100	–	–	20	–	–	6
Fluorene	EPA 8270D-SIM	µg/L	0.00152	0.0100	–	–	70	–	–	10
Indeno(1,2,3-cd)pyrene	EPA 8270D-SIM	µg/L	**0.00101**	**0.0100**	–	–	0.0013	–	–	0.00016
Pyrene	EPA 8270D-SIM	µg/L	0.00118	0.0100	–	–	30	–	–	8
Phthalates										
Bis(2-ethylhexyl)phthalate	EPA 8270D	µg/L	**0.345**[f]	**3.00**[g]	–	–	0.37	–	–	0.046

Table C-5. Surface water analytes, analytical methods, MDLs, RL goals, and WQC

Analyte	Method	Unit	MDL	RL	National Recommended AWQC			Washington State Criteria[a]		
					Aquatic Life		Human Health	Aquatic Life		Human Health
					Marine			Marine		
					CMC (Acute)	CCC (Chronic)	Consumption of Organism Only	Acute	Chronic	Consumption of Organism Only
Butyl benzyl phthalate	EPA 8270D	µg/L	**0.320**[f]	**1.00**[g]	–	–	0.10	–	–	0.013
Diethyl phthalate	EPA 8270D	µg/L	0.292[f]	1.00[g]	–	–	600	–	–	200
Dimethyl phthalate	EPA 8270D	µg/L	0.362[f]	1.00[g]	–	–	2,000	–	–	600
Di-n-butyl phthalate	EPA 8270D	µg/L	0.336[f]	1.00[g]	–	–	30	–	–	8
Other SVOCs										
1,2,4,5-Tetrachloro-benzene	EPA 8270D	µg/L	TBD[e,f]	**1.00**[g]	–	–	0.03	–	–	–
1,2-Diphenylhydrazine	EPA 8270D	µg/L	**0.269**[f]	**1.00**[g]	–	–	0.2	–	–	0.02
2,4,5-Trichlorophenol	EPA 8270D	µg/L	1.03[f]	5.00[g]	–	–	600	–	–	–
2,4,6-Trichlorophenol	EPA 8270D	µg/L	**0.934**[f]	**3.00**[g]	–	–	2.8	–	–	0.28
2,4-Dichlorophenol	EPA 8270D	µg/L	0.816[f]	3.00[g]	–	–	60	–	–	10
2,4-Dimethylphenol	EPA 8270D	µg/L	0.350[f]	3.00[g]	–	–	3,000	–	–	97
2,4-Dinitrophenol	EPA 8270D	µg/L	4.25[f]	20.0[g]	–	–	300	–	–	100
2,4-Dinitrotoluene	EPA 8270D	µg/L	**1.18**[f]	**3.00**[g]	–	–	1.7	–	–	0.18
2-Chloronaphthalene	EPA 8270D	µg/L	0.302[f]	1.0[g]	–	–	1000	–	–	100
2-Chlorophenol	EPA 8270D	µg/L	0.276[f]	1.0[g]	–	–	800	–	–	17
3,3'-Dichlorobenzidine	EPA 8270D	µg/L	**1.57**[f]	**5.00**[g]	–	–	0.15	–	–	0.0033
4,6-Dinitro-o-cresol	EPA 8270D	µg/L	3.41[f]	**10.0**[g]	–	–	30	–	–	7
4-Chloro-3-methylphenol	EPA 8270D	µg/L	1.00[f]	3.00[g]	–	–	2,000	–	–	36
Benzidine	EPA 8270D	µg/L	**5.00**[f]	**10.0**[g]	–	–	0.011	–	–	0.000023
bis(2-chloroethyl)ether	EPA 8270D	µg/L	**0.235**[f]	**1.00**[g]	–	–	2.2	–	–	0.06
bis(2-chloroisopropyl)ether	EPA 8270D	µg/L	0.191[f]	1.00[g]	–	–	4,000	–	–	900
bis(chloromethyl) ether	EPA 8270D	µg/L	TBD[e,f]	**1.00**[g,h]	–	–	0.017	–	–	–
Hexachlorobenzene	EPA 8270D	µg/L	**0.333**[f]	**1.00**[g]	–	–	0.000079	–	–	0.0000050
Hexachloroethane	EPA 8270D	µg/L	**0.244**[f]	**2.00**[g]	–	–	0.1	–	–	0.02
Hexachlorocyclopentadiene	EPA 8270D	µg/L	**1.49**[f]	**5.00**[g]	–	–	4	–	–	1
Isophorone	EPA 8270D	µg/L	0.222[f]	1.00[g]	–	–	1,800	–	–	110
n-Nitrosodiethylamine	EPA 8270D	µg/L	TBD[e,f]	1.00[g,h]	–	–	1.24	–	–	–
n-Nitrosodimethylamine	EPA 8270D	µg/L	**0.935**[f]	**3.00**[g]	–	–	3	–	–	0.34
n-Nitroso-di-n-butylamine	EPA 8270D	µg/L	TBD[e,f]	**1.00**[g,h]	–	–	0.22	–	–	–
n-Nitroso-di-n-propylamine	EPA 8270D	µg/L	**0.296**[f]	**1.0**[g]	–	–	0.51	–	–	0.058
n-Nitrosodiphenylamine	EPA 8270D	µg/L	0.252[f]	**1.00**[g]	–	–	6	–	–	0.69
n-Nitrosopyrrolidine	EPA 8270D	µg/L	TBD[e,f]	1.00[g,h]	–	–	34	–	–	–
Nitrobenzene	EPA 8270D	µg/L	0.202[f]	1.00[g]	–	–	600	–	–	100

