Lower Duwamish Waterway Group

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

LOWER DUWAMISH WATERWAY CLAM 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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Prepared by: Windward environmental LLC

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TITLE AND APPROVAL PAGE
CLAM COLLECTION AND CHEMICAL ANALYSES
QUALITY ASSURANCE PROJECT PLAN

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Windward QA/QC Manager	Name	4/2/18 Date
EPA Project Manager	ELLEN HALE Name	Digitally signed by ELLEN HALE Date: 2018.04.02 14:39:12 -07'00' Date
EPA QA/QC Manager	Don Matheny Name	Digitally signed by Don Matheny Date: 2018.04.02 13:59:16 -07'00' 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.

- Elly Hale, EPA Project Manager
- Kathy Godtfredsen, Windward Project Manager
- Susan McGroddy, Windward Task Manager
- Suzanne Replinger, Windward Field Lead
- Donald Brown, EPA QA/QC Manager
- Amara Vandervort, Windward QA/QC Manager
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  - Brian Anderson, Joe Flaherty (The Boeing Company)
  - Dave Schuchardt, Allison Crowley, Pete Rude (City of Seattle)
  - Jeff Stern, Debra Williston (King County)
  - Joanna Florer (Port of Seattle)

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Acronyms

%RSD	percent relative standard deviation
95UCL	95% upper confidence limit (on the mean)
ALS	ALS Environmental-Kelso
AOC	Administrative Order on Consent
ARI	Analytical Resources, Inc.
SGS-Axys	SGS-Axys Analytical Services Ltd.
BEHP	bis(2-ethylhexyl) phthalate
BHC	benzene hexachloride
CFR	Code of Federal Regulations
COC	chemical of concern
COPC	chemical of potential concern
cPAH	carcinogenic polycyclic aromatic hydrocarbon
CPUE	catch per unit effort
CTO	chemothermal oxidation
DCM	dichloromethane
DDD	dichlorodiphenyldichloroethane
DDE	dichlorodiphenyldichloroethylene
DDT	dichlorodiphenyltrichloroethane
DL	detection limit
DQI	data quality indicator
DQO	data quality objective
Ecology	Washington State Department of Ecology
EDL	estimated detection limit
EIM	Environmental Information Management
ENR	enhanced natural recovery
EPA	US Environmental Protection Agency
FC	field coordinator
FS	feasibility study

GC/ECD	gas chromatography / electron capture detection
GC/MS	gas chromatography / mass spectrometry
GPC	gel permeation chromatography
GPS	global positioning system
HCB	hexachlorobenzene
HDPE	high-density polyethylene
HG-AFS	hydride generation-atomic fluorescence spectrometry
HHRA	human health risk assessment
HpCDD	heptachlorodibenzo-*p*-dioxin
HpCDF	heptachlorodibenzofuran
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
IDW	inverse distance weighted
ISO	International Organizations for Standardization
LCS	laboratory control sample
LDW	Lower Duwamish Waterway
LDWG	Lower Duwamish Waterway Group
LLOQ	lower limit of quantitation
LMCL	lower method calibration limit
MDL	method detection limit
MLLW	mean lower low water
MNR	monitored natural recovery
MS	matrix spike
MSD	matrix spike duplicate
MW	molecular weight

NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
OCDD	octachlorodibenzo-*p*-dioxin
OCDF	octachlorodibenzofuran
ODEQ	Oregon Department of Environmental Quality
OSHA	Occupational Safety and Health Administration
PCB	polychlorinated biphenyl
PCP	pentachlorophenol
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
RAO	remedial action objective
RARE	Regional Applied Research Effort
RI	remedial investigation
RL	reporting limit
RM	river mile
RME	relative margin of error
ROD	Record of Decision
RPD	relative percent difference
SDG	sample delivery group
SGS-Axys	SGS-Axys Analytical Services Ltd.
SIM	selected ion monitoring

SM	Standard Methods
SOP	standard operating procedure
SRM	standard reference material
SVOC	semivolatile organic compound
T-117	Terminal 117
TBT	tributyltin
TCDD	tetrachlorodibenzo-*p*-dioxin
TCDF	tetrachlorodibenzofuran
TEF	toxic equivalency factor
TEQ	toxic equivalent
TM	task manager
TOC	total organic carbon
TTL	target tissue level
UCT-KED	universal cell technology-kinetic energy discrimination
Windward	Windward Environmental LLC
ww	wet weight

Acknowledgements

Windward Environmental LLC wishes to acknowledge the contributions of Dr. Jose Gomez-Eyles (Integral Consulting Inc.) in the support of the cPAH porewater investigation, and Lorraine Read (Terrastat Consulting) in the sampling design.

1 Introduction

This quality assurance project plan (QAPP) describes the quality assurance (QA) objectives, methods, and procedures for collecting baseline clam tissue samples from the Lower Duwamish Waterway (LDW) for chemical analyses, and for performing an *ex situ* porewater analysis for carcinogenic polycyclic aromatic hydrocarbons (cPAHs) to determine if porewater data are helpful in assessing the relationship between cPAHs in clam tissue and sediment.

As described in the *Pre-Design Studies Work Plan* (Windward and Integral 2017), hereafter referred to as the Work Plan, these activities are being conducted to address the third amendment to the Administrative Order on Consent (AOC) (EPA 2016c). The Work Plan presented the data quality objectives (DQOs) and conceptual study designs (Windward and Integral 2017). This QAPP includes those DQOs and presents the detailed study designs, including specifics 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 the *ex situ* passive sampler portion of the cPAH porewater investigation.

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 tissue for comparison to target tissue levels (TTLs). This QAPP addresses the baseline sampling of clam tissue, as well as the collection of *ex situ* porewater data to assist in assessing potential relationships between cPAHs in clam tissue and those in sediment.

For the purposes of this QAPP, two chemical lists were identified for the baseline clam tissue sampling:

- **Human health risk drivers** – As specified in the third amendment to the AOC (EPA 2016c), all clam tissue samples will be analyzed for remedial action objective (RAO) 1 (human health seafood consumption). These chemicals are the four chemicals identified as risk drivers in the human health risk assessment (HHRA) (i.e., polychlorinated biphenyls [PCBs], dioxins/furans, cPAHs, and inorganic arsenic). For clarity, it should be noted that these chemicals were referred to as risk drivers in the risk assessment, but as chemicals of concern (COCs) in the ROD. These four chemicals will be referred to as "human health risk drivers" throughout this QAPP.
- **Non-risk driver chemicals** – In addition, the third amendment to the AOC (EPA 2016c) specified that a subset of clam tissue samples would be analyzed for additional chemicals identified for RAO 1 in the ROD (ROD Tables 14 and 18). These chemicals include vanadium, tributyltin (TBT), select semivolatile organic compounds (SVOCs) (bis(2-ethylhexyl) phthalate [BEHP], carbazole, hexachlorobenzene [HCB], and pentachlorophenol [PCP]), and organochlorine pesticides. For clarity, it should be noted that these chemicals (which do not have TTLs) were referred to as COCs in the risk assessment, but as chemicals of potential concern (COPCs) in the ROD. These chemicals will be referred to as "non-risk driver chemicals" throughout this QAPP.

2.1 DATA QUALITY OBJECTIVES

As described in the Work Plan (Windward and Integral 2017), two DQOs were identified for the collection and analysis of baseline clam tissue samples, and one DQO was identified for the analysis of cPAHs in porewater. These DQOs are summarized in Table 2-1. In addition to addressing the DQOs, clam tissue sampling will support health risk communication related to human consumption of resident seafood (RAO 1) (EPA 2014b).

Table 2-1. Clam tissue and porewater DQOs

DQO Step	Clam Tissue DQO 1	Clam Tissue DQO 2	Porewater DQO 1
STEP 1: State the problem.	Site-wide tissue concentrations of human health risk drivers have not been measured since 2007, and data are needed to establish current site-wide 95UCL concentrations in clam tissue to serve as baseline conditions before the site-wide sediment remedy is conducted.	The baseline mean concentrations of the human health risk drivers and other non-risk driver chemicals in clam tissue need to be established before the site-wide remedy is conducted, in order to assess concentration trends following remediation.	The ROD stated that research will be conducted to further assess the relationship between cPAH concentrations in sediment and in clam tissue, and to assess whether remedial action can reduce clam tissue concentrations to achieve RAO 1. Analyses performed during the RI showed that relationships between cPAH concentrations in clam tissue and in sediment were not statistically significant. To further assess this relationship, porewater data will be collected, in addition to clam tissue and sediment data, to assess whether porewater data aid in assessing the relationship.
STEP 2: Identify the goals of the study.	The goal of clam tissue DQO 1 is to establish baseline site-wide 95UCL concentrations for comparison to TTLs for RAO 1 from the ROD.	The goal of clam tissue DQO 2 is to calculate baseline site-wide mean clam tissue concentrations to assess trends following sediment remediation for the human health risk drivers with TTLs and the non-risk driver chemicals without TTLs.	The goal of porewater DQO 1 is to assess the relationship among concentrations of cPAHs in clam tissue, porewater, and sediment to help evaluate whether achieving sediment cleanup levels for cPAHs will reduce concentrations in clam tissue toward TTLs.
STEP 3: Identify the information inputs.	Existing clam tissue collection information from the LDW (i.e., locations where clams have been previously collected) was used to determine the clam tissue collection areas. Information regarding the number of clams needed per composite was based on the weights of previously collected clams.		Existing clam collection information and cPAH sediment data were used to define the 20 cPAH candidate locations within clam tissue collection areas that cover the range of cPAH concentrations in sediment.
STEP 4: Define the boundaries of the study.	The boundary of the study was defined by the ROD. A total of 11 clam tissue collection areas that are based on the sampling and analysis conducted for the RI have been identified (Map 2-1); within these clam tissue collection areas, 20 smaller areas have been identified for cPAH evaluation (porewater DQO 1) (Map 2-2).		

DQO Step	Clam Tissue DQO 1	Clam Tissue DQO 2	Porewater DQO 1
STEP 5: Develop the analytical approach.	Clams collected from each of the clam tissue collection areas will be analyzed for the four human health risk drivers. cPAHs, PCBs, and dioxins/furans will be analyzed in whole-body composite samples. Inorganic arsenic will be analyzed in separate composite samples of siphon skin and remainder tissue, because inorganic arsenic is known to accumulate preferentially in the siphon skin tissue of the target species. In addition to samples analyzed for the human health risk drivers, whole-body intertidal segment-wide composite samples (i.e., one for each of the three intertidal segments; Map 2-1) will be analyzed for non-risk driver chemicals as specified in the ROD. These chemicals include vanadium, TBT, select SVOCs (BEHP, carbazole, HCB, and PCP), and organochlorine pesticides.		Individual cPAHs will be analyzed in clam tissue composite samples, co-located sediment samples, and selected *ex situ* porewater samples. As described previously, these samples will be collected from 20 candidate sampling locations (Map 2-2).
STEP 6: Specify performance or acceptance criteria.	Performance or acceptance criteria are described in Section 4.7, including field QC samples and laboratory QC. DQIs for laboratory analyses (i.e., precision, accuracy, representativeness, completeness, and comparability) will be met, as described in Section 4.6.		
STEP 7: Develop the detailed plan for obtaining data.	Composite clam samples will be collected from the 11 clam tissue collection areas within the LDW in May/June 2018. At each location, clams will be hand-collected by the field crew. Team members will focus their effort by digging for clams with a shovel where clam siphon holes ("shows") or other evidence of clam presence are observed. Consistent with past efforts, only *Mya arenaria* ≥ 2 cm wide (as measured from valve to valve) will be retained.		Clams will be hand collected, as described for clam tissue DQOs 1 and 2, and co-located sediment will be collected at the same locations. All clam tissue and co-located sediment samples will be analyzed for cPAHs, TOC, and black carbon (sediment) and lipids (tissue), and a minimum of 10 sediment samples with the desired range of cPAH concentrations in sediment will be selected for *ex situ* porewater testing for cPAHs.

95UCL – 95% upper confidence limit (on the mean)
BEHP – bis(2-ethylhexyl) phthalate
cPAH – carcinogenic polycyclic aromatic hydrocarbon
DQI – data quality indicator
HCB – hexachlorobenzene
DQO – data quality objective
LDW – Lower Duwamish Waterway
PCB – polychlorinated biphenyl
PCP – pentachlorophenol
QC – quality control
RI – remedial investigation
RAO – remedial action objective
ROD – Record of Decision
SVOC – semivolatile organic compound
TBT – tributyltin
TOC - total organic carbon
TTL – target tissue level

2.1.1 Clam tissue DQO 1

The first clam tissue DQO is to:

- Establish baseline site-wide 95% upper confidence limit (on the mean) (95UCL) concentrations of human health risk drivers for comparison to TTLs[1] for RAO 1.

RAO 1 establishes sediment cleanup objectives for human health risk associated with the consumption of resident seafood. The baseline site-wide 95UCL is the statistic selected in the ROD for comparison to TTLs to measure progress toward achieving RAO 1 (EPA 2014b). TTLs are not cleanup levels; rather, they are to be used for informational purposes to assess ongoing risks associated with the consumption of resident LDW fish and shellfish (EPA 2014b).

TTLs have been developed for English sole (fillet and whole body), shiner surfperch, Dungeness crab (edible meat and whole body), and Eastern softshell clam. There are TTLs for fish, crab, and clam for PCBs and dioxins/furans, and for clams for cPAHs and inorganic arsenic. The purpose of this investigation is to generate a baseline site-wide dataset for clams. The study design for the baseline dataset for fish and crab has been provided in a separate QAPP (Windward 2017).

Composite samples from each of the 11 clam tissue collection areas will be analyzed for the human health risk drivers (i.e., inorganic arsenic, cPAHs, PCBs, and dioxins/furans). If clams are available, 1 clam composite sample will be collected from each of the 11 clam collection areas.[2] These data will be used to calculate a site-wide 95UCL in tissue.

The number of clam tissue collection areas was determined in the remedial investigation (RI) based on the distribution of clam habitat and information regarding the presence of clams from past clam tissue collection efforts. It is acknowledged that habitat restoration, cleanup actions, and shoreline uses in the LDW will change over time. Therefore, future sampling may consider how to maintain consistency with the baseline dataset, as well as newly identified areas that may contain clams.

In addition, it should be noted that the clam tissue collection areas are a subset of the potential clamming areas, which are being sampled as described in Sections 2.1.3, 4.1.3.1, and 4.2.2.3 and as shown on Map 4-9 of the sediment QAPP (Windward 2018). Only the co-located sediment that will be collected as part of the cPAH *ex situ* porewater evaluation is discussed in this QAPP (see Section 4.1.2).

[1] As specified in ROD Table 21, *LDW Resident Fish and Shellfish Target Tissue Concentrations* (EPA 2014b).

[2] Clams may not be present in 2 of the 11 areas sampled in the RI (Terminal 117 [T-117] and Slip 4) that have recently been remediated as early actions. The Boeing Plant 2 and Jorgensen Forge intertidal areas have also been remediated but are not among the 11 areas where clams were collected during the RI sampling program.

2.1.2 Clam tissue DQO 2

The second clam tissue DQO is to:

- Calculate baseline site-wide mean clam tissue concentrations to assess trends following sediment remediation for contaminants with TTLs.

The baseline data collected to calculate site-wide 95UCLs will also be used to establish baseline site-wide mean concentrations for the human health risk drivers (i.e., inorganic arsenic, cPAHs, PCBs, and dioxins/furans) to assess trends following implementation of the sediment remedy. For the LDW non-risk driver chemicals, three segment-wide intertidal composite samples (Map 2-1) will be used to calculate the site-wide average concentrations for these chemicals. Each composite sample will be composed of equal portions of the whole-body tissue from each clam tissue collection area within the given intertidal segment. The mean of the composite samples will be used to calculate the site-wide average concentrations for these chemicals. The segment composites will also provide information on differences in concentrations among the segments.

2.1.3 Porewater DQO 1

The porewater DQO for this QAPP is to:

- Assess the relationship among concentrations of cPAHs in clam tissue, porewater, and sediment to help evaluate whether achieving sediment cleanup levels for cPAHs will reduce concentrations in clam tissue to TTLs.

In the cPAH porewater investigation, cPAH concentrations in co-located intertidal sediment, clam tissue, and porewater will be analyzed to assess the utility of porewater data in better understanding the clam tissue-sediment relationship. Co-located *M. arenaria* and sediment composite samples will be collected from 20 candidate locations within clam tissue collection areas, provided clams are available in suitable areas. The sediment and tissue samples will be analyzed for cPAHs within three weeks of sample collection.[3] The cPAH sediment and tissue data will be used to select a minimum of 10 locations[4] where freely dissolved concentrations of individual cPAHs in porewater will be determined using passive samplers exposed to the sediment *ex situ*. The final data analysis will involve evaluating the significance of the relationships among porewater, clam tissue, and sediment for individual cPAHs. The relationships will not be evaluated for the cPAH TEQ, because the TEQ is a weighted sum of a mixture calculated to estimate toxicity.

[3] The three-week timeframe will include one week for sample compositing (and shipment when necessary) and two weeks for sample analysis.

[4] A sample size of 10 is expected to be sufficient for developing a regression and to capture a range of cPAH toxic equivalents (TEQs).

2.2 PROJECT APPROACH AND SCHEDULE

Baseline clam tissue will be collected between river mile (RM) 0 and RM 5 of the LDW, as shown on Map 2-1. Clam tissue samples will be hand collected using shovels in the LDW during low tides in mid-May 2018 (Table 2-2). Because *M. arenaria* are primarily found near the low tide line, sampling will occur during the period when tides are at or below 0 ft mean lower low water (MLLW).

Table 2-2. Targeted sampling dates for clam collection

Date	Low Tide (ft MLLW)	Time of Low Tide	Approximate Time Range when Tides ≤ 0 ft MLLW	Duration of Sampling (hrs)
May 15, 2018 (Tuesday)	-1.66	11:46a	10:00am – 1:30pm	3.5
May 16, 2018 (Wednesday)	-2.40	12:37p	10:30am – 2:30pm	4.0
May 17, 2018 (Thursday)	-2.77	1:11p	11:00am – 3:30pm	4.5
May 18, 2018 (Friday)	-2.74	1:59p	11:45am – 4:15pm	4.5
May 19, 2018 (Saturday)	-2.30	2:49p	12:45pm – 5:00pm	4.25
May 20, 2018 (Sunday)	-1.51	3:43p	2:00pm – 5:30pm	3.5

Source: NOAA Tides and Currents (Duwamish Waterway, Eighth Avenue South; Station 9447029) (NOAA 2017).
MLLW – mean lower low water
NOAA – National Oceanic and Atmospheric Administration

Chemical analysis of the clam composite samples will be performed after compositing and homogenization have been completed, and will require approximately four weeks to perform. 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.