Table C-5. Surface water analytes, analytical methods, MDLs, RL goals, and WQC

Analyte	Method	Unit	MDL	RL	National Recommended AWQC			Washington State Criteria[a]		
					Aquatic Life		Human Health	Aquatic Life		Human Health
					Marine		Consumption of Organism Only	Marine		Consumption of Organism Only
					CMC (Acute)	CCC (Chronic)		Acute	Chronic	
Nonylphenol (mixed isomers)	EPA 8270D	µg/L	TBD[e,f]	1.00[g,h]	7	1.7	–	–	–	–
Pentachlorobenzene	EPA 8270D	µg/L	TBD[e,f]	**1.00**[g,h]	–	–	0.1	–	–	–
Pentachlorophenol	EPA 8270D	µg/L	**1.58**[f]	**10.0**[g]	13	7.9	0.04	13	7.9	0.002
Phenol	EPA 8270D	µg/L	0.154[f]	1.00[g]	–	–	300,000	–	–	70,000
Total dinitrophenols	EPA 8270D	µg/L	TBD[e,f]	3.0[g,h]	–	–	1000	–	–	–
Total nitrosamines	EPA 8270D	µg/L	0.935[f]	**3.0**[g]	–	–	1.24	–	–	–
PCBs										
Total PCB (congeners)	EPA 1668C	µg/L	0.000001[i]	0.000004[j]	–	0.03	0.000064	10.0	0.030	0.000007
Dioxins/furans										
2,3,7,8-TCDD	EPA 1613B	pg/L	**0.62**	**2.0**	–	–	0.0051	–	–	0.014
Pesticides - organochlorine										
4,4'-DDD	EPA 8081B	µg/L	**0.0186**[f]	**0.0500**[g]	–	–	0.00012	–	–	0.0000079
4,4'-DDE	EPA 8081B	µg/L	**0.0184**[f]	**0.0500**[g]	–	–	0.000018	–	–	0.00000088
4,4'-DDT	EPA 8081B	µg/L	**0.0169**[f]	**0.0500**[g]	0.13	0.001	0.00003	0.13	0.001	0.0000012
Aldrin	EPA 8081B	µg/L	**0.0103**[f]	**0.0250**[g]	1.3		0.00000077	0.71[k]	0.0019[k]	0.000000041
Dieldrin	EPA 8081B	µg/L	**0.0168**[f]	**0.0500**[g]	0.71	0.0019	0.0000012	0.71[k]	0.0019[k]	0.000000070
alpha-BHC	EPA 8081B	µg/L	**0.00850**[f]	**0.0250**[g]	–	–	0.00039	–	–	0.000048
beta-BHC	EPA 8081B	µg/L	0.00980[f]	**0.0250**[g]	–	–	0.014	–	–	0.0014
gamma-BHC	EPA 8081B	µg/L	0.0159[f]	0.0250[g]	0.16	–	4.4	0.16		0.43
Total chlordane	EPA 8081B	µg/L	**0.00950**[f]	**0.050**[g]	0.09	0.004	0.00032	0.09	0.004	0.000022
alpha-Endosulfan	EPA 8081B	µg/L	**0.00890**[f]	**0.0250**[g]	0.034[n]	0.0087[n]	30	0.034[l]	0.0087[l]	7
beta-Endosulfan	EPA 8081B	µg/L	**0.0139**[f]	**0.0250**[g]	0.034[n]	0.0087[n]	40	0.034[l]	0.0087[l]	10
Endosulfan sulfate	EPA 8081B	µg/L	0.0235[f]	0.0500[g]	–	–	40	–	–	10
Endrin	EPA 8081B	µg/L	**0.0167**[f]	**0.0500**[g]	0.037	0.0023	0.03	0.037	0.0023	0.002
Endrin aldehyde	EPA 8081B	µg/L	0.0163[f]	**0.0500**[g]	–	–	1	–	–	0.035
Heptachlor	EPA 8081B	µg/L	**0.0113**[f]	**0.0250**[g]	0.053	0.0036	0.0000059	0.053	0.0036	0.00000034
Heptachlor epoxide	EPA 8081B	µg/L	**0.00790**[f]	**0.0500**[g]	0.053	0.0036	0.000032	–	–	0.0000024
Hexachlorocyclohexane-G	EPA 8081B	µg/L	TBD[e,f]	**1.00**[g,h]	–	–	0.010	–	–	–
Methoxychlor	EPA 8081B	µg/L	**0.0744**[f]	**0.250**[g]	–	0.03	0.02	–	–	–
Mirex	EPA 8081B	µg/L	**0.0104**[f]	**0.0500**[g]	–	0.001	–	–	–	–
Toxaphene	EPA 8081B	µg/L	**0.220**[f]	**1.25**[g]	0.21	0.0002	0.00071	0.21	0.0002	0.000032

Table C-5. Surface water analytes, analytical methods, MDLs, RL goals, and WQC

Analyte	Method	Unit	MDL	RL	National Recommended AWQC			Washington State Criteria[a]		
					Aquatic Life		Human Health	Aquatic Life		Human Health
					Marine		Consumption of Organism Only	Marine		Consumption of Organism Only
					CMC (Acute)	CCC (Chronic)		Acute	Chronic	
Pesticides - organophosphate and carbamate										
Carbaryl	EPA 8321	µg/L	0.004	0.02	1.6	–	–	–	–	–
Chlorpyrifos	EPA 8141B	µg/L	**0.036**	**0.2**	0.011	0.0056	–	0.011	0.0056	–
Diazinon	EPA 8141B	µg/L	0.051	0.2	0.82	0.82	–	–	–	–
Malathion	EPA 8141B	µg/L	0.076	0.2	–	0.1	–	–	–	–

Bold underlined reporting limits and method detection limits are greater than the lowest criteria value.

[a] Washington State criteria include standards promulgated in WAC 173-201A and human health criteria consistent with the Washington Toxics Rule (40 CFR 131.45 as applied to Washington) and 40 CFR 131.36(d)(14), including the 40 CFR 131 criteria updated on November 28, 2016. These criteria were updated after publication of the ROD.

[b] Criteria applied to dissolved fraction.

[c] Total value will be compared to criterion for related chemical species.

[d] Methylmercury criterion is expressed as fish tissue concentration (mg/kg). *Water Quality Criterion for the Protection of Human Health: Methyl Mercury (*EPA-823-R-01-001) contains information for how the value is calculated using the criterion in EPA's 2000 Human Health Methodology.

[e] Laboratory to perform MDL study prior to analysis.

[f] SW846 no longer requires MDL values. The laboratories have the option to use these values to assess sensitivity for EPA 8000 series methods. ARI has continued to maintain MDL studies for these analytes.

[g] RL values are consistent with the LLOQ values required under EPA SW846.

[h] Estimated RL; laboratory will confirm RL prior to analysis.

[i] EDL is a sample-specific DL. The value provided here is an estimate, and the sample-specific values will vary based on sample mass and the analytical conditions at the time of analysis.

[j] Value represents laboratory-specific LMCL value for an individual PCB congener based on a 1-L sample.

[k] Criteria for sum of aldrin and dieldrin.

[l] Criteria for sum of alpha-Endosulfan and beta-Endosulfan.

ARI – Analytical Resources, Inc.
AWQC – ambient water quality criteria
BHC – benzene hexachloride
CCC – criterion continuous concentration
CFR – Code of Federal Regulations
CMC – criterion maximum concentrations
DDD – dichlorodiphenyldichloroethane
DDE – dichlorodiphenyldichloroethylene
DDT – dichlorodiphenyltrichloroethane
DL – detection limit
EPA – US Environmental Protection Agency
EDL – estimated detection limit
LLOQ – lower limit of quantification
LMCL – lower method calibration limit
MDL – method detection limit
na – not applicable
PAH – polycyclic aromatic hydrocarbon
PCB – polychlorinated biphenyl
RL – reporting limit
ROD – Record of Decision
SIM – selective ion monitoring
SVOC – semivolatile organic compound
TBD – to be determined via MDL study
TBT – tributyltin
TCDD – tetrachlorodibenzo-*p*-dioxin
WAC – Washington Administrative Code
WQC – water quality criteria

APPENDIX D. PASSIVE SAMPLER STANDARD OPERATING PROCEDURES

GUIDANCE DOCUMENT

Passive PE Sampling in Support of In Situ Remediation of Contaminated Sediments: Standard Operating Procedure for PE Analysis

ESTCP Project ER-200915

December 2012

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ICF International

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Reset

Standard Operating Procedure
for the Extraction and Analysis of Polyethylene (PE) Used
in Polyethylene Devices (PEDs)

1.0 SCOPE AND APPLICATION

1.1 This method describes procedures for chemical analysis of contaminants contained in polyethylene (PE) that has been deployed in polyethylene devices (PEDs) to sample hydrophobic organic compounds (HOCs) in aquatic and sediment environments.

1.2 This procedure generates extracts suitable for High Resolution Gas Chromatography/Mass Spectrometry (GCMS) analysis.

1.3 This extraction procedure is applicable to PE used in laboratory- or field-exposed PEDs.

2.0 SUMMARY OF METHOD

2.1 Upon recovery from the field exposure, the PE, while still in the PED, should be carefully cleaned (e.g. remove adhering sediment) and then cut into appropriate lengths (e.g., to obtain replicates or to acquire sections exposed to varying depths into a sediment bed). The PE pieces, usually 10 to 100 milligram quantities, are placed in pre-cleaned, amber, glass vials with a drop of water for shipping. Once received by the analytical laboratory, each sample is spiked with Surrogate standards (to assess analyte recoveries) and submerged in a suitable solvent (e.g., methylene chloride) for at least 12 hours. The extract is transferred to a large vessel suited for solvent evaporation, and then the PE is re-extracted three more times with methylene chloride, with the extracts combined for evaporative concentration and eventual GCMS (or suitable) instrumental analysis. After extraction, the PE is air-dried and weighed.

2.2 A shaker table or some other suitable mechanical agitation is recommended for the extractions to facilitate PE-solvent contact.

3.0 INTERFERENCES

3.1 PE is susceptible to contamination from atmospheric and surfaces, and so it must be handled using clean techniques.

3.2 While the formation of biofilms and epiphytic growth on PE surfaces does not compromise their behavior in the field during deployment, these coatings can substantially complicate subsequent chemical analysis. Careful removal of adhering sediment or surface growths via water-wetted Kimwipe® wiping may be necessary. Surface coatings of organic films on PE (e.g., oil or tar residues) can be removed by using solvent-saturated wipes (<minute contact times) followed by immediate Surrogate standard addition and solvent extraction.

4.0 APPARATUS AND MATERIALS

4.1 Extraction vessels: amber glass vials (foil-lined lids)

4.2 Concentrating vessels: 100 mL glass, pear-shaped flask with glass stopper; 250 mL glass, round-bottom flask with glass stopper or equivalent

4.3 Bottle/jar tumbler, shaker table, bottle roller or equivalent

4.4 Analytical balance - capable of weighing to 0.1 mg (i.e., small value relative to samplers weights that are typically between 10 and 100 mg.)

4.5 Food-grade aluminum foil

4.6 Stainless steel forceps

4.7 Single-edge razor blades

4.8 Teflon (or similar non-contaminating material) cutting board

4.9 Glass transfer pipettes.

4.10 Kimberly-Clark Kimwipe® or equivalent

5.0 REAGENTS

5.1 Methylene chloride, CH_2Cl_2, pesticide grad or equivalent (other solvent suited to analytes of interest).

5.2 Organic-free reagent water (as defined in SW-846 Chapter One)

5.3 Research grade surrogate and injection standard compounds certified >98+% pure or equivalent.

6.0 PREPARATION AND HANDLING

6.1 Upon recovery and return to a clean working environment, the PE should be surface cleaned prior to any cutting or extraction. The PE surface should be wiped and rinsed free of surface particles and coatings. This may include briefly (< minute) wiping with a hexane-soaked Kimwipe® (or equivalent) to remove oily or tarry exterior staining. If water wet, the PE surface should be blotted dry with a clean wipe.

6.2 Laboratory and field personnel should wear nitrile or latex gloves whenever handling PE to avoid cross-contaminating the PE.

6.3 Methylene chloride (pesticide grade) rinsed, stainless steel forceps and scissors are used when manipulation of PE is required.

6.4 Clean aluminum foil is used to cover any surface that PE may encounter.

7.0 PROCEDURE

7.1 Solvent Extraction: Laboratory and/or field blank and field-exposed PE is spiked with known quantities of surrogate compounds to assess analytical recoveries and extracted using organic solvents prior to analysis by GC/MS.

7.1.1 The PE is inspected for surface biofilms, particles, mud, or oily coatings. Biofilm mass should be removed by using a clean wipe followed by a rinse with organic-

free reagent water. Particles and sedimentary debris are removed by rinsing with organic-free reagent water and careful surface scraping if necessary to remove adhered/imbedded material. Oily coatings (e.g., coal tar staining or hydrocarbon slicks) are removed by soaking clean wipes in hexane and using forceps to hold and wipe both PE surfaces. This is not an exhaustive extraction and should be done quickly (<minute) and immediately prior to immersion in solvent. PE surfaces are blotted dry if water wet.

7.1.2 The PE is transferred to a pre-cleaned amber vial (size determined by dimensions of PE, typically 15-40mL). Vial must be large enough for complete immersion of PE without excessive PE folding.

7.1.3 Known masses of surrogate compounds (Appendix 1) in a methylene chloride-compatible solvent are added to the vial. Typical additions are: 2.5-20 ng for aqueous samples; 50-250 ng for sediment samples, depending on target HOCs and their expected concentrations in the PE.