The cPAH porewater investigation will be conducted using co-located clam tissue and sediment samples (Map 2-2). These samples will be collected during the same period as that outlined above for baseline clam tissue. The analysis of cPAHs in clam tissue and sediment will be conducted within three weeks of sample collection. The *ex situ* exposure of passive samplers to sediment will begin immediately following sample collection for all samples, and will continue for about one month. *Ex situ* exposure will be followed by analysis of the selected passive samplers (minimum of 10[5]) for cPAHs. The selection of passive samplers for analysis will be based on unvalidated cPAH TEQs in sediment and clam tissue. The laboratory report will be reviewed to identify any significant QA issues that would affect the usability of the data. Data validation will occur following analysis of each media type, and is expected to be complete approximately three weeks after the receipt of chemistry data. The cPAH passive

[5] The co-located tissue and sediment chemistry data will be reviewed to identify a minimum of 10 sediment samples for which the corresponding *ex situ* sample extracts will be analyzed. Samples to represent the range of cPAH TEQs in sediment and tissue (e.g., if two samples have similar tissue and sediment cPAH TEQs, individual cPAH distribution, and carbon content, one of these samples may be excluded) will be selected in consultation with EPA.

sampler data will then be used to estimate the freely dissolved cPAH concentrations in porewater.

A draft data report (Task 5 of the third amendment to the AOC (EPA 2016c)) will be submitted to EPA 21 days after receipt of all validated analytical results, including the results from the cPAH porewater investigation. A draft final data report will be submitted to EPA 30 days after receipt of EPA's comments on the draft report.

Final validated data will be submitted to the Washington State Department of Ecology's (Ecology's) Environmental Information Management (EIM) system and EPA's Scribe database within 30 days of approval of the final data report. Data will be evaluated in the data evaluation report (Task 6 of the third amendment to the AOC (EPA 2016c)), which will be due 60 days after the submittal of the last draft data report (except for the surface water data report).

3 Project Organization and Responsibilities

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

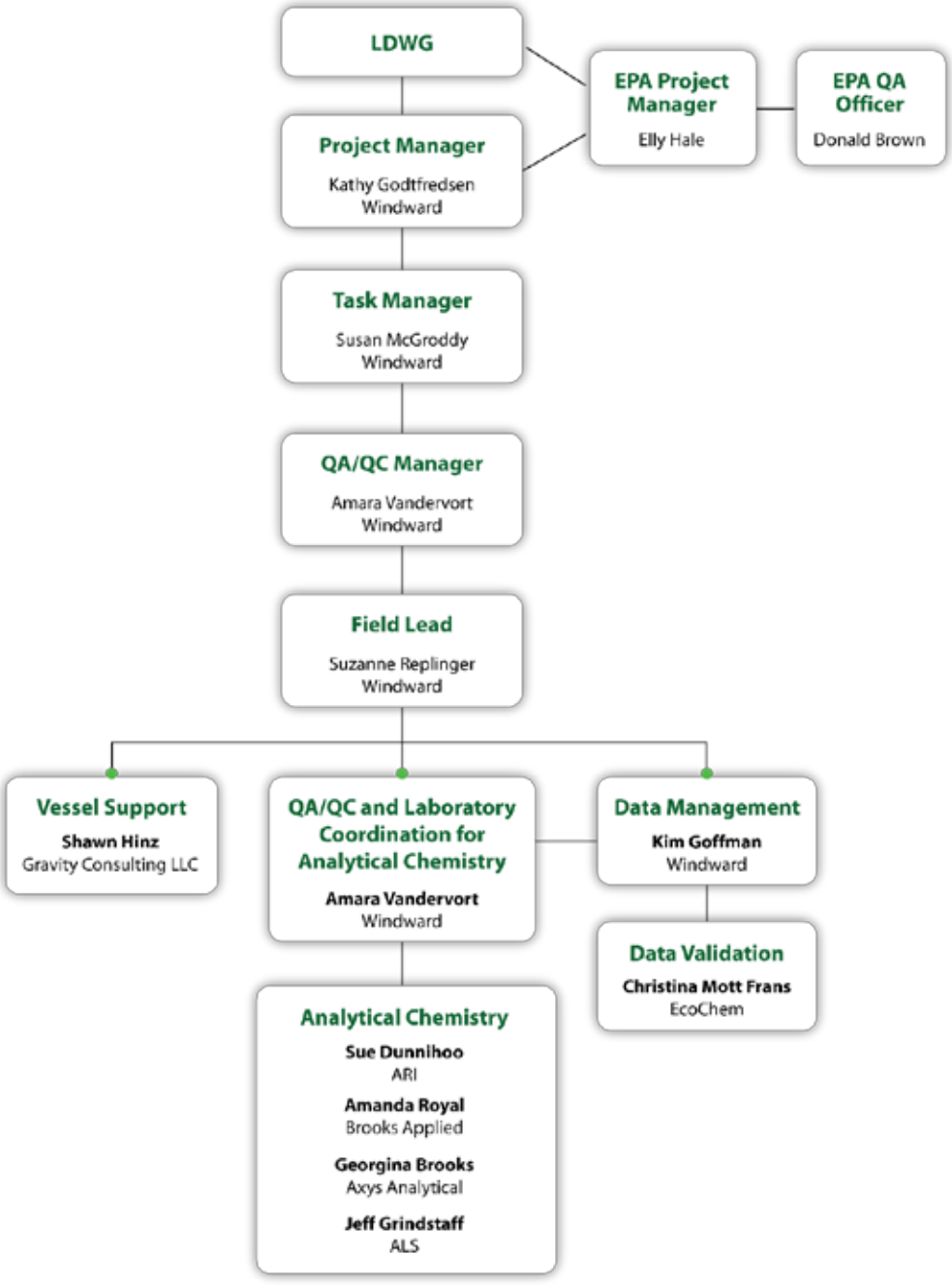

Figure 3-1.Project organization and team responsibilities

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

Suzanne Replinger is the Windward field coordinator (FC). As FC, she will be responsible for managing field sampling activities and general field and QA/quality control (QC) oversight. Jose Gomez-Eyles of Integral Consulting LLC will assist Ms. Replinger in overseeing the *ex situ* passive sampler exposures. Ms. Replinger 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 (e.g., by phone/email) and documented in the data report. Ms. Replinger can be reached as follows:

Ms. Suzanne Replinger
Windward Environmental LLC
200 West Mercer Street, Suite 401
Seattle, WA 98119
Telephone: 206.812.5435[6]
Email: suzanner@windwardenv.com

Shawn Hinz is the boat captain. He will be responsible for operating the boat and will coordinate closely with the FC. 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 clam and sediment samples, with the exception of analyses for PCB congeners, dioxins/furans, inorganic arsenic, organochlorine pesticides, and black carbon. SGS-Axys Analytical Services Ltd. (SGS-Axys) will perform analyses for PCB congeners and dioxins/furans, Brooks Applied Labs will perform analyses for inorganic arsenic, and ALS Environmental-Kelso (ALS) will perform analyses for organochlorine pesticides and black carbon. For the cPAH porewater investigation, ARI will provide the facilities for the *ex situ* exposures, and SGS-Axys will perform the preparation and required analysis of the passive samplers.

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 SGS-Axys can be reached as follows:

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

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

Ms. Amanda Royal
Brooks Applied Labs
18804 North Creek Parkway, Suite 100
Bothell, WA 98011
Telephone: 206.753.6111
Email: amanda@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, Brooks Applied Labs, and SGS-Axys have current environmental laboratory accreditation from Ecology for methods to be performed. ALS has current environmental accreditation from Ecology for organochlorine pesticides. Ecology does not offer accreditation for the black carbon method. However, ALS is International Organization for Standardization (ISO) accredited for the instrumental portion of black carbon analysis; this is the only accreditation available for this method.

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 sample 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:

- Clam collection form
- Sediment collection form (for co-located sediment samples for the cPAH porewater investigation)

- Forms for *ex situ* exposures:
  - Percent moisture benchsheet
  - Exposure setup benchsheet
  - Daily conditions benchsheet
- Protocol modification form

Information regarding equipment calibration and other sampling activities will be documented in the field logbook.

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 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
  - Weight used for analysis
  - Final dilution volumes or concentration factor for the sample
  - Identification of the instruments used for analysis

- Method detection limits (MDLs) and RLs[7]
- 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 will include the following information, as applicable:
  - 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.
  - 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 methods 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.

[7] The term MDL includes other types of detection limits (DLs), such as estimated detection limit (EDL) values calculated for PCB congeners and dioxin / furan congeners. RL values are consistent with the lower limit of quantitation (LLOQ) values required under EPA SW846.

- The standard reference material (SRM) analysis[8] 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 and the percent differences between the columns, as appropriate.
- The ion abundance ratio summary for samples analyzed by EPA methods 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
  - 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 blanks, passive sampler exposure 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

[8] SRMs will be analyzed for PCB congeners, dioxin / furans, cPAHs, and organochlorine pesticides. All other analyses will include a laboratory control sample (LCS). Specific information is listed in Section 4.7.2.2.

(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 will be the laboratory analyst's responsibility to reduce the data, which will be 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 of clams and co-located sediment (where applicable) reported in latitude and longitude to the nearest one-tenth of a second and in northing and easting to the nearest foot
- Summary of the chemical data QA / QC review
- Results from the analyses of field samples and *ex situ* passive samplers, 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 chain of custody 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 within 30 days of approval. The data will be exported in two formats: one that is compatible with Ecology's EIM 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

Clam samples, co-located sediment samples, and the *ex situ* 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

The following sections detail sampling design components for clam tissue DQOs 1 and 2 (Section 4.1.1) and porewater DQO 1 (Section 4.1.2). An overview of the samples to be collected for each of these DQOs is presented in Table 4-1, with details presented in the subsections below.

Table 4-1. Overview of samples to be collected by DQO

DQO	No. of Clam Tissue Collection Areas	Sample Types	No. of Samples
Clam tissue DQOs 1 and 2	11	whole-body composites to be analyzed for cPAHs, PCBs, and dioxins/furans	11[a]
		siphon skin and remainder tissue composites to be analyzed for inorganic arsenic	11[a]
		intertidal segment-wide whole-body composites to be analyzed for non-risk driver chemicals	3
Porewater DQO 1	20	whole-body clam composites to be analyzed for cPAHs	20[a]
		co-located sediment (0–10-cm) to be analyzed for cPAHs	20[a]
		ex situ porewater to be analyzed for cPAHs	≥ 10[b]

[a] Although efforts will be made to collect clams from all 11 clam tissue collection areas and 20 cPAH porewater investigation areas, it is unknown whether clams will be present in each of these areas, particularly in Slip 4 and near T-117, which has been recently remediated. A minimum of three samples is required to calculate a 95UCL. Details regarding contingencies are described in Section 4.2.

[b] A minimum of 10 samples is expected to be sufficient for developing a regression relationship, and to ensure sufficient coverage of the range of observed cPAH TEQs.

95UCL – 95% upper confidence limit (on the mean)
cPAH – carcinogenic polycyclic aromatic hydrocarbon
DQO – data quality objective
EPA – US Environmental Protection Agency
LDWG – Lower Duwamish Waterway Group
PCB – polychlorinated biphenyl
T-117 – Terminal 117
TEQ – toxic equivalent

4.1.1 Clam tissue samples (DQOs 1 and 2)

This section presents the sampling design for the clam composite samples that will be collected to evaluate clam tissue DQOs 1 and 2.

4.1.1.1 Targeted species and organism size

Based on the species sampled as part of the RI (Windward 2010) and the species with TTLs listed in Table 21 of the ROD (EPA 2014b), one species of clam (i.e., Eastern softshell clams [*M. arenaria*]) will be collected to establish LDW baseline conditions.

Target clam sizes for this QAPP are consistent with those of the LDW RI tissue dataset, and represent reasonable size ranges for seafood consumed by humans. The target size range for clams is ≥ 2 cm in width (as measured from valve to valve; Figure 4-1). If insufficient clams are available, smaller clams (e.g., ≥ 1.5 cm in width) will be collected and considered for analysis.

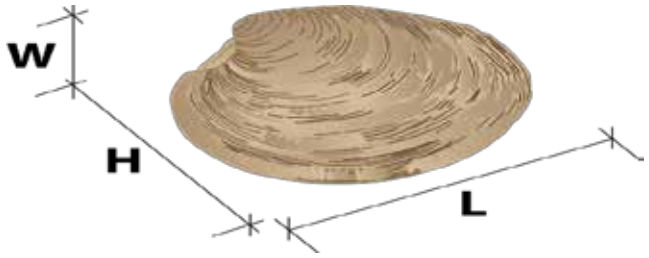

Figure 4-1. Clam dimension measurements

4.1.1.2 Clam tissue collection areas

Efforts will be made to collect clams from 11 clam tissue collection areas in the LDW (Map 2-1). Although efforts will be made to collect clams from all of these areas, it is unknown whether clams will be present in each of these areas, particularly in Slip 4 and near T-117, which has been recently remediated. Details regarding the maximum level of effort to be expended at each clam tissue collection area, as well as how clams will be divided into composites if an insufficient number of clams are collected at a given clam tissue collection area, are discussed in Section 4.2.

The locations where clams will be collected within each clam tissue collection area will be based primarily on evidence of clam presence (i.e., shows) during the field collection effort. The field team will search along the entire low tide line in each clam tissue collection area (including the candidate cPAH porewater investigation areas) to ensure that, to the extent possible, clams are spatially distributed throughout the area. Section 4.2.2 discusses collection methods and contingency plans that may be needed.

Individual clams collected in each of the 11 clam tissue collection areas will be composited by area (as described in Section 4.1.1.3), and the area composites will be analyzed for the human health risk drivers. The data will be used to calculate 95UCL concentrations for the LDW; these 95UCL concentrations will be used for comparison to TTLs for DQO 1, and to calculate the mean value across the LDW to serve as a baseline for trend analysis for DQO 2. In addition, for the non-risk driver chemicals, three intertidal segments have been identified for the creation of segment-wide composite samples. These three intertidal segments are from RM 0 to RM 1.3 (clam tissue collection areas 1 to 3), RM 1.3 to RM 2.6 (clam tissue collection areas 4 to 6), and above RM 2.6 (clam tissue collection areas 7 to 11) (Map 2-1). The average of the three segment-wide composite samples will be used to calculate the site-wide average for these chemicals. The segment composites will also provide information on differences in concentrations among the segments.

4.1.1.3 Number and location of composite samples

Clams collected in each of the 11 clam tissue collection areas will be used to create area-specific composites that will be analyzed for the human health risk drivers (i.e., inorganic arsenic, cPAHs, PCBs, and dioxins/furans) (Table 4-2). In each clam tissue collection area, the number of clams to be collected is based on the amount needed for the chemical analyses of both the clam area samples and the intertidal segment composite samples. Specifically, composites analyzed for cPAHs, PCBs, and dioxins/furans will consist of 10 whole-body clams (i.e., with the shell removed) to provide sufficient mass for analysis. For inorganic arsenic analysis, separate composites consisting of siphon skin tissue and remainder tissue (i.e., the remaining edible meat tissue) will be created from three clams and analyzed separately. This will be done because, as was reported by the Oregon Department of Environmental Quality (ODEQ) (Oregon DEQ 2015) and in the Regional Applied Research Effort (RARE) clam and arsenic study (Kerns et al. 2017), *M. arenaria* accumulate a larger fraction of both total and inorganic arsenic in their siphon skin (relative to the rest of the body). In addition, if available, up to five additional clams will be collected from each clam tissue collection area to provide additional options for compositing.

Table 4-2. LDW clam tissue sampling design for clam tissue DQOs 1 and 2

Chemical(s)	Tissue Type(s)	Composite Details	No. of Clams per Composite	No. of Composites
cPAHs, PCBs, dioxins/furans	whole body	separate composites for each of the 11 clam tissue collection areas	10[a]	11[b]
Inorganic arsenic	siphon skin	separate composites for each of the 11 clam tissue collection areas	3	11[b]
	remainder[c]			
Non-risk driver chemicals[d]	whole body	intertidal segment-wide composites across each of 3 segments	30–50[e]	3

Note: The number of clams required per composite was determined based on masses recorded from the 2017 cPAH siphon skin investigation (LDWG 2017). After removing the shell, the average per-clam weight of *M. arenaria* collected from the LDW was equal to 19 g for whole body, 3.1 g for siphon skin, and 16 g for remainder tissue (i.e., whole body minus siphon skin). Target numbers of clams were identified using conservative estimates of clam masses and the analytical mass requirements presented in Section 4.6.6.

[a] A composite of 10 clams will include sufficient mass for the analysis of both PCB Aroclors and congeners (see Section 4.6.6).

[b] One composite sample from each of the 11 potential clam tissue collection areas will be targeted; however, if enough clams cannot be collected for the composite sample, as many clams as possible will be collected, and EPA will be consulted to discuss prioritizing analytes.

[c] The remainder sample will be all the tissue remaining after the siphon skin has been removed (minus the shell). The whole-body concentrations will be calculated mathematically based on the fraction of the whole body represented by each tissue type.

[d] Non-risk driver chemicals for the LDW, as specified in the ROD (EPA 2014b), include vanadium, TBT, select SVOCs (BEHP, carbazole, HCB, and PCP), and organochlorine pesticides.

[e] A portion of the whole-body clam homogenate (i.e., the composite created for cPAHs, PCBs, and dioxins/furans) from each of the three to five clam tissue collection areas within a segment will be used to create a segment-wide composite sample.