7.1.4 Methylene chloride is added to the vial to completely submerge the PE for a period of at least 12 hours.

7.1.5 The extract is transferred to a pre-cleaned glass concentration vessel. A second aliquot of methylene chloride is added to the extraction vial and agitated for >10 minutes. This step is repeated two more times.

7.1.6 After the final extract transfer, the PE is allowed to air dry in the extraction vial and weighed on an analytical balance until a consistent PE mass is obtained. This result is used to calculate the final target HOC concentrations measured in the PE sampler in units of HOC mass per PE mass.

7.2 Extracts are concentrated using rotary evaporation (or equivalent) down to suitable volumes for GCMS analysis; the resultant concentrated extracts are transferred to smaller vials (e.g., for autosamplers) according to standard laboratory practices. Before analysis, appropriate injection standards are added to the final extracts to allow for evaluation of the total volume of extract analyzed (Appendix 1).

Typical final extract volumes are:

50-250 μL for water column-exposed PE

1-10 mL for contaminated sediment bed-exposed PE

8.0 QUALITY CONTROL

8.1 Method blanks, field blanks, matrix spikes, and/or replicate samples should be subjected to exactly the same analytical procedures as those used on field/lab-exposed samples.

8.2 QA/QC metrics, that are specific to the type of target HOCs of interest and the analytical methods used to quantify them, should be applied. Typical values for targets like PAHs and PCBs that are analyzed by capillary gas chromatography-low resolution mass spectrometry, in which picogram/uL detection is common, are:

8.2.1 Freshly prepared polyethylene and trip blanks: <0.1 ng / g PE

Freshly cleaned PE samples, and samples of PE that traveled to and from the field site ("trip blank"), should have no significant peaks where PRCs, surrogate standards, injection standards, and target analytes elute.

8.2.2 PRC-loaded polyethylene reproducibility (±1σ/mean, N=6): <10%
Individual batches of PE loaded with PRCs should exhibit reproducible PRC concentrations in the PE before deployment.

:

8.2.3 Recoveries of Surrogate Standards: >70% to < 120%
Surrogate standards should be recovered from PE samples at 100%, plus or minus analytical precision. An exception may be relatively volatile compounds (e.g., mono-, di-chlorobiphenyls) that may be significantly lost when extracts are evaporated (e.g., recovery down to 60%).

8.2.4 Precision of replicate PE extract analyses (N≥3): <20%.
The reproducibility of all analytes (injection standards, surrogate standards, PRCs, and target compounds) determined with multiple instrumental analyses of the same PE sample extract, even run on different dates, should fall with suitably narrow bounds.

8.2.5 Detection limits using PE samples: <1 ng / g PE
Assuming 100 mg PE samples and 100 uL final extract volumes, target analytes such as PAHs and PCBs analyzed by GCMS (or methods with like sensitivity) should have <ppb detection limits.

9.0 METHOD PERFORMANCE

9.1 The method performance is assessed by determining the recovery and reproducibility in analyzing surrogate compounds (Appendix 1). All other lab-specific QA/QC metrics should be adhered to.

9.2 Successful PE deployment is achieved when significant (>method precision) losses of PRCs occurred, allowing one to use their behavior to adjust target compound levels in the PE up to equilibrium concentrations (Fernandez et al. 2009).

10.0 REFERENCES

Fernandez L.A., Harvey, C.F., and Gschwend, P.M. Using performance reference compounds in polyethylene passive samplers to deduce sediment pore water concentrations for numerous target chemicals. Environ. Sci. Technol., 43, 8888-8894, 2009.

Appendix 1 Suggested Performance Reference Compounds (PRCs), Surrogate Compounds (Recovery Standards), and Injection Standards. The lab preparing the PEDs must coordinate PRC choices with the lab doing the PE analyses to avoid conflicting uses.

A. PRCs, suitable for polycyclic aromatic hydrocarbon (PAH) determinations when Capillary Gas Chromatography-Mass Spectrometry (GCMS) is used for analysis include, but are not restricted to, deuterated PAHs. One subset should be used as PRCs, while reserving others for use as surrogate (recovery) and injection standards. Unlabeled compounds such as terphenyl can be used as injection standards if they are readily resolved from the other analytes.

Targets: PAHs	**Method: GCMS**	**Detection Limit ~ 100 pg / 100 mg PE**	
PRCs	d10-phenanthrene	d10-pyrene	d12-chrysene
Surrogates	d10-anthracene	d10-fluoranthene	d12-benz(a)anthracene
Injection Standards	d10-acenaphthene	d14-*m*-terphenyl	d12-perylene

B. PRCs and surrogate compounds suitable for polychlorinated biphenyl (PCB) determinations when GCMS is the method separation and detection include, but are not restricted to, ^{13}C-labeled or deuterated PCB congeners. One subset, for example including tri-, tetra-, penta-, hexa-, and heptachloro-biphenyls, can be used as PRCs while reserving different tri-, tetra-, penta-, hexa-, and heptachloro-biphenyl congeners to serve as surrogate compounds. Still other compounds such as deuterated PAHs or rare PCBs (not contained in Aroclor/Clophan mixtures such as: PCB-39, PCB-55, PCB-104, PCB-150 and PCB-188) can be used as injection standards.

Targets: PCBs	**Method: GCMS**	**Detection Limit ~ 100 pg / 100 mg PE**			
PRCs	^{13}C PCB-28	^{13}C PCB-52	^{13}C PCB-101	^{13}C PCB-153	^{13}C PCB-180	
Surrogates	^{13}C PCB-19	d_6 PCB-77	^{13}C PCB-105	^{13}C PCB-167	^{13}C PCB-170	^{13}C PCB-194
Injection Standards	d17-39	d22-104	d34-55	d40-150	d52-188	

C. When analyzing for organochlorine pesticides such as DDT using GCMS, ^{13}C labeled compounds can serve as PRCs. However, since DDT has been seen to degrade to form DDE or DDD in certain situations, one should use the 4,4'- isomer of DDT and the 2,4'-isomers of DDE and DDD as PRCs to allow appearance of 13C-labelled 4,4'-DDE of 4,4'-DDD to be interpreted as arising from reaction the DDT PRC during the deployment. Deuterated or ^{13}C labeled PCBs can be used as surrogate (recovery) and injection standards.