BEHP – bis(2-ethylhexyl) phthalate
cPAH –carcinogenic polycyclic aromatic hydrocarbon
PCB – polychlorinated biphenyl
PCP – pentachlorophenol

EPA – US Environmental Protection Agency
HCB – hexachlorobenzene
LDW – Lower Duwamish Waterway
na – not applicable
ROD – Record of Decision
SVOC – semivolatile organic compound
TBT – tributyltin

In addition to analyzing the 11 area-specific composites for the human health risk drivers, a portion of the whole-body clam homogenate from each clam tissue collection area (i.e., the composite created for cPAHs, PCBs, and dioxins/furans) will be used to create a segment-wide composite sample that will be analyzed for the non-risk driver chemicals for the LDW, as specified in the ROD (EPA 2014b) (Table 4-2; Figure 4-2). These segment-wide composite samples will contain equal portions of tissue from each of the clam tissue collection areas within the given segment (Map 2-1).

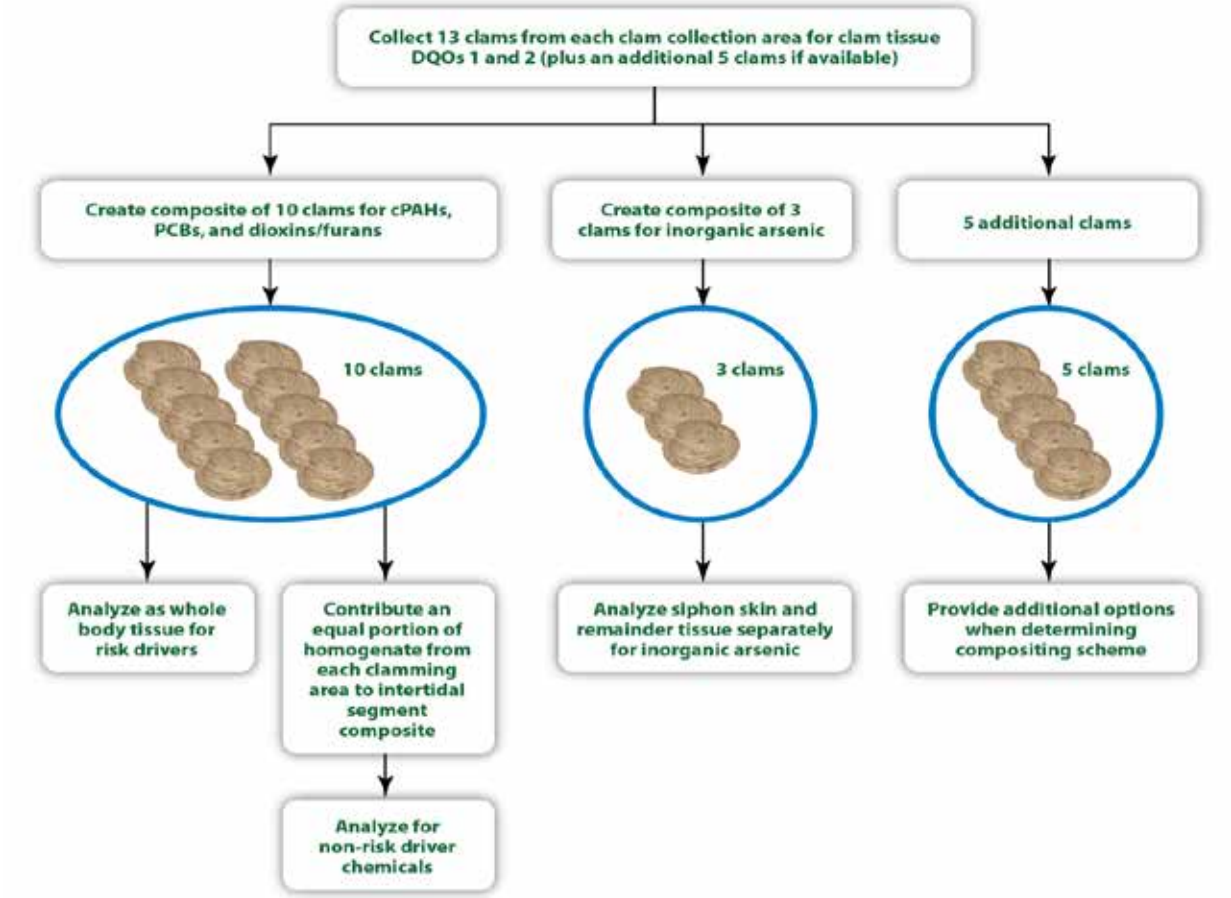

Figure 4-2.Clam compositing for clam tissue DQOs 1 and 2

Data from the composite samples will be used to estimate the site-wide mean and its 95UCL.[9] Clams included in the composite to be analyzed for inorganic arsenic will be separated into siphon skin and remainder components, which will be mathematically combined to represent whole-body clams based on the fraction of the whole body represented by each tissue type for the three clams in that composite. To calculate the inorganic arsenic concentrations in whole-body clams for comparison to the TTLs (ROD Table 21 (EPA 2014b)), reconstituted whole-body clam concentrations will be calculated using following Equation 1:

$$C_{WB} = (C_{siphon} \times F_{siphon}) + (C_{remainder} \times F_{remainder}) \qquad \textbf{Equation 1}$$

Where:

C_{WB} = estimated whole-body tissue concentration
C_{siphon} = siphon skin tissue concentration
F_{siphon} = average fraction of whole-body weight that is siphon skin
$C_{remainder}$ = remainder tissue concentration
$F_{remainder}$ = average fraction of whole-body weight that is remainder

4.1.2 Porewater DQO 1

In the cPAH porewater investigation, cPAHs will be analyzed in co-located intertidal sediment, clam tissue, and porewater. An overview of the proposed study design is provided in Figure 4-3 and discussed in the subsections that follow. In brief, co-located *M. arenaria* (3 clams per composite) and sediment composite samples will be collected from 20 candidate intertidal locations throughout the LDW (Map 2-2). Target species and organism sizes will be the same as those described in Section 4.1.1.1. These clam and tissue samples will be analyzed for cPAHs,[10] and a minimum of 10 locations—to be selected to represent the range of cPAHs in both sediment and tissue samples[11]—will be selected for analysis of cPAHs in passive samplers following *ex situ* exposures. A minimum of 10 samples was determined to be a reasonable number, both to allow for sufficient data to develop a regression relationship, and to ensure sufficient coverage of the range of observed cPAH concentrations. The final data analysis will involve evaluating the significance of the relationships among porewater, clam tissue, and sediment for individual cPAHs.

[9] Once these data are available, the distribution will be assessed using goodness of fit tests and probability plots. The 95UCL will be calculated using the most appropriate methods based on the observed distributional characteristics (i.e., distributional form, number of non-detects).

[10] Clam tissue will also be analyzed for lipids, and bulk sediment will also be analyzed for total organic carbon (TOC) and black carbon.

[11] Based on previously collected data, the cPAH TEQ in sediment ranged from 4.3 to 1,900 µg/kg in enhanced natural recovery/monitored natural recovery (ENR/MNR) areas (Table 4-3), although this range may have changed over time as a result of natural processes. No specific target range of cPAH TEQs in sediment has been identified for the cPAH porewater investigation, but coverage of as large a range as possible is desired. The selection of passive samplers for analysis will be based on unvalidated data for sediment and clam tissue.

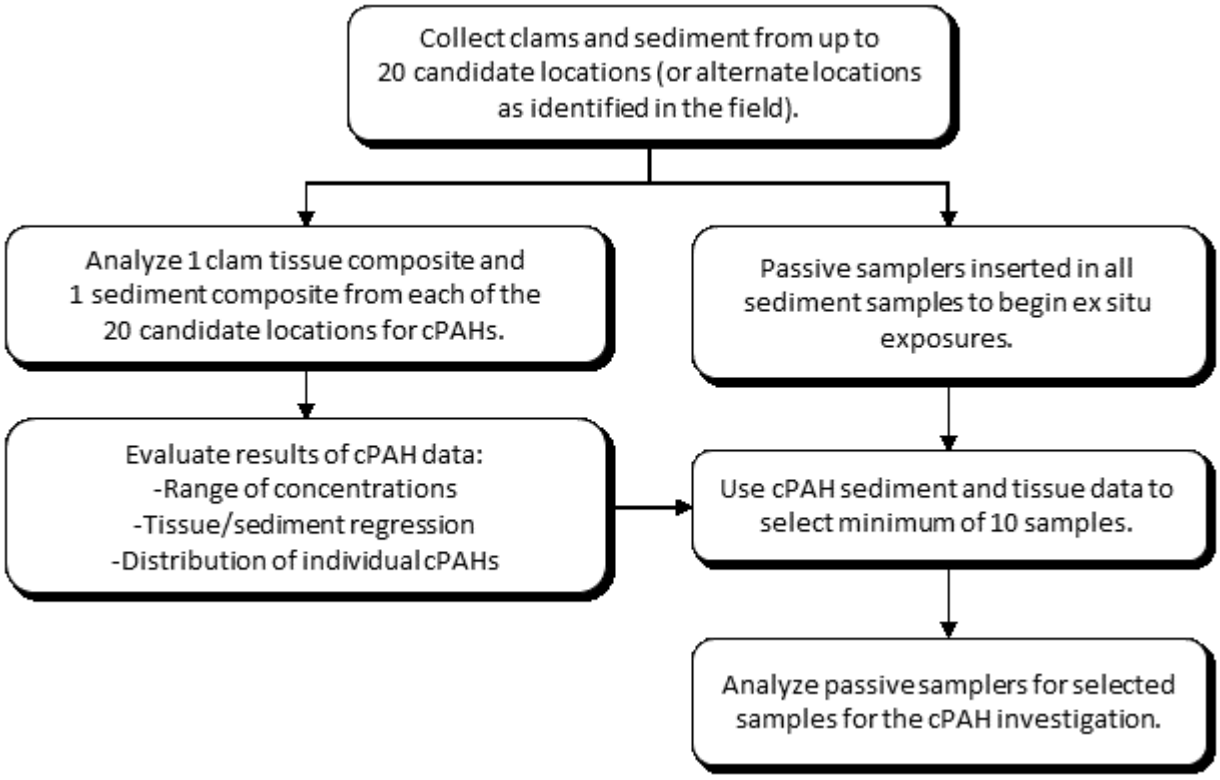

Figure 4-3. Conceptual cPAH porewater sampling design

4.1.2.1 Selection of sampling locations

Twenty candidate cPAH porewater investigation areas have been identified within the clam tissue collection areas in the LDW (Table 4-3, Map 2-2) based on the following criteria:

- Locations within clam tissue collection areas, with preference given to those locations with higher clam densities based on previous sampling efforts
- Locations with expected concentrations within the relevant range[12] of cPAH TEQs in ENR / MNR areas

[12] cPAH TEQs in ENR / MNR areas range from approximately 4.3 to 1,900 µg/kg, based on the LDW RI surface sediment dataset. This range is relevant because these areas will not be dredged or capped during the remedy.

Table 4-3. cPAH porewater sampling areas in order of increasing cPAH TEQ

Candidate cPAH Porewater Investigation Area	RM	Clam Tissue Collection Area	Estimated cPAH TEQ in Sediment based on RI/FS IDW Interpolation (µg/kg dw)		Remedy Type
			Estimated Concentration Category	Estimated Average TEQ[a]	
2	0.2	1	< 60	13	MNR
14	3.0	9	< 60	32	MNR
6	0.85	2	< 60	34	MNR
12	2.8	8	60–90	72	ENR
19	3.8	10	60–90	85	MNR
11	2.1	6	60–150	108	MNR
13	2.9	9	90–150	110	MNR
20	3.95	10	90–150	110	MNR
16	3.35	9	90–150	118	MNR
15	3.1	9	90–150	140	MNR
5	0.7	3	90–380	200	MNR
4	0.7	2	150–380	220	MNR
9	1.8	5	150–380	260	MNR
10	1.8	5	380–900	520[b]	MNR
8	1.5	4	380–1,500	750	dredge[c]
1	0.15	1	380–1,500	1,200	dredge[c]/MNR
7	1.45	4	380–1,500	1,300	dredge[c]
17	3.7	11	900–1,500	1,300	dredge[c]
18	3.8	11	> 1,500	1,900	dredge[c]
3	0.6	3	> 1,500	3,000	dredge
Summary of cPAH TEQ in candidate porewater investigation areas:			**Mean = 574 µg/kg Range = 13 to 3,000 µg/kg**		-
cPAH TEQ in site-wide ENR/MNR areas:			**Mean = 273 µg/kg Range = 4.3 to 1,900 µg/kg**		-

[a] Estimated average cPAH TEQs were calculated by averaging the interpolated cPAH TEQ values within each of the porewater sampling areas.

[b] No data were available within the candidate cPAH porewater investigation area; the closest sample had a cPAH TEQ of 520 µg/kg dw.

[c] Some sampling areas are in dredge areas (per Figure 18 in the ROD) to ensure the collection of a sufficient range of cPAH TEQs. It is acknowledged that the remedial boundaries and technology assignments portrayed in ROD Figure 18, titled *Selected remedy*, are likely to change following design. Thus, any reference to areas refers to preliminary area designations.

cPAH – carcinogenic polycyclic aromatic hydrocarbon
dw – dry weight
ENR – enhanced natural recovery
IDW – inverse distance weighted
MNR – monitored natural recovery
RI/FS – remedial investigation/feasibility study
RM – river mile
ROD – Record of Decision
TEQ – toxic equivalent

These 20 candidate locations were selected to represent a range of cPAH TEQs in sediment where clams may be present in reasonably high densities. Although the objective of this cPAH investigation is to represent the range of cPAHs observed in the

ENR/MNR areas, the 20 candidate locations were placed both in ENR/MNR areas and candidate dredge areas. The higher cPAH TEQs in the candidate dredge areas were included to help ensure that a wide range of cPAH concentrations is targeted, acknowledging that some degree of natural recovery may have occurred since the RI dataset was generated.

As needed, the locations may be modified in the field in order to utilize locations where clams can be collected in close proximity to one another. The selection of sampling locations will be based on the available information regarding the cPAH TEQs (Map 2-2) and the density of clams. Although the 11 clam collection areas (i.e., those identified on Maps 2-1 and 2-2) likely cover most available clam habitat in the LDW, some adjacent areas (e.g., north of clam tissue collection area 3) may also contain clams. If necessary to make optimal composite samples for the cPAH investigation, crews may collect and use clams found outside of the 11 clam collection areas, subject to EPA field approval. Utilizing locations with greater clam density will reduce the differences in cPAH concentrations to which the clams were exposed, and will improve the representativeness of the co-located sediment samples.

At each of the cPAH porewater investigation areas circled on Map 2-2, clam tissue and co-located sediment samples for the cPAH porewater investigation will be collected during the baseline clam tissue collection effort. The exact cPAH sampling locations within each cPAH porewater investigation area will be selected in the field based on clam density, so that sufficient clam tissue (three clams) can be collected from as small an area as possible. In addition to the global positioning system (GPS) coordinates for all clams, the approximate distance between clams included in the composite will be recorded in the field notes. Sufficient co-located sediment will also be collected and composited (one composite for each area, as described in detail in Section 4.2.2) to allow for bulk sediment and *ex situ* porewater measurements of selected composite samples.

4.1.2.2 Selection of passive samplers for analysis following ex situ *exposure*

In order to select which cPAH porewater investigation areas will be included in the porewater analysis, clam tissue and sediment collected from each area will be analyzed[13] for cPAHs and TOC in sediment, with an expedited analytical turnaround time. All 20 sediment samples collected will have passive samplers inserted into the sample jars and the jars will be placed on the shaker table at the laboratory. When exposure is complete (28 days[14]), the passive samplers will be removed and shipped to SGS-Axys. The samplers will then be extracted, and the extracts will be stored in sealed vials; sediment samples will be stored frozen.

[13] Sediment will also be analyzed for black carbon, and tissue will also be analyzed for lipids, but these analyses will not be expedited.

[14] All polyethylene (PE) strips will be exposed for the same duration and extracted on the same date.

The unvalidated co-located tissue and sediment chemistry data will be reviewed to identify a minimum of 10 sediment samples for which the corresponding *ex situ* sample extracts will be analyzed. Samples will be selected in consultation with EPA to represent the range of cPAH TEQs in sediment and tissue (e.g., if two samples have similar tissue and sediment cPAH TEQs, individual cPAH distribution, and carbon content, one of these samples may be excluded). Sample extracts not selected for analysis will be held until approval of the data evaluation report.

4.1.3 Compositing scheme for all DQOs

Because clams for clam tissue DQOs 1 and 2 and porewater DQO 1 will be collected at the same time, the compositing scheme must take into account the sampling needs of all DQOs.

As discussed in Section 4.1.1.3 and presented in Table 4-2 for the clam tissue DQOs, and discussed in Section 4.1.2 for the porewater DQO, the number of clams required per composite sample differs for each sampling objective. To determine which individual clams from a given area will be composited, consideration will be given to both the size of the clam (i.e., width) and the location of its collection within the clam tissue collection area.

- **Clam tissue DQOs 1 and 2** – Both composite samples (the whole-body composite [10 clams] and inorganic arsenic composite [3 clams]) will, to the extent possible, include clams from throughout the area where clams were found so that each composite is representative of the overall clam tissue collection area. In addition, only clams of the targeted size range (> 2 cm in width) will be used. The consideration of clam size and collection location in the compositing approach is expected to result in a more precise estimate of the population mean concentration for individual clam tissue collection areas and the whole LDW.
- **Porewater DQO 1** – Each composite will include three clams from as small an area as possible to improve the representativeness of the co-located sediment sample.

Because of the need to collect co-located sediment for the clams in the candidate cPAH porewater investigation area composites, clams to be included in these composites will be selected in the field, as described in Section 4.2. After each day of clamming, the clam tissue collection areas sampled and the numbers of clams collected will be summarized and shared with LDWG and EPA for informational purposes. At the conclusion of the overall sampling event, all clams, except those included in the candidate cPAH porewater investigation area composites, will be archived, frozen; a compositing memorandum will be prepared for EPA review to determine the clams to be included in the composites for clam tissue DQOs 1 and 2.

4.2 SAMPLING METHODS

Sample identification and field sampling will be performed following the protocols described in this section. Contingencies may arise during activities that will require modification of the general procedures outlined herein. 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

This section presents sample identification information for individual clams and clam composite samples, as well as co-located sediment samples and passive samplers for the cPAH porewater investigation.

4.2.1.1 Individual clam specimen ID

Unique alphanumeric IDs will be assigned to each individual clam (see Section 4.2.2.1) in the field and recorded on the target clam species form. The sample ID for individual clams will include the following:

- Project area ID (i.e., LDW) and two-digit year (18)
- Clam tissue collection area (i.e., C01 through C11)
- Two-letter species code (i.e., CL for clam) and three-digit number indicating the sequential number of the specimen captured during the sampling event

For example, the 11th clam collected in clam tissue collection area 1 will be identified as LDW18-C01-CL011. All relevant information for each individually wrapped and labeled clam—including specimen ID, width, sample date, sample time, and location (including GPS coordinates[15])—will be recorded manually on the target clam species collection form (Appendix B) or electronically. This information will be included as an appendix to the data report. Therefore, all pertinent data associated with each individual clam specimen will be tracked.

4.2.1.2 Clam composite sample ID

Composite clam samples will be identified using a similar convention; their IDs will include the following:

- Project area ID (i.e., LDW) and two-digit year (18)
- Clam tissue collection area (i.e., C01 through C11)

[15] High-accuracy GPS units (e.g., units estimated to have an accuracy of 1 ft under optimal conditions) will be used during clam tissue sampling. However, accuracy under typical field conditions can be diminished by structures and other circumstances.

- Species code (i.e., CL for clam) and a two-letter tissue type code (i.e., WB, SP, or RM for whole body, siphon skin, or remainder [after removal of the siphon skin], respectively)
- Composite ID (i.e., comp and a one-digit sequential composite number)

For example, the first whole-body clam composite sample collected from clam tissue collection area 1 will be identified as LDW18-C01-CLWB-comp1.

For the segment-wide intertidal composite samples that will be analyzed for the non-risk driver chemicals, the composite IDs will be similar to those for the clam composites, except that the clam tissue collection area portion of the ID will be replaced by an intertidal segment ID (i.e., S1, S2, and S3 for segment 1 [RM 0 to RM 1.3], segment 2 [RM 1.3 to RM 2.6], and segment 3 [above RM 2.6], respectively). For example, the whole-body clam composite sample collected from intertidal segment 2 will be identified as LDW18-S2-CLWB-comp1.

For the clam composite samples collected for the cPAH porewater investigation, IDs will include the following:

- Project area ID (i.e., LDW) and two-digit year (18)
- cPAH porewater investigation area (i.e., A01 through A20)
- Species code (i.e., CL for clam) and a two-letter tissue type code (i.e., WB for whole body)
- Composite ID (i.e., comp and a one-digit sequential composite number)

For example, the first whole-body clam composite sample collected from cPAH porewater investigation area 5 will be identified as LDW18-A05-CLWB-comp1.

4.2.1.3 Sediment samples for cPAH porewater investigation

For the co-located sediment samples for the cPAH porewater investigation, the sample IDs will include the following:

- Project area ID (i.e., LDW) and two-digit year (18)
- Sample type (i.e., SSCL for surface sediment co-located with clam samples)
- cPAH porewater investigation area ID (i.e., A01 through A20)

For example, the sediment sample collected from cPAH porewater investigation area 9 will be identified as LDW18-SSCL-A09.

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

4.2.1.4 Passive samplers

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

- Project area ID (i.e., LDW) and two-digit year (18)
- Sample type (i.e., PWPS for porewater passive sampler)
- cPAH porewater investigation area ID (i.e., A01 through A20)

For example, the passive sampler associated with cPAH porewater investigation area 5 will be labelled LDW18-PWPS-A05. The porewater concentrations calculated from those passive sampler results will be LDW18-PW-A05.

4.2.2 Field sampling methods

This section describes the methods used to collect clams (for clam tissue DQOs 1 and 2 and porewater DQO 1), as well as the method used to collect co-located surface sediment (for porewater DQO 1 only). The methods to determine porewater cPAH concentrations using PE passive samplers are described in Section 4.5.

4.2.2.1 Clam search and level of effort

Upon arriving at a given clam tissue collection area, field team members will begin searching for clams. Because *M. arenaria* are primarily located near the low tide line, search efforts will focus on that vicinity. Team members will search near the low tide line for the length of the clam tissue collection area to ensure that, to the extent possible, clams are spatially distributed throughout the area where they are present. Parts of the clam tissue collection areas where substrate is too soft to allow team members to search safely for clams (and in which clams are unlikely to be present) will be avoided during sample collection.[16] In addition, team members will ensure that the designated candidate cPAH porewater investigation areas are searched. However, as specified in the Work Plan (Windward and Integral 2017) and discussed in Section 4.1.2, the cPAH porewater investigation areas may be modified in the field depending on where clams are found. Any modification of these areas will also take into consideration the estimated cPAH TEQs in sediment, as shown on Map 2-2, to increase the likelihood that the modified locations successfully cover the range of cPAH TEQs.

For each clam tissue collection area, a maximum level of effort to collect the target number of clams has been identified based on the approximate area length in river miles. Although it is likely that the field team will successfully locate the target numbers of clams in each area in less than the maximum allotted time, the specified maximum level of effort provides a cutoff in the case that relatively few clams are

[16] Specifically, field staff members will not attempt to collect clams in soft substrate areas where they sink to deeper than mid-calf.

present in a given clam tissue collection area. Assuming a three-person field team, the maximum level of effort for each clam tissue collection area is as follows:

- **Small areas** (≤ 0.1 miles in length) – The three-person field team will search for clams for a maximum of two hours (i.e., six person-hours[17]).
- **Medium-sized areas** (> 0.1 to ≤ 0.3 miles in length) – The three-person field team will search for clams for a maximum of three hours (i.e., nine person-hours).
- **Large areas** (> 0.3 miles in length) – The 3-person field team will search for clams for a maximum of 4 hours (i.e., 12 person-hours).

Based on these criteria, the maximum level of effort for each of the clam tissue collection areas is shown in Table 4-4. If fewer than the target number of clams is found at a given beach (as specified in Section 4.2.2.2), the field team will continue searching for the duration of the maximum level of effort specified.[18] However, if no shows have been observed by the three-person field team after the first hour of searching within a given clam tissue collection area, the field crew will stop searching in that area and proceed to the next area. In this case, no clam tissue composites will be collected from the area in question. If any shows are observed or if any clams are collected, the field crew will continue searching for the duration of the maximum level of effort for a given area. A discussion of the prioritization of clam tissue analyses is presented in Section 4.2.2.3; prioritization may become relevant if insufficient clams are found at a given beach.

Table 4-4. Maximum level of effort by clam tissue collection area

Clam Tissue Collection Area	cPAH Porewater Investigation Area(s)	Determination of Maximum Level of Effort		
		Approximate Area Length (miles)	Area Size Category[a]	Maximum Level of Effort Assuming a 3-Person Field Team[b, c]
1	1, 2	0.2	medium	3 hours (i.e., 9 person-hours)
2	4, 6	0.35	large	4 hours (i.e., 12 person-hours)
3	3, 5	0.2	medium	3 hours (i.e., 9 person-hours)
4	7, 8	0.1	small	2 hours (i.e., 6 person-hours)
5	9, 10	0.1	small	2 hours (i.e., 6 person-hours)
6	11	0.05	small	2 hours (i.e., 6 person-hours)
7	none	0.15	medium	3 hours (i.e., 9 person-hours)
8	12	0.1	small	2 hours (i.e., 6 person-hours)
9	13, 14, 15, 16	0.45	large	4 hours (i.e., 12 person-hours)

[17] One person-hour is defined as the time spent searching by one individual for one hour.

[18] Although not anticipated, if the field team identifies an additional intertidal area just outside the clam tissue collection area that appears to potentially contain clams, the field team may determine that a higher maximum level of effort is required in that area (i.e., based on the new size of the clam collection area).

Clam Tissue Collection Area	cPAH Porewater Investigation Area(s)	Determination of Maximum Level of Effort		
		Approximate Area Length (miles)	Area Size Category[a]	Maximum Level of Effort Assuming a 3-Person Field Team[b, c]
10	19, 20	0.45	large	4 hours (i.e., 12 person-hours)
11	17, 18	0.1	small	2 hours (i.e., 6 person-hours)

[a] Areas were categorized as small (≤ 0.1 miles in length), medium (> 0.1 to ≤ 0.3 miles in length), or large (> 0.3 miles in length) for the purposes of establishing the maximum level of effort for each clam tissue collection area.

[b] The maximum level of effort is based on a 3-person field team. If a different size field team is utilized during field collection efforts, the total number of person-hours (i.e., 1 person-hour is defined as the time spent searching by 1 individual for 1 hour) will be the same as specified herein.

[c] If no shows have been observed by the three-person field team after the first hour of searching within a given clam tissue collection area (including any adjacent areas identified as potentially containing clams; see Section 4.1.2.1), the field crew will stop searching in that area and proceed to the next area. In this case, the maximum level of effort will be 1 hour (i.e., 3 person-hours). In such cases, the logbook will include a description of the search in the area and the absence of clam shows, and will include a description of substrate and other site characteristics that may be relevant to clam habitat.

cPAH – carcinogenic polycyclic aromatic hydrocarbons

4.2.2.2 Clam collection

Clams will be hand collected using shovels in the same manner as described in the benthic invertebrate QAPP for the RI (Windward 2004). Clams will be collected at low tide (e.g., ideally targeting days with low tides of -1.5 ft MLLW or lower, see Section 2.2) following the catch per unit effort (CPUE) method used in 2003 during the clam abundance survey and during subsequent clam collection efforts. This method involves field crew members actively searching for and collecting clams from areas within the intertidal clam tissue collection areas where clams are present, as determined by evidence of shows. Unbroken (i.e., intact) clams ≥ 2 cm in width (as measured from valve to valve; Figure 4-1) will be retained. If insufficient clams are available from a given area, smaller clams (e.g., ≥ 1.5 cm in width) will be collected and considered for analysis.

At each location where a show is observed, field team members will:

- Carefully remove sediment around the clam using a shovel or small hand tool (e.g., trowel) and retain the clam.
- Place a pre-labeled survey flag (e.g., numbered 1 through 20) to serve as a temporary identifier of the clam's location and record coordinates.
- Rinse excess sediment off the clam (using site water), wrap the clam in foil, and place the clam in a resealable plastic bag.
- Label the bag containing the clam with the number on the survey flag (i.e., temporary identifier) to track the clam collection location.
- Place the bagged and labeled clam in a cooler on ice and hold, in the dark, at ≤ 4 ± 2°C to await further processing once collection efforts in the clam collection area have been finished.

Because of the need for clams from a given area to be distributed into different composite samples, the field team will need to document where all clams from a given clam tissue collection area were collected prior to leaving that area. Table 4-5 presents a summary of the number of clams needed in each clam tissue collection area, including the clams needed for cPAH porewater investigation. Figure 4-4 presents an example compositing scheme for a single clam tissue collection area.

Table 4-5. Target number of clams per tissue collection area

Clam Tissue Collection Area	Intertidal Segment-wide Composite	cPAH Porewater Investigation Area(s)	No. of Clams Needed by Composite			Target No. of Clams Needed[b]
			Clam Tissue DQOs 1 and 2		Porewater DQO 1	
			Clams for Primary Composite[a]	Clams for Arsenic Composite	Clams for cPAH Porewater Investigation Composite	
1	1	1, 2	10	3	6 (3 per area)	19
2		4, 6	10	3	6 (3 per area)	19
3		3, 5	10	3	6 (3 per area)	19
4	2	7, 8	10	3	6 (3 per area)	19
5		9, 10	10	3	6 (3 per area)	19
6		11	10	3	3	16
7	3	none	10	3	0	13
8		12	10	3	3	16
9		13, 14, 15, 16	10	3	12 (3 per area)	25
10		19, 20	10	3	6 (3 per area)	19
11		17, 18	10	3	6 (3 per area)	19

[a] Target analytical mass for the area-specific composite includes sufficient mass for contribution to the intertidal segment composites to be analyzed for non-risk driver chemicals (including QC analyses).

[b] In addition to the target numbers of clams specified, five additional clams may be retained to provide additional options for compositing.

cPAH – carcinogenic polycyclic aromatic hydrocarbons
DQO – data quality objective
LDW – Lower Duwamish Waterway
QC – quality control

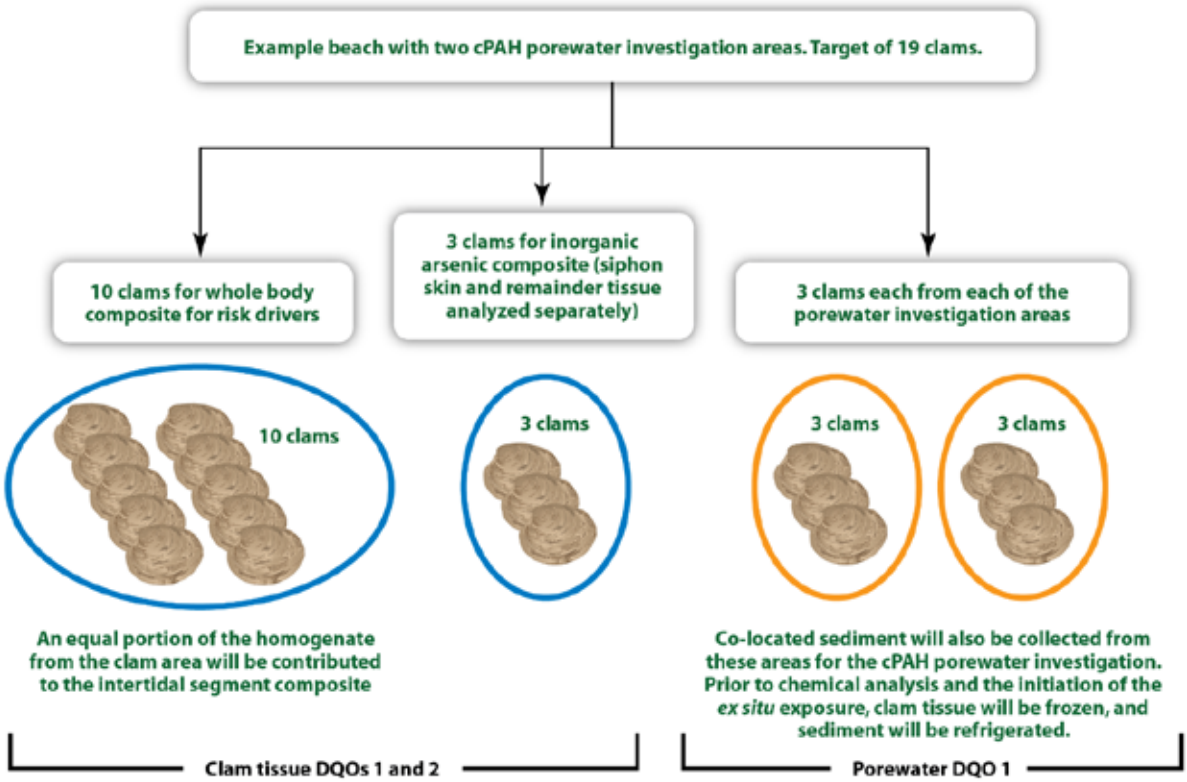

Figure 4-4. Compositing scheme for clams collected from an example clam tissue collection area

4.2.2.3 Field processing of clams

Once sufficient clams have been located for a given area (i.e., the target numbers of clams in Table 4-5 have been collected), or the maximum level of effort has been reached at a given clam tissue collection area (defined by the size of the area, as shown in Table 4-4), the field crew will begin processing clams. Field-processing of the clams will include the following steps (see Figure 4-4):

- **Identification of clams for cPAH porewater investigation area** – Three clams collected from as small an area as possible within a candidate cPAH porewater investigation area will be identified for each cPAH composite. If clams are not found in a target area, an alternate location where clams are found within close proximity to one another (and also as close as possible to the original cPAH porewater investigation area) will be identified by the field team.
- **Collection of co-located sediment** – At the location where the clams that will be included in the cPAH porewater investigation area composite are found, co-located sediment (0–10 cm deep) will also be collected, as described in Section 4.2.2.4. Sediment will be collected from as near as possible to the location

from which the clam was collected (e.g., from the side of the hole) to ensure that representative material from the full vertical extent (i.e., 0–10 cm) is collected.

- **Processing of individual clams** – All clams will be processed individually (i.e., assigned a sample ID, measured, and bagged with a label that contains this information). Location information (i.e., GPS coordinates) will be recorded for each clam to provide general information regarding the extent of the clam collection within a given area, and to assist in compositing decisions.

At the conclusion of the sampling event, all individuals will be held frozen to avoid deterioration of the clam tissue prior to processing and analysis (see Sections 4.3.3 and 4.4 for details).

If insufficient clams are found in a given clam tissue collection area, the selection of clams for inclusion in the clam tissue DQOs 1 and 2 composites vs. the porewater DQO 1 cPAH composite will consider the following:

- Sufficient clams for the clam tissue DQOs 1 and 2 composites will generally be prioritized. As specified previously, a total of 13 clams will be needed to fulfill this portion of the sampling objectives. Decisions regarding the compositing of clams will be determined as part of a compositing memorandum, which will be prepared for EPA review. This memorandum will also discuss prioritizing analytes if sufficient clams are not collected.
- Because of the need to collect co-located sediment samples for the cPAH porewater investigation composites (i.e., porewater DQO 1), clams to be included in these composites must be identified in the field. The FC (or designee) will consult with the PM or TM to determine whether, in certain areas, clams should be selected for the cPAH porewater investigation composites (rather than for the clam tissue DQOs 1 and 2 composites). This may occur to ensure that, based on the estimated cPAH TEQs in sediment (Table 4-3), clam tissue and co-located sediment samples are likely to cover the range of cPAH concentrations found in the LDW.

4.2.2.4 Collection of co-located sediment samples

In each of the cPAH porewater investigation areas where three clams are collected, a co-located sediment sample will be collected for analysis and for *ex situ* passive sampler exposure. The required sediment volume for each sample will be 52 oz., which will provide sufficient volume for both the *ex situ* exposure and chemical analyses (see Section 4.6.6).