Targets: DDTs	**Method: GCMS**	**Detection Limit ~ 200 pg / 100 mg PE**	
PRCs	^{13}C 2,4'-DDE	^{13}C 2,4'-DDD	^{13}C 4,4'-DDT
Surrogates	^{13}C-PCB111	^{13}C-PCB153	^{13}C PCB 178
Injection Standards	d6 PCB 77	^{13}C PCB 105	^{13}C PCB 167

GUIDANCE DOCUMENT

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Reset

Standard Operating Procedure for the Preparation of Polyethylene (PE) and Polyethylene Devices (PEDs) Used for Passive Sampling

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for preparing and handling polyethylene (PE) films that will be cut into strips and used in polyethylene devices (PEDs) to passively sample hydrophobic organic compounds (HOCs) in environmental media.

1.2 This method generates PE that can be deployed within PEDs for passive sampling of HOCs in atmospheric, aqueous, or sediment-porewater systems.

1.3 PE that is prepared by this method is suitable for laboratory or *in situ* field deployment.

2.0 SUMMARY OF METHOD

2.1 A known mass of low density polyethylene (LDPE) sheet, usually gram quantities, is cleaned by sequentially extracting with methylene chloride, methanol, and ultrapure water in a closed glass vessel.

2.2 Clean PE is equilibrated with performance reference compounds (PRCs) dissolved in water or methanol-water (see Appendix 1 for possible PRCs).

2.3 Prepared PE is stored in contaminant-free, sealed, glass vessels.

2.4 Shortly before deployment, the PE is cut into strips and either placed in aluminum mesh bags for water sampling water or aluminum frames for sediment sampling. PEDs are transported to the field wrapped in clean aluminum foil.

2.5 In the field, the PE is exposed to the environmental medium of concern. HOCs in the medium diffuse into the PE, while PRCs diffuse out.

3.0 INTERFERENCES

3.1 PE is susceptible to contamination from atmospheric vapors and contact with surfaces (e.g., worker hands), so it must remain in clean sealed vessels until deployment.

4.0 APPARATUS AND MATERIALS

4.1 Extraction vessels: 1-L glass bottles or screw capped jars (foil-lined lids).

4.2 Storage vessels: bottles with glass stoppers or amber jars (foil-lined lids).

4.3 Bottle/jar tumbler, shaker table, bottle roller, or equivalent.

4.4 Low density polyethylene (LDPE): commercial grade, large sheet at 25μm (1 mil) or 51μm (2 mil) thickness. The thickness is chosen to be strong enough to withstand stresses during deployment (e.g., insertion into sediment), but thin enough to exchange a significant fraction (e.g., >20%) of its PRCs during the deployment time to be used.

4.5 Food grade aluminum foil (solvent cleaned and/or combusted to remove any organic residue from foil production)

4.6 Stainless steel forceps

4.7 Teflon (or similar non-contaminating material) cutting board

5.0 REAGENTS

5.1 Methylene chloride, CH_2Cl_2, pesticide grade or equivalent

5.2 Methanol, CH_3OH, pesticide grade or equivalent

5.3 Organic-free reagent water (as defined in SW-846 Chapter 1)

5.4 Research grade PRCs certified >98+% pure.

Note: Specific standard materials, concentrations, solvents, and solvent purity requirements will be determined based upon that target HOCs of concern for the particular application

6.0 PRESERVATION AND HANDLING

6.1 Clean PE should be stored in clean sealed glass vessels.

6.2 Until deployment, prepared PE (PE loaded with PRCs) is stored in sealed glass containers with a few mL of organic-free reagent water added to maintain 100% relative humidity within the storage vessels (minimizing sorptive losses of PRCs to glass vessel walls).

6.3 Laboratory and field personnel should wear nitrile or latex gloves whenever handling clean PE.

6.4 Methylene chloride-rinsed, stainless steel forceps and scissors are used when manipulation of clean PE is required.

6.5 Methylene chloride-rinsed, aluminum foil is used to cover any surface that clean PE may encounter.

7.0 PROCEDURE

7.1 Polyethylene Cleaning Procedure: LDPE is purchased from hardware/painting stores in large sheets ('dropcloth or plastic tarp' material) with thickness of 25μm (1 mil) or 51μm (2 mil), depending on the user's need for strength (choose thicker) and desire to use short deployment times (used thinner). The sheet is cut into strips sized for environment and frames to be used. An organic solvent cleaning sequence is then used to prepare the PE. This process ensures that extractable oligomers, plasticizers, and contaminating organic chemicals are removed from the PE prior to use. All extractions are performed sequentially in the same container.

7.1.1 Methylene chloride is placed into the extraction vessel, and the PE strips are immersed in the container for 24 hours to enable time for diffusive transfers out of the PE. The initial methylene chloride extract is discarded and a second methylene chloride extraction is performed for 24 hours. The second methylene chloride extract is discarded and replaced by methanol in order to remove methylene chloride from the PE. Methanol immersion is also done for 24 hours. The initial methanol extract is discarded and followed by a second methanol soak for 24 hours. Finally, the second methanol extract is discarded and the PE undergoes three 24-hour soaks with organic-free reagent water (within the same

extraction vessel) to remove residual methanol from the PE.

7.1.2 The cleaned PE is stored in organic-free reagent water in the extraction vessel until further processing.

7.2 Polyethylene Preparation with Performance Recovery Compounds (PRCs)***:*** PRCs are loaded into the clean PE, prior to its field deployment, by utilizing either aqueous (Fernandez et al. 2009) or 80:20 methanol:water equilibrations (Booij et al., 2002). Depending on the hydrophobic organic compounds of interest, PRCs should be chosen which mimic mass transfer phenomena governing exchanges during field deployments. It is important to avoid adding PRCs that the analytical laboratory already uses as surrogate or injection standards. PRC loading is performed by placed the PE in pre-cleaned glass vessels containing known PRC solutions made up in organic-free reagent water with or without pesticide-grade methanol. The PE user should estimate the expected accumulation of target compounds in the passive sampler and seek to load with similar levels of PRCs to facilitate the eventual chemical analyses. Sufficient PRC equilibration time during this PE preparation step is necessary to ensure uniform PE loading across the entire PE thickness; hence thicker PE sheet is more robust for field use, but takes longer to load with PRCs.