For this sample, the field crew will collect an equal volume of sediment from a depth of 0 to 10 cm at each of the three locations where clams are collected, so that sufficient sediment will be retained (see Section 4.6.6 for details). Samples will be hand collected from the hole dug for the clam using a stainless steel trowel (or other similar tool), and the field crew will homogenize the sediment from each of the three clam collection locations in stainless steel bowls. Large gravel/rocks and shell debris will be excluded

from the homogenized sample to the extent practicable. Following homogenization, sediment will be distributed into jars as specified in Section 4.6.6.

If three clams are not collected for a given cPAH porewater investigation area (or alternate area identified by the field crew), as discussed in Section 4.2.2.3, no sediment sample will be collected from this area.

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 names / initials of responsible individuals performing the analyses, dates of sample extraction / preparation and analysis, and types of analyses being performed.

4.3.2 Sample custody procedures

Samples will be 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 chain of custody form will accompany all samples to the analytical laboratory. Each person who has custody of the samples will sign the chain of custody 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

The FC or designee 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 chain of custody forms prior to removing samples from the clam tissue collection area. At the end of each day, and prior to sample transfer, chain of custody 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. Chain of custody forms, which will accompany all samples, will be signed at each point of transfer. Copies of all chain of custody 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 chain of custody forms are properly signed upon receipt of the samples, and will note questions or observations concerning sample integrity on the chain of custody forms. The laboratories will contact the FC and project QA / QC coordinator immediately if discrepancies are discovered between the chain of custody forms and the sample shipment upon receipt.

4.3.3 Shipping requirements

Clams and sediment will be transported directly to ARI (i.e., by field staff or a courier). Sediment will be stored, refrigerated, prior to initiation of the *ex situ* porewater exposure. Clams will be stored frozen at ARI until compositing. Sample processing will occur as described in Section 4.4. Once clam tissue composite samples have been homogenized and frozen, subsamples will be transported to ALS, Brooks Applied Labs, and SGS-Axys (Figure 4-5).

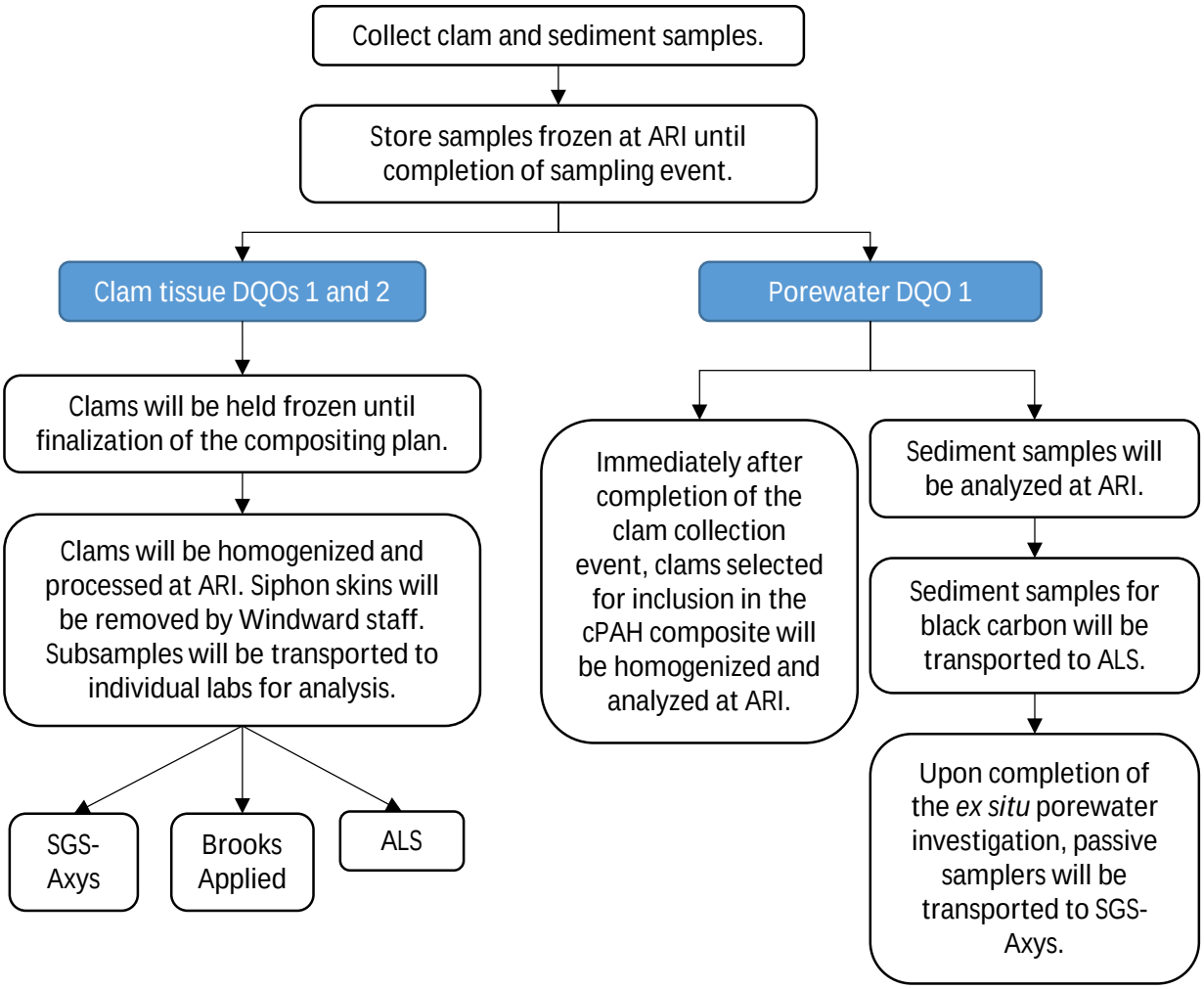

Figure 4-5.Sample shipping and handling process

Sediment samples will be transported directly to ARI (i.e., by field staff or a courier). Sediment samples for black carbon will be transported to ALS, and passive samplers will be transported to SGS-Axys. Prior to shipping, containers with sediment samples will be securely packed inside a cooler with ice packs. Passive samplers will be wrapped in foil, placed in resealable plastic bags, and securely packed inside a cooler with ice packs.

The original signed chain of custody forms for all samples 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 containing the clam tissue samples, sediment, and passive samplers will be checked by the laboratory upon receipt of the samples. The laboratory will specifically note any cooler that does not contain ice packs, or that is

not sufficiently cold (≤ 4 ± 2°C)[19] upon receipt. All samples will be handled so as to prevent contamination or sample loss. Any remaining tissue and sediment samples will be disposed of upon receipt of written notification by the Windward PM. Passive sampler extracts will be held until the laboratory is notified by the Windward PM.

4.3.4 Decontamination procedures

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. Ice chests will be scrubbed clean with Alconox® detergent and rinsed with distilled water after use to prevent potential cross contamination. To avoid contamination from melting ice, the wet ice will be placed in separate plastic bags. Prior to each use, sampling equipment (i.e., bowls and spoons used to collect co-located sediment) will be cleaned with Alconox® phosphate-free detergent and rinsed with deionized water.

4.3.5 Field-generated waste disposal

Excess sediment, generated equipment rinsates, and decontamination water[20] 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

Clam samples will be stored at ARI and held frozen until all clams have been collected. At the conclusion of the clam collection effort, the following will occur:

- Clams selected for inclusion in the cPAH porewater investigation composite samples will be homogenized and composited at ARI in preparation for the expedited analysis (as described in Section 4.1.2.2).

[19] As stated in validation guidance documents, sample shipping coolers should arrive at the laboratory with an internal temperature within the advisory range of 4 ± 2°C; however, due to the short transit distance and time from the site to ARI, the samples may not have reached this temperature by the time they arrive at the laboratory.

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

- All other individual clams will remain frozen until finalization of the compositing memorandum, at which point clams will be organized into composite groups by Windward or its designee. The clams to be included in each composite sample will be determined based on the compositing scheme described in Section 4.1.3, as well as any required modifications determined in consultation with EPA.
- For clams identified for inclusion in the inorganic arsenic composite, dissection of siphon tissue will be performed by Windward staff.

During the compositing and homogenization process, tissue specimens from each clam tissue collection area will be kept separate from one another and processed one at a time to ensure that individual specimens are tracked properly.

4.4.1.1 Compositing of clam tissues

Clam samples will be at least partially thawed before processing. Clams will be rinsed with deionized water and opened. The main body of each clam will be removed from the shell, rinsed, weighed, and placed into a pre-labeled composite jar. The siphon skin of each clam to be analyzed for inorganic arsenic will be carefully dissected from the main body of clam tissue and rinsed. Following the dissection, both the remainder tissue and siphon skin for each clam will be weighed prior to being placed in a pre-labeled composite jar. The creation of the intertidal segment- composites will involve combining equal aliquots of the homogenized whole-body clam sample from each clam tissue collection area within a given segment (see Section 4.1.1.2). Each segment composite will require 90 g for analysis. Within each segment, an equal aliquot will be taken from each area in that segment in order to obtain a 90-g composite sample. For example, if there are three areas within a segment then, 30 g will be taken from each area sample to obtain a final mass of 90 g.

Equipment will be cleaned between composites to avoid contaminating tissue samples during processing.

4.4.1.2 Clam homogenization

Clam composite samples will be homogenized using a blender or chopper following the ARI SOP. Homogenized samples will be blended into a creamy paste with no discernable bits remaining. ARI will transport frozen subsamples of clam tissue homogenates to SGS-Axys, Brooks Applied Labs, and ALS for analyses, as presented in Section 4.4.2.

4.4.2 Analytical methods

Chemical analyses of clam tissue will be conducted at four different laboratories (SGS Axys, ARI, Brooks Applied Labs, and ALS), and sediment samples will be analyzed at two laboratories (ARI and ALS) (Table 4-6). Chemical analyses of passive samplers will be performed by SGS-Axys (see Section 4.5.3). Analytical methods and sample handling requirements for all measurement parameters are presented in Table 4-7.

Table 4-6. Procedures to be conducted at each analytical laboratory

Laboratory	Analyses to be Conducted	Individual Analytes
Clam tissue		
SGS-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	lipids and percent solids
	metals	vanadium
	PCB Aroclors	Aroclor 1016, Aroclor 1221, Aroclor 1232, Aroclor 1242, Aroclor 1248, Aroclor 1254, and Aroclor 1260
	cPAHs	benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene
	SVOCs	bis(2-ethylhexyl) phthalate, PCP, carbazole, and HCB
	TBT	TBT
Brooks Applied Labs	inorganic arsenic	inorganic arsenic
ALS	organochlorine pesticides	aldrin, alpha-BHC, beta-BHC, total chlordane (alpha-chlordane, cis-nonachlor, gamma-chlordane, oxychlordane, trans-nonachlor), total DDTs (2,4'-DDD, 2,4'-DDE, 2,4'-DDT, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT) dieldrin, gamma-BHC, heptachlor, and heptachlor epoxide
Sediment		
ARI	conventionals	percent solids, TOC
	cPAHs	benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene
ALS	black carbon	black carbon
Passive samplers		
SGS-Axys	cPAHs	benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene

ALS – ALS Environmental-Kelso
ARI – Analytical Resources, Inc.
cPAH –carcinogenic polycyclic aromatic hydrocarbon
DDD – dichlorodiphenyldichloroethane
DDE - dichlorodiphenyldichloroethylene
DDT - dichlorodiphenyltrichloroethane
HCB – hexachlorobenzene
HpCDD – heptachlorodibenzo-*p*-dioxin
HpCDF – heptachlorodibenzofuran
HxCDD – hexachlorodibenzo-*p*-dioxin
HxCDF – hexachlorodibenzofuran
OCDD – octachlorodibenzo-*p*-dioxin
OCDF – octachlorodibenzofuran
PCB – polychlorinated biphenyl
PCP – pentachlorophenol
PeCDD – pentachlorodibenzo-*p*-dioxin
PeCDF – pentachlorodibenzofuran
SGS-Axys – SGS-Axys Analytical Services Ltd.
SVOC – semivolatile organic compound
TBT - tributyltin
TOC – total organic carbon
TCDD – tetrachlorodibenzo-p-dioxin
TCDF – tetrachlorodibenzofuran

Table 4-7. Analytical methods and sample handling requirements for clam tissue and sediment samples

Parameter[a]	Method	Reference	Extraction Solvent	Cleanup	Laboratory	Container	Preservative	Sample Holding Time
Clam tissue								
Lipids	gravimetric extraction	Bligh and Dyer (1959) (mod)	DCM/ acetone	na	ARI	aluminum foil (whole clams) glass jar (tissue homogenate and sediment)	freeze to ≤ -10°C	1 year
Percent solids	drying oven	PSEP (1997)	na	na	ARI	aluminum foil (whole clams) glass jar (tissue homogenate)	freeze to ≤ -10°C	6 months
Inorganic arsenic	HG-AFS	EPA 1632	na	na	Brooks Applied Labs	aluminum foil (whole clams) glass jar (homogenate)	freeze to ≤ -10°C	1 year
Vanadium	ICP-MS	EPA 6020A UCT-KED	na	na	ARI	aluminum foil (whole clams) glass jar (homogenate)	freeze to ≤ -10°C	6 months
TBT	GC/MS	EPA 3350-C Mod EPA 8270-SIM	0.10% tropolone/ DCM	hexylmagnesium bromide in diethyl ether alumina or silica gel	ARI	aluminum foil (whole clams) glass jar (homogenate)	freeze to ≤ -10°C	1 year to extract; extract within 14 days of thawing; analyze within 40 days of extraction
cPAHs	GC/MS	EPA 3350-C Mod EPA 8270D-SIM	DCM/ acetone	GPC (optional) silica gel (manual)	ARI	aluminum foil (whole clams) glass jar (homogenate)	freeze to ≤ -10°C	1 year to extract; extract within 14 days of thawing; analyze within 40 days of extraction
PCB Aroclors	GC/ECD	EPA 3350-C Mod EPA 8082A	DCM/ acetone	GPC (optional) acid	ARI	aluminum foil (whole clams) glass jar (homogenate)	freeze to ≤ -10°C	1 year to extract; extract within 14 days of thawing; analyze within 1 year of extraction
Other SVOCs	GC/MS	EPA 3350-C Mod EPA 8270D	DCM/ acetone	GPC	ARI	aluminum foil (whole clams) glass jar (homogenate)	freeze to ≤ -10°C	1 year to extract; extract within 14 days of thawing; analyze within 40 days of extraction

Parameter[a]	Method	Reference	Extraction Solvent	Cleanup	Laboratory	Container	Preservative	Sample Holding Time
PCB congeners	HRGC/ HRMS	soxhlet extraction EPA 1668C	DCM	biobead multi-layered acid/base silica alumina florisil	SGS-Axys	aluminum foil (whole clams) glass jar (homogenate)	freeze to ≤ -10°C	1 year to extract; extract within 14 days of thawing; analyze within 1 year of extraction if extracts are stored in the dark at < -10°C
Dioxins/ furans	HRGC/ HRMS	soxhlet extraction EPA 1613B	DCM/ hexane	biobead multi-layered acid/base silica florisil alumina carbon/celite	SGS-Axys	aluminum foil (whole clams) glass jar (homogenate)	freeze to ≤ -10°C	1 year to extract; extract within 14 days of thawing; analyze within 1 year of extraction if extracts are stored in the dark at < -10°C
Organochlorine pesticides	GC/MS	EPA 3541 EPA 8270D/1699 Mod	DCM	GPC carbon	ALS	aluminum foil (whole clams) glass jar (homogenate)	freeze to ≤ -10°C	1 year to extract; extract within 14 days of thawing; analyze within 40 days of extraction
Sediment								
Percent solids	drying oven	PSEP (1997)	na	na	ARI	glass jar	sediment - cool to ≤ 4 ± 2°C	6 months
TOC	high-temperature combustion	EPA 9060	na	na	ARI	glass jar	cool to ≤ 4 ± 2°C	28 days
cPAHs	GC/MS	EPA 3550C/ EPA 8270D-SIM	DCM/ acetone	silica gel	ARI	glass jar	freeze to ≤ -10°C	1 year to extract if frozen;14 days until extraction if refrigerated or when thawed, 40 days after extraction; store extracts at ≤ ≤ 4 ± 2°C and in the dark
Black carbon	infrared	Gustafsson (2001) - CTO Pretreatment/ Combustion (950°C)/ EPA 440.0	na	na	ALS	glass jar	cool to ≤ 4 ± 2°C	no established holding time; samples kept cold until drying at 105°C, which prevents potential biological action from occurring

Note: Analytical methods for passive samplers are discussed in Section 4.5.3.

[a] Individual analytes are listed in Table 4-6.

ALS – ALS Environmental-Kelso

ARI – Analytical Resources, Inc.

cPAH - carcinogenic polycyclic aromatic hydrocarbon

CTO – chemothermal oxidation

DCM – dichloromethane

EPA – US Environmental Protection Agency

GC/ECD – gas chromatography/electron capture detection

GC/MS – gas chromatography/mass spectrometry

GPC – gel permeation chromatography

HG-AFS – hydride generation-atomic fluorescence spectrometry

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

ICP-MS – inductively coupled plasma-mass spectrometry

na – not applicable

PCB – polychlorinated biphenyl

PSEP – Puget Sound Estuary Program

SGS-Axys – SGS-Axys Analytical Services Ltd.

SIM – select ion monitoring

SVOC – semivolatile organic compound

TBT – tributyltin

TOC – total organic carbon

UCT-KED – universal cell technology-kinetic energy discrimination

As was discussed in Sections 2 and 4.1.1, clam tissue composite samples will be analyzed for the human health risk drivers (inorganic arsenic, cPAHs, PCBs, and dioxins / furans) (Table 4-8). Lipids and percent solids will also be analyzed in each composite sample, and PCB congeners will be analyzed in six[21] composite samples in order to calculate PCB TEQs. In addition to the four human health risk drivers, to serve as a baseline for long-term monitoring, three intertidal segment-wide composite samples will be analyzed for the non-risk driver chemicals listed in ROD Table 14 (see Section 2). These chemicals include vanadium, TBT, select SVOCs (BEHP, carbazole, HCB, and PCP), and organochlorine pesticides. For the porewater DQO 1 (as discussed in Section 4.1.2), whole-body clam composites, co-located sediment samples, and passive samplers will be analyzed for cPAHs (Table 4-8). Co-located sediment samples will also be analyzed for TOC, black carbon, and percent solids, and clam tissue composites will also be analyzed for lipids and percent solids. The methods for all analytes are listed in Table 4-7.

Table 4-8. Numbers of composite samples to be analyzed in each analyte group

Analyte	Clam Tissue DQOs 1 and 2			Porewater DQO 1		
	Clams (Whole Body)	Clams (Siphon Skin)	Clams (Remainder)	Clams (Whole Body)	Sediment	Passive Samplers
Human health risk driver chemicals:						
PCB Aroclors	11	-	-	-	-	-
PCB Congeners	6	-	-	-	-	-
Dioxins/furans	11	-	-	-	-	-
cPAHs	11	-	-	20	20	≥ 10
Inorganic arsenic	-	11	11	-	-	-
Non-risk driver chemicals:						
Vanadium	3	-	-	-	-	-
TBT	3	-	-	-	-	-
Selected SVOCs	3	-	-	-	-	-
Organochlorine pesticides	3	-	-	-	-	-
Conventionals:						
Lipid	11	-	-	20	-	-
Percent solids	11	3	3	20	20	-
TOC	-	-	-	-	20	-
Black carbon	-	-	-	-	20	-

cPAH – carcinogenic polycyclic aromatic hydrocarbon
DQO – data quality objective
PCB – polychlorinated biphenyl
SVOC – semivolatile organic compound
TBT – tributyltin
TOC – total organic carbon

[21] In addition to the six clam tissue composites to be analyzed for PCB congeners, if none of the PCB Aroclors are detected in a sample, then the sample will be submitted for analysis of PCB congeners.

4.5 *EX SITU* POREWATER METHODS

This section describes the *ex situ* methods to be followed for the cPAH porewater investigation.

4.5.1 Passive sampler preparation

Passive samplers will be prepared for exposure to the 20 sediment samples collected for the cPAH porewater investigation, as discussed in Section 4.1.2. SGS-Axys will prepare the passive samplers and the test exposures will be conducted at ARI.

Using methods based on those outlined by Gschwend et al. (2012), SGS-Axys will prepare the passive samplers by cleaning a known mass of 25-µm-thick PE sheeting using sequential extractions with solvent (e.g., dichloromethane [DCM], methanol) (Appendix D).

The cleaned PE sheeting will be loaded with PRCs to allow non-equilibrium conditions between the PE and the sediment porewater to be quantified. The degree of equilibrium reached by the PRCs during the exposure will be used to calculate the degree of equilibrium reached by the target cPAH analytes. This information will be used to correct for non-equilibrium conditions, as described in Section 4.5.4. The deuterated PAHs to be used for PRCs are d10-fluoranthene and d14-dibenzo(a,h)anthracene. d10-fluoranthene has a molecular weight (MW) of 212 and d14-dibenzo(a,h)anthracene has a MW of 288. The PRC MW range is comparable to the MW range for the target cPAH compounds of 228-276.

The PRCs will be loaded by equilibrating the clean PE sheets with a methanol / water PRC solution in a glass container for at least seven days. Prior to delivery to ARI, the loaded PE sheets will be submerged in ultra-clean water for three days to remove the methanol.

To accurately determine initial pre-exposure PRC concentrations, three 0.1-g PE strips will be cut from the PE sheets after the PRC loading is complete, wrapped in aluminum foil, and stored, frozen, at SGS-Axys. These day-zero PE strips will be analyzed along with the PE strips retrieved from the porewater exposure batch tests (Section 4.5.2). Pre- and post-exposure PRC concentrations will be used either to confirm that equilibrium has been reached for all cPAHs, or to allow for the correction of non-equilibrium conditions between the PE and the sediment porewater.

The remaining PE sheets will be wrapped in aluminum foil and placed in a resealable plastic bag at ≤ 4 ± 2°C for shipment to ARI for use in the porewater exposures. Upon delivery, ARI will store the PE sheets in the refrigerator until the exposures are started.

4.5.2 Porewater exposure batch tests

Exposures will be conducted in accordance with design guidelines laid out by EPA et al. (2017), as detailed in Appendix D. The range of targeted cPAH and TOC concentrations has been used to determine the appropriate PE sampler mass. The

sampler mass must be sufficient to accumulate detectable cPAH concentrations, but not so large as to deplete the sediment cPAH concentrations (i.e., less than 1% of the mass of cPAHs in sediment). In the event that any exposure exceeds the 1% mass target, corrections for depletion will be made assuming a linear relationship for partitioning characteristics of the sediment organic matter, as described in Fagervold et al. (2010) and Ghosh et al. (2014).

Each sediment sample will be thoroughly homogenized, and approximately 1 kg ww of each sample will be placed in a wide-mouth glass jar with a Teflon™-lined cap. A 2-g/L sodium azide (biocide) solution will be added to each jar to achieve a well-formed slurry (80% water content) and inhibit microbial activity. A pre-weighed PE strip (0.1 g) will then be inserted into each jar. Sealed jars will be agitated in the dark on an orbital shaker table for one month to enhance contaminant mass transfer from the sediment porewater to the passive sampler, accelerating sampler equilibration rates. After the 28-day exposure period, the PE strips will be removed from their respective jars, rinsed with laboratory-grade deionized water, and gently wiped with clean laboratory wipes to remove any attached sediment. They will then be shipped to SGS-Axys as described in Section 4.3.3.

4.5.3 Passive sampler analysis

The PE strips will be extracted and analyzed for cPAHs following modified EPA method 8270 (Table 4-7). The passive sampler handling protocols are provided in Appendix D.

The lowest possible DLs for cPAHs in water based on the results from the PE passive samplers will be calculated using the laboratory analytical DLs for the PE strips, the partition coefficients between water and PE (from Gschwend et al. 2014), and any needed non-equilibrium corrections. Preliminary DLs calculated for each cPAH (assuming 100% equilibrium) are provided in Appendix D; however, these estimated DLs may be low (the actual DLs may be higher). Specifically, the high molecular weight cPAHs may not achieve equilibrium. The actual DLs will be greater than those calculated for any cPAH that does not reach equilibrium within the exposure period. Chemical analyses of the passive samplers will be performed by SGS-Axys (Table 4-9).

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

Parameter	Method	Reference	Extraction Solvent	Cleanup	Laboratory	Container	Preservative
cPAHs	GC/ LRMS	Soxhlet extraction modified EPA method 8270	DCM	biobead silica base wash/alumina (optional)	SGS-Axys	wire mesh holder tightly wrapped in foil and in sealable bag	refrigerate at ≤ 4 ± 2°C, can freeze after deployment

cPAH – carcinogenic polycyclic aromatic hydrocarbon
DCM – dichloromethane
EPA – US Environmental Protection Agency
GC/LRMS – gas chromatography/low-resolution mass spectrometry
SGS-Axys – Axys Analytical Services Ltd.

4.5.4 Calculation of freely dissolved cPAH concentrations from PE concentrations

Following analysis of the PE strips by SGS-Axys, validated cPAH concentrations in the PE strips will be used to calculate the concentrations of freely dissolved cPAHs in the sediment porewater, as summarized in Figure 4-6.

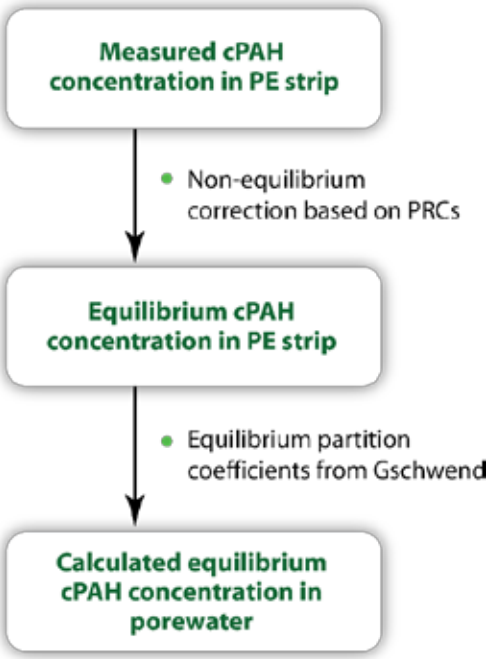

Figure 4-6. Calculation method for freely dissolved cPAHs in porewater from passive sampler

The first step to convert the measured PE concentrations to equilibrium PE concentrations will be based on the PRC concentrations in the samplers. PRC concentrations remaining in the PE sampler after the *ex situ* exposures will be used to estimate the degree of equilibrium between the sampler and the sediment porewater.

PRCs of different hydrophobicities have been selected, because the rates of mass transfer in and out of the sampler will depend on the hydrophobic properties of each cPAH. 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 cPAH using a PRC correction calculator accessed via a graphical user interface, as described by EPA et al. (2017).

Appendix D presents the physical and chemical properties that will be used to correct for non-equilibrium conditions. PRC calculator default values will be used for the properties of the cPAHs. 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 porewater in that exposure (Gschwend et al. 2014). The equilibrium PE cPAH 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 D), will then be used to calculate the freely dissolved cPAH concentrations in porewater (C_{PW}) using the Equation 2:

$$C_{PW} = \frac{C_{PE}}{K_{PEW}} \qquad \textbf{Equation 2}$$

Where:

C_{PE} = equilibrium PE cPAH concentration
C_{PW} = freely dissolved cPAH concentration in porewater
K_{PEW} = PE-to-water partition constant

4.6 ANALYTICAL DATA QUALITY OBJECTIVE AND CRITERIA

The analytical DQO for clam tissue and sediment samples and passive samplers 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 are presented in Section 4.6.6.

4.6.1 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 4.6.6). Equations 3a and 3b are used to express precision:

$$RPD = \frac{(\text{measured conc} - \text{measured duplicate conc})}{(\text{measured conc} + \text{measured duplicate conc}) / 2} \times 100$$ **Equation 3a**

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

Where:

$$SD = \sqrt{\frac{\sum (D_n - D_{ave})^2}{(n-1)}}$$ **Equation 3b**

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

4.6.2 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 4.6.6). Equation 4 is used to express accuracy for spiked samples:

$$\text{Percent recovery} = \frac{\text{spike sample result} - \text{unspiked sample result}}{\text{amount of spike added}} \times 100$$ **Equation 4**

4.6.3 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.

4.6.4 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.

4.6.5 Completeness

Completeness is a measure of the amount of data that is determined to be valid in proportion to the amount of data collected. Equation 5 is used to calculate completeness:

$$\textbf{Completeness} = \frac{\textbf{number of valid measurements}}{\textbf{total number of data points planned}} \times \mathbf{100} \qquad \textbf{Equation 5}$$

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.

4.6.6 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[22] will be used as the measure of sensitivity for each measurement process. Table 4-10 lists specific DQIs for laboratory analyses of clam tissue, sediment, and passive samplers.

Table 4-10. Data quality indicators for laboratory analyses

Parameter[a]	Units	Precision[b]	Accuracy[b]		Completeness
			SRM/LCS[c]	Spiked Samples	
Clam tissue					
Lipids	%	± 30%	na	na	90%
Percent solids	%	± 20%	na	na	90%
Inorganic arsenic	mg/kg ww	± 35%	na	65–135%	90%
Vanadium	mg/kg ww	± 30%	na	75–125%	90%
TBT	µg/kg ww	± 35%	na	20–130%	90%
cPAHs	µg/kg ww	± 35%	20–130%	20–130%	90%
PCB Aroclors[d]	µg/kg ww	± 35%	na	30–150%	90%
Other SVOCs	µg/kg ww	± 35%	na	20–130%	90%
PCB congeners	ng/kg ww	± 50%	40–145%	10–145%	90%
Dioxins/furans congeners	ng/kg ww	± 50%	70–130%	17–130%	90%
Organochlorine pesticides	µg/kg ww	± 50%	30–150%	30–150%	90%
Sediment					
cPAHs	µg/kg dw	± 35%	30–160%	30–160%	90%
Percent solids	%	± 20%	na	na	90%

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

Parameter[a]	Units	Precision[b]	Accuracy[b]		Completeness
			SRM/LCS[c]	Spiked Samples	
TOC	%	± 20%	80–120%	na	90%
Black carbon	wt%	± 20%	80–120%	na	90%
Passive samplers					
cPAHs	ng/g PE	± 20% of mean equivalent to 40% RPD	50–200%	15–130%	90%

[a] Individual analytes are listed in Table 4-6.

[b] Values listed are performance-based limits provided by ARI, ALS, SGS-Axys, and Brooks Applied Labs.

[c] An LCS may be used to assess accuracy when an SRM is unavailable. A tissue SRM will be analyzed for PCB congeners, dioxins/furans, cPAHs, and organochlorine pesticides.

[d] If a tissue sample has no detected PCB Aroclors, then the sample will be submitted for analysis of PCB congeners by EPA method 1668C with an estimated RL of 0.002 µg/kg.

ALS – ALS Environmental-Kelso
ARI – Analytical Resources, Inc.
cPAH - carcinogenic polycyclic aromatic hydrocarbon
dw – dry weight
LCS – laboratory control sample
na – not applicable
RL – reporting limit
RPD – relative percent difference
PCB – polychlorinated biphenyl
PE – polyethylene
SGS-Axys – SGS-Axys Analytical Services Ltd.
SRM – standard reference material
SVOC – semivolatile organic compound
TBT - tributyltin
TOC – total organic carbon
ww – wet weight

The laboratory MDL and RL values for each analytical method are compared to their respective TTL values in Table 4-11. All of the analytical methods are sufficiently sensitive, with the exception of the PCB Aroclor method. The PCB congener method will be used for all samples that do not have at least one detected PCB Aroclor, so the combination of these methods will ensure that the PCB concentrations are sufficiently sensitive relative to the PCB TTL. The sensitivity of the methods for cPAH and dioxin/furan TEQs is difficult to assess, because TEQs are calculated values and not analytes. The analytical methods for cPAHs and dioxins/furans are the most sensitive available, and cPAHs and dioxins/furans typically have high detection frequencies in clam tissues.

Table 4-11. Summary of clam tissue analytes, methods, and RL goals for each analyte

Analyte	Method	Laboratory MDL	RL	TTL (ROD Table 21)
Human Health Risk Drivers				
Inorganic arsenic (mg/kg ww)	EPA 1632	0.004	0.01	0.09
cPAH TEQ (µg/kg ww)	EPA 8270D-SIM	na[a]	na[b]	0.24
Total PCBs (µg/kg ww)	EPA 8082A (Aroclors)	2.37[c]	4[d,e]	0.42
PCB congeners (sum) (µg/kg ww)	EPA 1668C	0.0002[f]	0.002[g]	0.42
Dioxin/furan TEQ (ng/kg ww)	EPA 1613B	na[h]	na[i]	0.71

Analyte	Method	Laboratory MDL	RL	TTL (ROD Table 21)
Non-risk Drivers				
Metals and organometals				
Vanadium (mg/kg ww)	EPA 6020A	na[j]	0.004	na
TBT (µg/kg ww)	EPA 8270D-SIM	0.450	3.86	na
SVOCs				
BEHP (µg/kg ww)	EPA 8270D	28.0[c]	50.0	na
Carbazole (µg/kg ww)	EPA 8270D	7.37[c]	20.0	na
HCB (µg/kg ww)	EPA 8270D	31.3[c]	20.0	na
PCP (µg/kg ww)	EPA 8270D	4.74[c]	100	na
Organochlorine pesticides				
Aldrin (µg/kg ww)	EPA 8270D/1699 Mod	0.22	1.0	na
alpha-BHC (µg/kg ww)	EPA 8270D/1699 Mod	0.26	1.0	na
beta-BHC (µg/kg ww)	EPA 8270D/1699 Mod	0.4	1.0	na
Total chlordane[k] (µg/kg ww)	EPA 8270D/1699 Mod	0.13	2.0	na
Total DDTs[l] (µg/kg ww)	EPA 8270D/1699 Mod	0.46	2.5	na
Dieldrin (µg/kg ww)	EPA 8270D/1699 Mod	0.22	1.0	na
gamma-BHC (µg/kg ww)	EPA 8270D/1699 Mod	0.17	1.0	na
Heptachlor (µg/kg ww)	EPA 8270D/1699 Mod	0.09	1.0	na
Heptachlor epoxide (µg/kg ww)	EPA 8270D/1699 Mod	0.061	1.0	na

[a] cPAH TEQ is a calculated value and not an analyte. The MDL values for the cPAH compounds used in the calculation of the TEQ range from 0.488 to 1.53 µg/kg ww (see Appendix C).

[b] cPAH TEQ is a calculated value and not an analyte. The RL values for the cPAH compounds used in the calculation of the TEQ range from 5 to 10 µg/kg ww (see Appendix C).

[c] EPA SW846 methods no longer require 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.

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

[e] If a sample has no detected PCB Aroclors, then the sample will be submitted for analysis of PCB congeners by EPA Method 1668C with an estimated RL of 0.002 µg/kg.

[f] The PCB congener EDL is based on the laboratory-estimated DL from SGS-Axys and represents the value for an individual PCB congener. Individual congener EDLs are listed in Appendix C. EDL is a sample-specific DL. The value provided is an estimate, and the sample-specific values will vary by sample

[g] The PCB congener LMCL is based on the laboratory minimum calibration level from SGS-Axys and represents the value for an individual PCB congener. Individual congener LMCLs are listed in Appendix C. The LMCL is SGS-Axys's lowest calibration limit. Detected values below the LMCL will be J-qualified. The reported LMCL will be adjusted based on the sample mass of each sample.

[h] Dioxin/furan TEQ is a calculated value and not an analyte. The EDL value for the dioxin/furan congeners used in the calculation of the TEQ was 0.05 ng/kg ww (Appendix C). The value provided is an estimate, and the sample-specific values will vary by sample mass and the analytical conditions at the time of analysis.

[i] Dioxin/furan TEQ is a calculated value and not an analyte. The LMCL values for the dioxin/furan congeners used in the calculation of the TEQ range from 0.2 to 2.0 ng/kg ww (see Appendix C). The LMCL is SGS-Axys's lowest calibration limit. Detected values below the LMCL will be J--qualified. The reported LMCL will be adjusted based on the sample mass of each sample.

[j] EPA SW846 methods no longer require MDL values.

[k] The components of total chlordane include alpha-chlordane, cis-nonachlor, gamma-chlordane, oxychlordane, and trans-nonachlor. Individual component MDLs and RLs are listed in Appendix C.