7.2.1 Isotopically labeled compounds are useful internal standards when Gas Chromatography-Mass Spectrometry (GCMS) is the method of separation and detection. For example, deuterated polycyclic aromatic hydrocarbons (PAHs) and C13-labeled PCBs are effective methodological standards for PE passive sampling. One subset of compounds, distributed across the range of PAHs to be assessed (e.g., d10-phenanthrene, d10-pyrene, and d12-chrysene), should be used as PRCs, while another set (e.g., d10-anthracene, d10-fluoranthene, and d12-benz(a)anthracene) is used as surrogate (recovery) compounds during later analysis of field-deployed PE. Finally, compounds such as d10-acenaphthene, d14-*m*-terphenyl, and d12-perylene can be used as injection standards. Similar sets of labeled compounds should be used for other compound classes (see Appendix 1). Note: if PE samples are eventually to be analyzed at a contract laboratory, PRC choices must be made so as not to conflict with recovery and injection standards used by that laboratory.

7.2.2 As subsequent analysis (e.g., GCMS) is best achieved with both PRCs and target HOCs present at like concentrations in the PE extracts, the optimal concentration level of the PRC loaded into the PE is dependent on the environment in which the PE is to be deployed. For example, if a target HOC is expected to occur in the water or pore water near 1 ng/L levels, one can use that compound's LDPE-water partition coefficient (e.g., Fernandez et al., 2009; Lohmann, 2012) to estimate the expected levels in the PE after deployment:

$$\text{Concentration in PE (ng/kg)} \sim K_{LDPE\text{-}water} * \text{concentration in (pore)water (ng/L)}$$

So if the $K_{LDPE\text{-}water}$ for the target HOC of interest is 10^5 (L/kg), then the concentration of the target HOC in the PE will approach 100 ug/kg. Based on this estimate, the PRCs are loaded into the PE at similar concentrations. Appendix 2 shows a typical calculation used to design a PRC-containing MeOH:H_2O solution of PCBs suited for causing an 0.82 g strip of PE to acquire about 100 ug of each PRC per kg of PE (equivalent to 100 ng/g PE).

7.2.3 Aqueous PRC Loading: A solvent-cleaned and dried glass container is filled with ultrapure water that has been spiked with known concentrations of PRCs (e.g., using calculations like those shown in Appendix 2). A known mass of pre-cleaned PE is then added and weighted to insure complete PE submersion. The vessel is agitated to remove any air pockets adhering to the submerged PE. Equilibration times vary for different PRC/PE thickness combinations and the PE-water phase ratio. For PAHs and PCBs, use at least 30 days to insure homogeneous distributions of the PRCs throughout the entire thickness of the PE film unless faster equilibration has been confirmed. Confirmation can be done by time course measures of PRC concentrations in the PE or by showing that concentrations of PRCs are the same for films of different thicknesses, but the same masses. Generally, PE is stored in the PRC solution until it is to be deployed.

7.2.4 Methanol-Aided PRC Loading: A solvent-cleaned and dried glass container is filled with an 80:20 mixture of pesticide grade methanol and ultrapure water that has been spiked with known concentrations of PRCs (e.g., see calculations in Appendix 2). A known mass of pre-cleaned PE is then added and weighted to insure complete submersion. The vessel should be agitated to remove any air pockets adhering to the submerged PE. Equilibration times vary for different PRC/PE thickness combinations and the PE-solvent phase ratio, but typically this step is completed within 7 days since methanol swells the PE and thereby speeds PRC diffusion into the polymer sheet (Booij et al., 2002). Generally, the PE is stored in the PRC solution until shortly before it is to be deployed. Before deployment, the PRC-loaded PE is rinsed with ultrapure water, and then it is soaked in ultrapure water for 24 h to remove methanol from the PE. This methanol leaching step is repeated twice to insure complete methanol removal.

7.3 PED Assembly

7.3.1 PEDs can be pre-assembled with prepared PE strips up to a few days prior to deployment depending on the target compounds of interest.

7.3.2 FOR WATER SAMPLING WITH PE IN A STAINLESS STEEL MESH BAG. Since PE that is openly exposed in the water column has been observed to be eaten by aquatic organisms, the PE must be protected by deploying it in a mesh bag.

7.3.2.1 Cut rectangles from the mesh that are larger than the piece of PE to be deployed. Clean the mesh with methylene chloride, methanol, and water.

7.3.2.2 Wearing nitrile gloves, and using solvent-rinsed stainless steel forceps, lay a piece of the mesh on a clean surface such as an aluminum-foil covered lab bench. Remove the PE strip from its container and lay it on top of a stainless steel mesh. Place the second mesh on top. The two meshes are sealed together by folding the edges over on one another, and then sewing them together with nylon fishing line. Grommets can be added to the upper corners to facilitate mesh labeling and attachments in the field.

7.3.3 FOR SEDIMENT BED SAMPLING WITH PE IN AN ALUMINUM SHEET METAL FRAME. In order to insert the PE strips into a sediment bed, the PE must be carried by an aluminum frame (Figure 1).

7.3.3.1. Aluminum sheet metal is cut into two complementary pieces that can be bolted together such that a piece of PE sheet is held in place. After cutting, these pieces of aluminum must be washed with organic solvents (e.g., methylene chloride and methanol) and then rinsed with water.

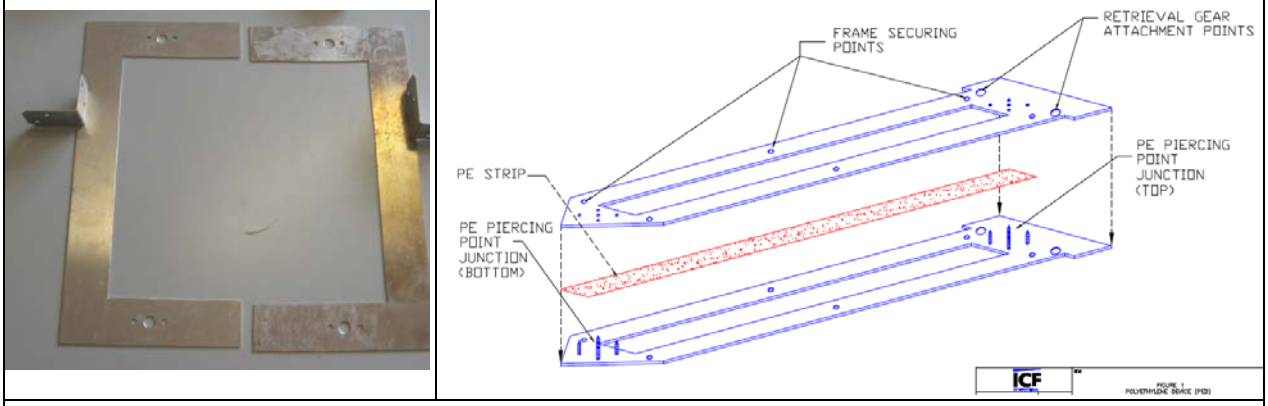

Figure 1.
(left panel) Aluminum sheet cut into two "C-shaped" pieces allowing the investigator to mount and hold ~25 cm strips of PE an open window when the two pieces are overlapped and bolted together.
(right panel) Drawing of two aluminum sheet pieces cut so as to sandwich a strip of PE and expose about 50 cm of length.