[l] The components of total DDT include 2,4'-DDD, 2,4'-DDE, 2,4'-DDT, 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT. Individual component MDLs and RLs are listed in Appendix C.

BEHP – bis(2-ethylhexyl) phthalate
BHC – benzene hexachloride
COC – chemical of concern
cPAH – carcinogenic polycyclic aromatic hydrocarbon
DDD – dichlorodiphenyldichloroethane
DDE – dichlorodiphenyldichloroethylene
DDT – dichlorodiphenyltrichloroethane
DL – detection limit
EDL – estimated detection limit
EPA – US Environmental Protection Agency
HCB – hexachlorobenzene
J – estimated concentration
LLOQ – lower limit of quantitation
LMCL – lower method calibration limit
MDL – method detection limit
na – not available
PCB – polychlorinated biphenyl
PCP – pentachlorophenol
RL – reporting limit
ROD – Record of Decision
SGS-Axys – SGS-Axys Analytical Services Ltd.
SIM – selected ion monitoring
SVOC – semivolatile organic compound
TBT – tributyltin
TCDD – tetrachlorodibenzo-*p*-dioxin
TEF – toxic equivalency factor
TEQ – toxic equivalent
TTL – target tissue level
ww – wet weight

Standard tissue mass requirements are specified to meet RLs for each particular analytical method. Table 4-12 summarizes the tissue masses needed for clam tissue. The masses listed include the masses required for QC samples. The total mass required for standard analyses (i.e., excluding QC samples) is 92 g of clam tissue. The total masses targeted for the clam tissue sampling (i.e., including QC samples) are 3.5 g for the inorganic arsenic samples, 107.5 g for the other human health risk driver samples (including sufficient mass for PCB congeners in a subset of samples), 70 g for the non-risk driver chemicals samples, and 10 g for conventionals.

Table 4-12. Tissue mass required for analysis

Analyte	Tissue Mass[a] (g)	Total for Composite Sample (g)
Human health risk drivers		
Inorganic arsenic	3.5	3.5 (inorganic arsenic)
cPAHs	30	107.5 (other human health risk drivers)
PCB Aroclors	37.5	
PCB congeners and dioxins/furans	40	
Non-risk drivers		
SVOCs	37.5	70 (non-risk driver chemicals)
TBT	15	
Vanadium	7.5	
Organochlorine pesticides	10	
Conventionals		
Lipids	taken from PCB Aroclor or SVOC extract[b]	na
Percent solids	10	10

[a] Tissue mass listed includes mass required for QC samples.
[b] Solvent extraction with acetone/DCM for both PCB Aroclors and SVOCs.

cPAH – carcinogenic polycyclic aromatic hydrocarbon
DCM – dichloromethane
PCB – polychlorinated biphenyl
QC – quality control
SVOC – semivolatile organic compound
TBT – tributyltin

Table 4-13 summarizes the sample volume needed for each sample type for the co-located sediment samples. The masses listed include those required for QC samples.

Table 4-13. Sediment mass required for analysis and *ex situ* exposure

Analyte	Sediment Mass (g ww)	Laboratory-requested Jar Size
TOC	30	4-oz. wide-mouth glass
Percent solids	45	
cPAHs	60	8-oz. wide-mouth glass
Black carbon	30	8-oz. wide-mouth glass
Ex situ exposure	1,000	2 16-oz. wide-mouth glass[a]

[a] Two 16-oz. jars will be required for 1 kg of sediment for the *ex situ* exposure.

cPAH – carcinogenic polycyclic aromatic hydrocarbon
TOC – total organic carbon
ww – wet weight

4.7 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.

4.7.1 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. For the clam tissue sampling, rinsate blanks are not relevant. Field duplicate clam composite samples will not be collected, although matrix replicates of homogenized tissue samples will be analyzed as described in the following section. In addition, one sediment field duplicate will be collected.

A passive sampler exposure blank will be used to assess possible contamination due to the high sorptive capacity of the passive samplers. The exposure blank will be prepared at the same time and following the same methods as the passive samplers. It will be agitated with distilled water for the duration of the porewater exposure in the laboratory.

4.7.2 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 spiked samples.

4.7.2.1 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 4-14. 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 4-14. 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
Clam tissue									
Lipids	na	na	na	na	1 per 20 samples or per batch	na	na	na	na
Percent solids	na	na	na	na	1 per 20 samples or per batch	na	na	na	na
Inorganic arsenic	prior to analysis	after initial calibration	every 10 samples	na	1 per batch or SDG	1 per batch or SDG	1 per batch or SDG	1 per prep batch	na
Vanadium	prior to analysis	after initial calibration	every 10 samples	na	1 per batch or SDG	1 per batch or SDG	1 per batch or SDG	1 per prep batch	na
TBT	prior to analysis	after initial calibration	every 10 samples	na	na	1 per batch or SDG	1 per batch or SDG	1 per prep batch	each sample
cPAHs	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
PCBs Aroclors	prior to analysis	after initial calibration	every 10–20 analyses or 12 hours	na	na	1 per batch or SDG	1 per batch or SDG	1 per prep batch	each sample
SVOCs	prior to analysis	after initial calibration	every 10–20 analyses or 12 hours	na	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[c]	1 per batch or SDG	na	na	1 per prep batch	each sample
Dioxins/furans congeners	prior to analysis	after initial calibration	every 12 hours	1 per prep batch[c]	1 per batch or SDG	na	na	1 per prep batch	each sample
Organochlorine pesticides	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

Analysis Type	Initial Calibration	Initial Calibration Verification (second source)	Continuing Calibration Verification	SRM or LCS[a]	Laboratory Replicates	MSs	MSDs	Method Blanks	Surrogate Spikes
Sediment									
Percent solids	Na	na	na	na	1 per 20 samples or per batch	na	na	na	na
TOC	Na	na	na	1 per 20 samples or per batch[d]	1 per 20 samples or per batch	1 per 20 samples or per batch	na	1 per 20 samples or per batch	na
cPAHs	prior to analysis	after initial calibration	every 12 hours	1 per prep batch[d]	na	1 per batch or SDG	1 per batch or SDG	1 per prep batch	each sample
Black carbon	prior to analysis	after initial calibration	every 20 samples and at the end of run	3 (1 high and 2 low range) per batch or SDG	1 per batch or SDG	na	na	1 per batch or SDG	na
Passive Sampler									
cPAHs	prior to analysis	after initial calibration	every 10–20 analyses or 12 hours	1 per prep batch[d]	1 per 20 samples	na	na	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 to exceed 20 samples.

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

[b] SRM 1974c will be used to assess accuracy for cPAHs and organochlorine pesticides.

[c] CARP-2 will be used to assess accuracy for PCB congeners and dioxin/furans.

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

cPAH – carcinogenic polycyclic aromatic hydrocarbon
LCS – laboratory control sample
MS – matrix spike
MSD – matrix spike duplicate
na – not applicable or not available
PCB – polychlorinated biphenyl
SDG – sample delivery group
SRM – standard reference material
SVOC – semivolatile organic compound
TBT – tributyltin
TOC – total organic carbon

4.7.2.2 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; 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 4-14 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.

SGS-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.[23] 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.

[23] 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 PCB congeners, dioxins/furans, cPAHs, and organochlorine pesticides. An LCS sample can be used to assess accuracy if an appropriate SRM is not available. An LCS will be analyzed for conventional, inorganic, SVOC, and PCB Aroclor 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 separate samples, 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. For the passive samplers, one sediment sample will be identified for replicate analysis. Two passive sampler samples will be inserted into the single sediment sample and analyzed as replicates.

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 of tissue and sediment, 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. An MS/MSD pair will not be analyzed for passive sampler samples.

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 to calibrate and quantify 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-labelled cPAHs prior to deployment. The deuterated PAHs to be used for PRCs will include d10-fluoranthene and d14-dibenzo(a,h)anthracene. The change in PRC concentration during deployment will be used to help quantify the non-equilibrium conditions between the porewater and the PE for various compounds.

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 samplers 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 4.5.

4.8 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 differential GPS unit[24] 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.

[24] High-accuracy GPS units (e.g., units estimated to have an accuracy of 1 ft under optimal conditions) will be used during clam tissue sampling. However, accuracy under typical field conditions can be diminished by structures and other circumstances.

4.9 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 to be 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.

A Trimble© SPS461 or similar GPS receiver unit (i.e., a unit estimated to have an accuracy of 1 ft under optimal conditions) will be employed to document clam collection locations. 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.

4.10 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.

4.11 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 will be 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 4-10) 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 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 DQIs specified in this QAPP.

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

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 1 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
- Ion abundance ratio compared to theoretical ratios for samples analyzed by EPA methods 1613b and 1668c

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 chemistry data will be performed in accordance with the QA

requirements of the project, the technical specifications of the analytical methods indicated in Table 4-7, 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. 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 data report. Only validated data with appropriate qualifiers will be released for general use.

6.2 RECONCILIATION WITH DATA QUALITY INDICATORS

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 DQIs were not met will be identified. The usability of the data will be determined in terms of the magnitude of the DQI exceedance.

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Harbor I.

Clam Tissue Area 1

Clam Tissue Area 3

Clam Tissue Area 2

Kellogg I.

Slip 1

Clam Tissue Area 4

Slip 2

Clam Tissue Area 5

MATCH LINE MIDDLE PANEL

Clam Tissue Area 5

LEFT PANEL MATCH LINE

Clam Tissue Area 6

Slip 3

Clam Tissue Area 8

Slip 4

Clam Tissue Area 7

Clam Tissue Area 9

Clam Tissue Area 10

MATCH LINE RIGHT PANEL

Clam Tissue Area 10

MIDDLE PANEL MATCH LINE

Slip 6

Upper Turning Basin

Clam Tissue Area 11

Clam tissue sampling area[a]

Clam tissue intertidal segments

- Segment 1
- Segment 2
- Segment 3

Intertidal segment boundary

Early Action Area

LDW Superfund Boundary

Navigation Channel

River mile

[a] Based on LDW RI clam tissue sampling areas.

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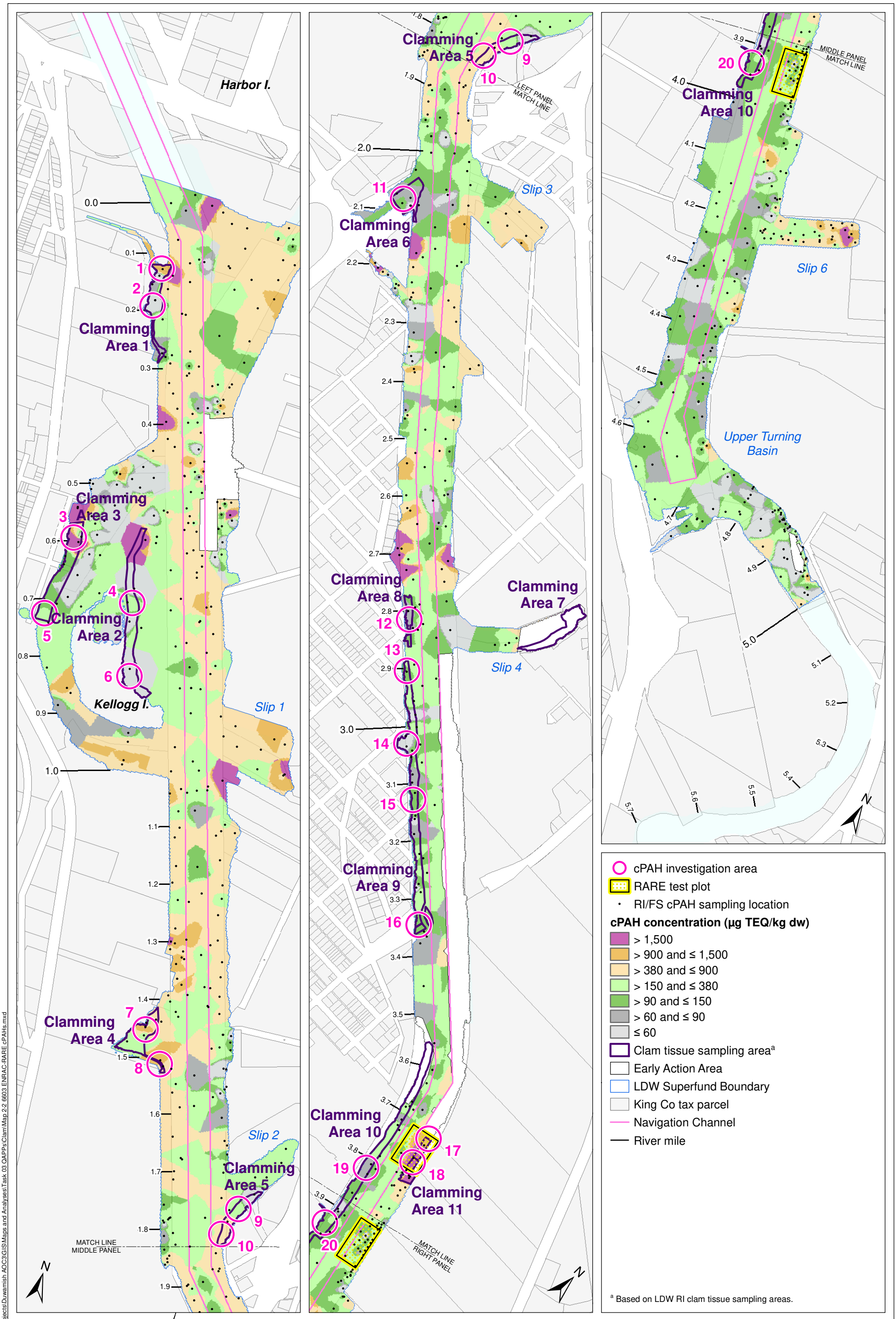
0 0.1 0.2 Miles

0 0.2 0.4 Kilometers

Scale is the same for each inset map

Map 2-1. Clam tissue collection areas and intertidal segments

Prepared by craigh, 11/21/2017; W:\Projects\Duwamish AOC3\GIS\Maps and Analyses\Task 03 QAPPs\Clam\Map 2-1 6523 Clam sampling plan.mxd



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0 0.1 0.2 Miles

0 0.2 0.4 Kilometers

Scale is the same for each inset map

Map 2-2. cPAH porewater investigation areas and RI/FS cPAH interpolation

Prepared by craigh, 1/5/2018; W:\Projects\Duwamish AOC3\GIS\Maps and Analyses\Task 03 QAPPs\Clam\Map 2-2 6603 ENRAC-RARE cPAHs.mxd

Lower Duwamish Waterway Group

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LOWER DUWAMISH WATERWAY CLAM 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 Clam Collection 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

4/2/18
Date

Name
Corporate Health and Safety Manager

4/2/18
Date

Name
Field Coordinator/Health and Safety Officer

4/2/18
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 clam and co-located sediment 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 clam and co-located sediment samples
- 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 under wet or rainy conditions or on the shoreline where slick rocks are found requires careful attention to minimize the risk of falling. Slips can be minimized by wearing boots with good tread, made of material that does not become overly slippery when wet. The same care should be used when on a boat or vessel that may be used to access the sampling site.

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.

4.1.2 Sampling equipment

No hazards from using the sampling equipment during this project are anticipated. Clams will primarily hand-collected by digging with a shovel or trowel, and co-located sediment will also be hand-collected using a stainless steel towel (or other similar tool) and bowl, as described in Section 4.2.2 of the QAPP.

4.1.3 Falling overboard

Sampling locations along the shoreline may be accessed from a boat. 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 travelling from site to site by 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.

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

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.

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, the chemicals of concern in sediment 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, water, tissue, 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 water is not considered a major route of exposure for this project. Crew is advised to take care to minimize exposure.

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 water or 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.

4.3 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 sampling.

Table A-1. Activity hazard analysis

Activity	Hazard	Control
Clam and co-located sediment sampling[a]	Slips and trips	Use extra care when walking along uneven and unstable surfaces along the shoreline, and under wet/slippery conditions. Wear boots with good tread.
	falling overboard	Use care in boarding/departing from the vessel. Wear a PFD.
	skin contact with contaminated sediments or liquids	Wear modified Level D PPE.
	back strain	Use appropriate lifting technique when lifting sample coolers, or seek help.
	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.
	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.

[a] Boating hazards are also included because a boat will be used to transport crew members to sampling sites.

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 near the intertidal sampling area. 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.

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

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 available. 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
- 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 clam and co-located sediment samples (e.g., shovels, trowels, stainless steel spoons, and stainless steel bowls) will be scrubbed with Alconox® detergent 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 sediment collected for the samples will be returned to sampling site.