7.3.3.2 Wearing nitrile gloves, lay a piece of the aluminum frame containing the PE piercing points (sheet metal screws, see Figure 1), sharp side up, on a sheet of solvent-rinsed aluminum foil.

7.3.3.3 Using solvent-rinsed stainless steel forceps, remove the PE strip from its container and lay the strip lengthwise across both sets of PE piercing point junctions. PE strips should have been sized to fit the frame with a little extra length, allowing the investigator to cut a small strip of PE from one end to serve as sample for PRC concentration measures before the sampler is deployed. At one end of the PED frame, gently push the remainder of the PE strip onto the PE piercing points so all points penetrate the PE strip. Gently pull the other end of the PE strip over the adjacent PE piercing points, keeping the PE strip taut, and push that end of the PE strip into the PE piercing points. The tautness of the PE strip should have as minimal deflection as possible between the two PE piercing point junctions, but not too tight so that movement of the PE causes it to rip or tear. Place the other PED frame over the PED frame containing the PE strip so that each of the PE piercing point junctions meet and both PED frames are flush against each other. Secure the two frames together using the appropriate hardware (stainless steel machine screws, locking washers, and cap nuts).

7.3.3.4 Wrap the entire PED frame in solvent-rinsed aluminum foil to prevent exposure during transport and field preparation activities.

7.4 PE and PED Storage and Shipment*:*

7.4.1 Prepared PEDs in their foil envelops may be stored a few days at ambient temperature prior to deployment. Freezing or excessive heat should be avoided to minimize the likelihood of changing the polymer crystallinity. It is recommended that PEDs be hand carried or shipped in a timely fashion (Overnight or Next Day if possible) to minimize chances sampler contamination or damage.

7.4.2 If PE is to be shipped to another location for PED assembly, it is recommended that the PE strips are individually sealed in pre-cleaned glass vials that contain a little water. Freeze shipping should be avoided, but cold (refrigeration temperature) packing may be necessary depending on time of season and individual laboratory handling/quality control procedures.

8.0 QUALITY CONTROL

8.1 PRC Loading Validation: At least six representative samples of prepared PE should be collected (e.g., 6 x 10 mg pieces), extracted, and analyzed prior to field deployment to validate that the PRC concentrations are consistent with their intended loadings and these standards have uniform concentrations in a batch of PE.

8.2 Target HOC Blanks: Subsamples of prepared PE, commensurate in size with the planned environmental PE samples (e.g., 10 cm wide by 5 cm long by 25 um thick and therefore weighing about 120 mg), should be be collected, extracted, and analyzed prior to field deployment to demonstrate that other substances have not contaminated the PE which would contribute to interfering background for the target HOCs.

9.0 METHOD PERFORMANCE

9.1 PRC data, obtained from PE samples collected from >six parts of the prepared PE, should be consistent within about 10% (i.e., 100 x standard deviation / mean).

9.2 Target HOC concentrations should be undetectable in the prepared PE (e.g., < 1 ng/g PE assuming 100 mg PE subsamples).

10.0 REFERENCES

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Appendix 1 Suggested Performance Reference Compounds (PRCs), Surrogate Compounds (Recovery Standards), and Injection Standards.

A. PRCs, suitable for polycyclic aromatic hydrocarbon (PAH) determinations when Gas Chromatography-Mass Spectrometry (GCMS) is the preferred method of detection, include, but are not restricted to, deuterated PAH compounds. One subset should be used as PRCs, while reserving others for use as surrogate (recovery) compounds. Still other compounds such as terphenyl can be used as injection standards.

Targets: PAHs	**Method: GCMS**	**Detection Limit ~ 100 pg / 100 mg PE**	
PRCs	d10-phenanthrene	d10-pyrene	d12-chrysene
Surrogates	d10-anthracene	d10-fluoranthene	d12-benz(a)anthracene
Injection Standards	d10-acenaphthene	d14-*m*-terphenyl	d12-perylene

B. PRCs and surrogate compounds suitable for polychlorinated biphenyl (PCB) determinations when GCMS is the preferred method of detection include, but are not restricted to, ^{13}C-labeled or deuterated PCB congeners. One subset, for example including a tri-, tetra-, penta-, hexa-, and heptachloro-biphenyl, can be used as PRCs while reserving different tri-, tetra-, penta-, hexa-, and heptachloro-biphenyl congeners to serve as surrogate compounds. Still other compounds such as deuterated PAHs or rare PCBs (not contained in Aroclor/Clophan mixtures such as: PCB-39, PCB-55, PCB-104, PCB-150 and PCB-188) can be used as injection standards.

Targets: PCBs	**Method: GCMS**		**Detection Limit ~ 100 pg / 100 mg PE**			
PRCs	^{13}C PCB-28	^{13}C PCB-52	^{13}C PCB-101	^{13}C PCB-153	^{13}C PCB-180	
Surrogates	^{13}C PCB-19	d_6 PCB-77	^{13}C PCB-105	^{13}C PCB-167	^{13}C PCB-170	^{13}C PCB-194
Injection Standards	d17-39	d22-104	d34-55	d40-150	d52-188	

C. When analyzing for organochlorine pesticides such as DDT using GCMS, ^{13}C labeled compounds can serve as PRCs and surrogate standards. Since DDT has been seen to degrade to form DDE or DDD in certain situations, one should use the 4,4'- isomer of DDT and the 2,4'-isomers of DDE and DDD as PRCs to allow appearance of ^{13}C-labelled 4,4'-DDE of 4,4'-DDD to be interpreted as arising from reaction of the DDT PRC during the deployment. Deuterated or ^{13}C labeled PCBs can be used as surrogate (recovery) and injection standards.

Targets: DDTs	**Method: GCMS**	**Detection Limit ~ 200 pg / 100 mg PE**	
PRCs	^{13}C 2,4'-DDE	^{13}C 2,4'-DDD	^{13}C 4,4'-DDT
Surrogates	^{13}C-PCB111	^{13}C-PCB153	^{13}C 2,4'-DDT
Injection Standards	d6 PCB 77	^{13}C PCB 105	^{13}C PCB 167

Appendix 2. Example of spreadsheet used to design solution needed to impregnate PE with Performance Reference Compounds (PRCs) for PCB sampling. The leftmost section uses data from Booij et al. (2002) to establish a correlation between log K(polyethylene-80:20 MeOH:H2O) values and log K_{ow} values from Hawker and Connell (1988). With this relationship, the second section shows is use to estimate the PE-MeOH:H2O partition coefficients for PRCs of interest. Using these partition coefficients and a user-chosen mass of PE to prepare (here 0.82 g), the third section allows the user to find the PRC spiking solution concentration needed to obtain any desired initial PE concentration (here set to be 100 ng each PRC per g PE); for example, for congener 52, one needs to have 11 ng/mL of the initial 80:20 MeOH:H_2O solution to end up with about 100 ng/g PE. Finally, the right-most section uses the polyethylene-water partition coefficients (from Lohmann 2012) to check the importance of PRC losses from the PE when the MeOH is leached out in three successive steps after PRC loading. Successive calculations are described in the text below.

Example spreadsheet calculation for spiking PCBs into LDPE with 80:20 methanol-water solutions.

	Training data for estimation of Kpe-meoh:H2O		13C-labelled PRCs		use correlation to estimate	fraction in PE for PE mass (g)	0.82042	Solution concentration needed in ng/mL in order to get 100 ng/g PE			fraction in PE after each water soak to remove MeOH		
PCB congener	log Kpe-meoh:water (ref 1)	log Kow (ref 2)	congener	log Kow (ref 2)	log Kpe-meoh:water(80:20)	with VMeOH:water (mL)	125	ng/mL MeOH:H2O	congener	estim log Kpe-w log Kpew = 1.14*log Kow-1.14 (ref 3)	1st leach using	2nd leach 1000	3rd leach mL water
4	0.20	4.65	**52**	5.84	0.97	0.058		11.29	**52**	5.52	0.9966	0.9932	0.9898
29	1.05	5.6	**101**	6.38	1.26	0.107		6.15	**101**	6.13	0.9990	0.9980	0.9971
155	1.29	6.41	**153**	6.92	1.55	0.188		3.49	**153**	6.75	0.9997	0.9994	0.9991
204	1.67	7.3	**180**	7.36	1.78	0.284		2.31	**180**	7.25	0.9999	0.9998	0.9997
			28	5.67	0.88	0.048		13.75	**28**	5.32	0.9950	0.9900	0.9850
			47	5.85	0.98	0.059		11.16	**47**	5.53	0.9967	0.9934	0.9901
			111	6.76	1.46	0.160		4.10	**111**	6.57	0.9996	0.9992	0.9988
			153	6.92	1.55	0.188		3.49	**153**	6.75	0.9997	0.9994	0.9991
			178	7.14	1.66	0.233		2.82	**178**	7.00	0.9998	0.9997	0.9995

use to find following correlaltion:

log Kpe-mw(80:20) = 0.532 (+/- 0.094) * log Kow(Hawker) - 2.133 (+/- 0.572)

N = 4, R2 = 0.94, S.E. 0.18

PE mass

number of strips	1
PE density (g/cm3)	0.95
PE thickenss (cm)	0.00254 for 1 mil sheet
PE length (cm)	68
PE width (cm)	5
length*width*thickness *number of strips*density	
mass of PE (g)	**0.82**

references

1. Booij, K, Smedes, F., van Weerlee, E.M., Chemosphere 2002, 46, 1157-1161.
2. Hawker DW and Connell DW. 1988. Environ. Sci. Technol. 22: 382-387.
3. Lohmann, R. Environ. Sci. & Technol.; 2012, 46, 606–618.

Step 1: find/estimate PE-spiking solvent partition coefficients for PRCs in solvents of interest. Here 80:20 MeOH:H_2O values from Booij et al. (2002) are used to develop a LFER with K_{ow} values from the literature (Hawker and Connell, 1988); this relation is then used to estimate $K_{pe\text{-}meoh:h2o}$ values for other PCB congeners.

Step 2: choose the size of PE needed for the sampling exercise (here a single 1 mil-thick strip of 5 cm width and 68 cm length) and solve for the PE mass (here 0.82 g). Also choose a vessel which is large enough in volume to fit the PE inside without extensive PE-PE surface contact, but small enough so that unacceptably expensive masses of the labeled PRCs are not used (here 125 mL ground glass stopped flask). For this PE mass and solution volume, use the PE-solution partition coefficients from step 1 to solve for the fractions of each PRC that will be in the PE at equilibrium using:

$$\text{fraction in PE} = 1 - (1 / (1+\text{Mass}_{pe}*K_{pe\text{-}solution}/\text{Volume}_{solution}))$$

(e.g., 5.8% for congener #52)

Step 3. solve for spiking solution concentrations of PRCs that result in desired PRC loadings in the PE (here 100 ng/g_{PE}) using:

$$C_{initial\ spiking\ solution} = C_{desired\ in\ PE} * \text{Mass}_{pe} / \text{fraction in PE} / \text{Volume}_{solution}$$

(e.g., here find need about 11.3 ng congener #52 per mL to achieve 100 ng/g PE; this is concentration of the spiking solution that the investigator must make up to prepare PE for subsequent sampling at sites where it is expected that the (pore)water will cause the PE to accumulate about 10 to 100 ng of target PCBs/g_{PE}).

Step 4. PE is stored in the PRC loading solution until shortly before passive sampling use.

Step 5. if spiking solutions that contain organic cosolvents like MeOH were used, this MeOH must be leached out of the PE before it can be used for passive sampling. To insure that MeOH leaching will not substantially change PRC loading, calculate whether substantial fractions of the PRCs will be lost in subsequent steps required to leach the co-solvent from the PE. Since the leaching steps involve use of H_2O, use the PE-water partition coefficients; for PCBs, these are derived from a LFER found in the review by Lohmann (2012). With these values, we can solve for the fractional losses of individual PRCs to the leach water (assumes negligible MeOH builds up in the leach water) contained in 1000 mL ground glass stoppered flasks, using:

$$\text{fraction remaining in PE after a single leach step} = 1 - (1 / (1+K_{pe\text{-}H2O}*\text{Mass}_{pe} / \text{Volume}_{H2O}))$$

(e.g., in this case for congener #52, one finds 99.66% of the PRC remains in the PE after the first leach. Two additional leaches lower this to 99.32% and 98.98%, respectively. More hydrophobic congeners are leached even less.)