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 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. She will designate her replacement during those times when she is not present 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	
Suzanne Replinger	206.812.5435

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, she 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:

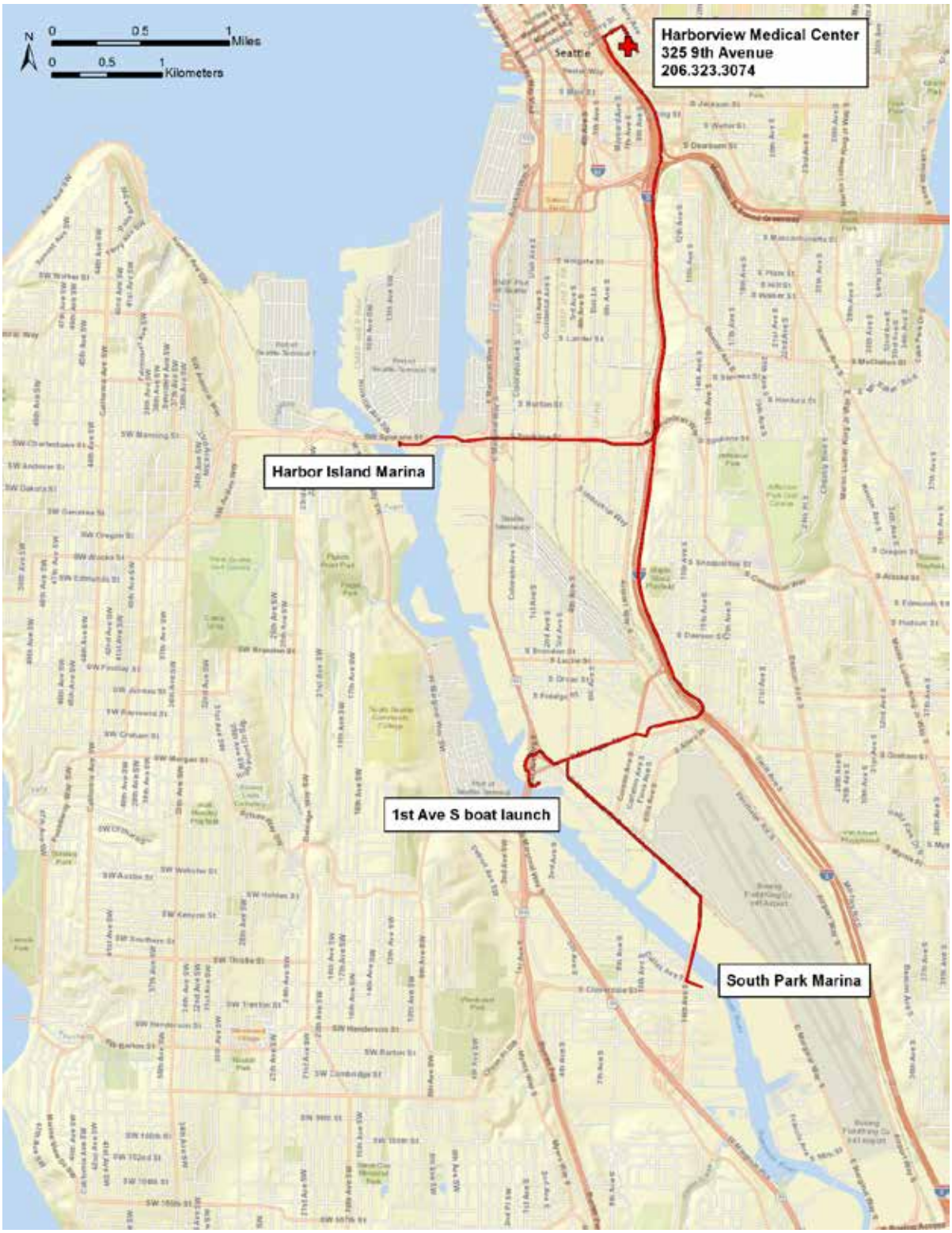
- Drive east on South River Street.
- Turn left on Occidental Avenue South.
- Turn left on East Marginal Way South.
- Turn right on South Michigan Street.
- Look for entrance ramps to I-5 Northbound.
- Drive north on I-5.
- Take the James Street exit.
- Drive east on James Street to 9th Avenue.
- Turn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



Map A-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

- Clam Collection Form
- Surface Sediment Collection Form
- Forms for *ex situ* exposures:
  - Percent Moisture Benchsheet
  - Exposure Setup Benchsheet
  - Daily Conditions Benchsheet
- Protocol Modification Form

CLAM COLLECTION FORM

Project Name: _____ **Task No.:** _____

Date: _____ **Start/Stop Time:** _____

Weather: _____ **Clam Area ID:** _____

Sampling Method: _____ **cPAH Area ID(s):** _____

Crew: _____ _____

Clam ID	Width (mm)	Coordinates		Composite type				Comment
		Latitude	Longitude	cPAH, PCBs, D/F	Inorganic arsenic	cPAH -porewater	Extra	

SURFACE SEDIMENT COLLECTION FORM

Project Name: _____ **Project no.:** _____

Date: _____ **Weather:** _____

Sampling Method: _____ **Crew:** _____

LOCATION	**Location ID:**			
Latitude/Northing(Y):				**Longitude/Easting(X):**
Time of sample	**Bottom depth (m)**	**Penetration depth (cm)**	**Acceptable sample (Y/N)**	**Comments**
SAMPLE DATA	**Sample ID:**			
Sediment type	**Sediment color**	**Sediment odor**		**Comments:**
cobble	brown surface	none	H_2S	
gravel	drab olive	slight	petroleum	
sand (F M C)	brown	moderate	other:	
silt	gray	strong		
clay	black			

LOCATION	**Location ID:**			
Latitude/Northing(Y):				**Longitude/Easting(X):**
Time of sample	**Bottom depth (m)**	**Penetration depth (cm)**	**Acceptable sample (Y/N)**	**Comments**
SAMPLE DATA	**Sample ID:**			
Sediment type	**Sediment color**	**Sediment odor**		**Comments:**
cobble	brown surface	none	H_2S	
gravel	drab olive	slight	petroleum	
sand (F M C)	brown	moderate	other:	
silt	gray	strong		
clay	black			

PERCENT MOISTURE BENCHSHEET

Pan ID	Sample ID	Tare (g)	Wet Wt. (g)	Tare + Dry Wt. (g)	Dry Wt. (g)	% Moisture

Oven ID: _____ **Thermometer ID:** _____

Date/Time In: _____ **Temp In:** _____

Date/Time Out: _____ **Temp Out:** _____

Analyst: _____ **Balance ID:** _____ **Calibration Date** _____

EXPOSURES SETUP BENCHSHEET

Sample ID	Sediment Mass (g ww)	Passive Sampler Mass (g)	Biocide Solution Volume (mL)

Start Date: _____

Stop Date: _____

Analyst: _____

DAILY CONDITIONS BENCHSHEET

Date	Room Temperature	Orbital Shaker Performance Acceptable (Y/N)	Jars and Lids Intact (Y/N)	Comments	Analyst

Thermometer ID:_____

Orbital Shaker ID:_____

PROTOCOL MODIFICATION FORM

Project Name and 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 Officer: _____ Date: _____

QA Officer: _____ Date: _____

APPENDIX C. ANALYTICAL METHODS AND REPORTING LIMITS

Tables

Table C-1. Method detection limits and reporting limits for PCB Aroclors, cPAHs, metals, TBT, organochlorine pesticides, SVOCs, and conventionals in tissue

Analyte	Method	Unit	MDL	RL
PCBs as Aroclors				
Aroclor 1016	EPA 8082A	µg/kg ww	2.37[a]	4.00[b]
Aroclor 1221	EPA 8082A	µg/kg ww	2.37 [a]	4.00 [b]
Aroclor 1232	EPA 8082A	µg/kg ww	2.37 [a]	4.00 [b]
Aroclor 1242	EPA 8082A	µg/kg ww	2.37 [a]	4.00 [b]
Aroclor 1248	EPA 8082A	µg/kg ww	2.37 [a]	4.00 [b]
Aroclor 1254	EPA 8082A	µg/kg ww	2.37 [a]	4.00 [b]
Aroclor 1260	EPA 8082A	µg/kg ww	1.06 [a]	4.00 [b]
cPAHs				
Benzo(a)anthracene	EPA 8270D-SIM	µg/kg ww	0.537	5.00
Benzo(a)pyrene	EPA 8270D-SIM	µg/kg ww	0.915	5.00
Total benzofluoranthenes	EPA 8270D-SIM	µg/kg ww	1.00	10.0
Chrysene	EPA 8270D-SIM	µg/kg ww	0.488	5.00
Dibenzo(a,h)anthracene	EPA 8270D-SIM	µg/kg ww	1.53	5.00
Indeno(1,2,3-cd)pyrene	EPA 8270D-SIM	µg/kg ww	0.575	5.00
Metals				
Inorganic Arsenic	EPA 1632	mg/kg ww	0.004	0.010
Vanadium	EPA 6020A	mg/kg ww	na[c]	0.004
TBT	EPA 8270D-SIM	µg/kg ww	0.450	3.86
Organochlorine Pesticides				
Aldrin	EPA 8270D/1699 Mod	µg/kg ww	0.22	1.0
alpha-BHC	EPA 8270D/1699 Mod	µg/kg ww	0.26	1.0
beta-BHC	EPA 8270D/1699 Mod	µg/kg ww	0.4	1.0
Dieldrin	EPA 8270D/1699 Mod	µg/kg ww	0.22	1.0
gamma-BHC	EPA 8270D/1699 Mod	µg/kg ww	0.17	1.0
Heptachlor	EPA 8270D/1699 Mod	µg/kg ww	0.09	1.0

Table C-1. Method detection limits and reporting limits for PCB Aroclors, cPAHs, metals, TBT, organochlorine pesticides, SVOCs, and conventionals in tissue

Analyte	Method	Unit	MDL	RL
Heptachlor epoxide	EPA 8270D/1699 Mod	µg/kg ww	0.061	1.0
alpha-Chlordane[d]	EPA 8270D/1699 Mod	µg/kg ww	0.12	1.0
cis-Nonachlor[d]	EPA 8270D/1699 Mod	µg/kg ww	0.13	1.0
gamma-Chlordane[d]	EPA 8270D/1699 Mod	µg/kg ww	0.13	1.0
Oxychlordane[d]	EPA 8270D/1699 Mod	µg/kg ww	0.77	2.5
trans-Nonachlor[d]	EPA 8270D/1699 Mod	µg/kg ww	0.094	1.0
2,4'-DDD[e]	EPA 8270D/1699 Mod	µg/kg ww	0.31	2.5
2,4'-DDE[e]	EPA 8270D/1699 Mod	µg/kg ww	0.42	2.5
2,4'-DDT[e]	EPA 8270D/1699 Mod	µg/kg ww	0.46	1.0
4,4'-DDD[e]	EPA 8270D/1699 Mod	µg/kg ww	0.13	1.0
4,4'-DDE[e]	EPA 8270D/1699 Mod	µg/kg ww	0.7	2.5
4,4'-DDT[e]	EPA 8270D/1699 Mod	µg/kg ww	0.35	1.0
SVOCs				
BEHP	EPA 8270D	µg/kg ww	28.0 [a]	50.0 [b]
Carbazole	EPA 8270D/1699 Mod	µg/kg ww	7.37	20.0
PCP	EPA 8270D	µg/kg ww	31.3 [a]	100 [b]
Hexachlorobenzene	EPA 8270D	µg/kg ww	4.74 [a]	20.0 [b]
Conventionals				
Total solids	PSEP 1986	% dw	na	0.040
Lipids	Bligh and Dyer (mod)	% ww	na	0.010

[a] SW 846 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 SW 846

[c] SW 846 no longer requires MDL values.

[d] Components chlordane sum.

[e] Components of total DDx sum.

BEHP – bis(2-ethylhexyl) phthalate
BHC – benzene hexachloride
cPAH – carcinogenic polycyclic aromatic hydrocarbon
DDD – dichlorodiphenyldichloroethane
DDE – dichlorodiphenyldichloroethylene
DDT – dichlorodiphenyltrichloroethane
EPA – US Environmental Protection Agency
MDL – method detection limit
na – not available
PCB – polychlorinated biphenyl
PCP – pentachlorophenol
PSEP - Puget Sound Estuary Program
RL – reporting limit
SIM – selective ion monitoring
SVOC – semivolatile organic compounds
TBT – tributyltin
total DDx – DDT isomers (2,4′-DDD, 4,4′-DDD, 2,4′-DDE, 4,4′-DDE, 2,4′-DDT and 4,4′-DDT)
ww – wet weight

Table C-2. EDL and LMCL values for dioxins/furan congeners

Analyte	EPA Method 1613B	
	Tissue (ng/kg ww) based on 10-g sample	
	EDL[a]	LMCL[b]
2,3,7,8-TCDD	0.05	0.20
1,2,3,7,8-PeCDD	0.05	1.00
1,2,3,4,7,8-HxCDD	0.05	1.00
1,2,3,6,7,8-HxCDD	0.05	1.00
1,2,3,7,8,9-HxCDD	0.05	1.00
1,2,3,4,6,7,8-HpCDD	0.05	1.00
OCDD	0.05	2.00
2,3,7,8-TCDF	0.05	0.20
1,2,3,7,8-PeCDF	0.05	1.00
2,3,4,7,8-PeCDF	0.05	1.00
1,2,3,4,7,8-HxCDF	0.05	1.00
1,2,3,6,7,8-HxCDF	0.05	1.00
1,2,3,7,8,9-HxCDF	0.05	1.00
2,3,4,6,7,8-HxCDF	0.05	1.00
1,2,3,4,6,7,8-HpCDF	0.05	1.00
1,2,3,4,7,8,9-HpCDF	0.05	1.00
OCDF	0.05	2.00

[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 sample mass of each sample.

Axys – Axys Analytical Services Ltd.
DL – detection limit
EPA – US Environmental Protection Agency
EDL – estimated detection limit
HpCDD – heptachlorodibenzo-*p*-dioxin
HpCDF – heptachlorodibenzofuran
HxCDD – hexachlorodibenzo-*p*-dioxin
HxCDF – hexachlorodibenzofuran
J – estimated concentration
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
ww – wet weight

Table C-3. EDL and LMCL values for PCB congeners

Analyte	EPA Method 1668C Tissue (ng/kg ww) based on 10-g sample	
	EDL[a]	LMCL[b]
PCB-1	0.1	2.0
PCB-2	0.1	2.0
PCB-3	0.1	2.0
PCB-4	0.2	2.0
PCB-5	0.2	2.0
PCB-6	0.2	2.0
PCB-7	0.2	2.0
PCB-8	0.2	2.0
PCB-9	0.2	2.0
PCB-10	0.2	2.0
PCB-11	0.2	2.0
PCB-12/13	0.2	2.0
PCB-14	0.2	2.0
PCB-15	0.2	2.0
PCB-16	0.1	2.0
PCB-17	0.1	2.0
PCB-19	0.1	2.0
PCB-21/33	0.1	2.0
PCB-22	0.1	2.0
PCB-23	0.1	2.0
PCB-24	0.1	2.0
PCB-25	0.1	2.0
PCB-26/29	0.1	2.0
PCB-27	0.1	2.0
PCB-28/20	0.1	2.0
PCB-30/18	0.1	2.0
PCB-31	0.1	2.0
PCB-32	0.1	2.0
PCB-34	0.1	2.0
PCB-35	0.1	2.0
PCB-36	0.1	2.0
PCB-37	0.1	2.0
PCB-38	0.1	2.0
PCB-39	0.1	2.0
PCB-41/40/71	0.1	2.0
PCB-42	0.1	2.0

Table C-3. EDL and LMCL values for PCB congeners

Analyte	EPA Method 1668C	
	Tissue (ng/kg ww) based on 10-g sample	
	EDL[a]	LMCL[b]
PCB-43	0.1	2.0
PCB-44/47/65	0.1	2.0
PCB-45/51	0.1	2.0
PCB-46	0.1	2.0
PCB-48	0.1	2.0
PCB-50/53	0.1	2.0
PCB-52	0.1	2.0
PCB-54	0.1	2.0
PCB-55	0.1	2.0
PCB-56	0.1	2.0
PCB-57	0.1	2.0
PCB-58	0.1	2.0
PCB-59/62/75	0.1	2.0
PCB-60	0.1	2.0
PCB-61/70/74/76	0.1	2.0
PCB-63	0.1	2.0
PCB-64	0.1	2.0
PCB-66	0.1	2.0
PCB-67	0.1	2.0
PCB-68	0.1	2.0
PCB-69/49	0.1	2.0
PCB-72	0.1	2.0
PCB-73	0.1	2.0
PCB-77	0.1	2.0
PCB-78	0.1	2.0
PCB-79	0.1	2.0
PCB-80	0.1	2.0
PCB-81	0.1	2.0
PCB-82	0.1	2.0
PCB-83/99	0.1	2.0
PCB-84	0.1	2.0
PCB-88/91	0.1	2.0
PCB-89	0.1	2.0
PCB-92	0.1	2.0
PCB-94	0.1	2.0
PCB-95/100/93/102/98	0.1	2.0
PCB-96	0.1	2.0

Table C-3. EDL and LMCL values for PCB congeners

Analyte	EPA Method 1668C	
	Tissue (ng/kg ww) based on 10-g sample	
	EDL[a]	LMCL[b]
PCB-103	0.1	2.0
PCB-104	0.1	2.0
PCB-105	0.1	2.0
PCB-106	0.1	2.0
PCB-108/124	0.1	2.0
PCB-109/119/86/97/125/87	0.1	2.0
PCB-107	0.1	2.0
PCB-110/115	0.1	2.0
PCB-111	0.1	2.0
PCB-112	0.1	2.0
PCB-113/90/101	0.1	2.0
PCB-114	0.1	2.0
PCB-117/116/85	0.1	2.0
PCB-118	0.1	2.0
PCB-120	0.1	2.0
PCB-121	0.1	2.0
PCB-122	0.1	2.0
PCB-123	0.1	2.0
PCB-126	0.1	2.0
PCB-127	0.1	2.0
PCB-128/166	0.1	2.0
PCB-130	0.1	2.0
PCB-131	0.1	2.0
PCB-132	0.1	2.0
PCB-133	0.1	2.0
PCB-134/143	0.1	2.0
PCB-136	0.1	2.0
PCB-137	0.1	2.0
PCB-138/163/129/160	0.1	2.0
PCB-139/140	0.1	2.0
PCB-141	0.1	2.0
PCB-142	0.1	2.0
PCB-144	0.1	2.0
PCB-145	0.1	2.0
PCB-146	0.1	2.0
PCB-147/149	0.1	2.0
PCB-148	0.1	2.0

Table C-3. EDL and LMCL values for PCB congeners

Analyte	EPA Method 1668C	
	Tissue (ng/kg ww) based on 10-g sample	
	EDL[a]	LMCL[b]
PCB-150	0.1	2.0
PCB-151/135/154	0.1	2.0
PCB-152	0.1	2.0
PCB-153/168	0.1	2.0
PCB-155	0.1	2.0
PCB-156/157	0.1	2.0
PCB-158	0.1	2.0
PCB-159	0.1	2.0
PCB-161	0.1	2.0
PCB-162	0.1	2.0
PCB-164	0.1	2.0
PCB-165	0.1	2.0
PCB-167	0.1	2.0
PCB-169	0.1	2.0
PCB-170	0.1	2.0
PCB-171/173	0.1	2.0
PCB-172	0.1	2.0
PCB-174	0.1	2.0
PCB-175	0.1	2.0
PCB-176	0.1	2.0
PCB-177	0.1	2.0
PCB-178	0.1	2.0
PCB-179	0.1	2.0
PCB-180/193	0.1	2.0
PCB-181	0.1	2.0
PCB-182	0.1	2.0
PCB-183/185	0.1	2.0
PCB-184	0.1	2.0
PCB-186	0.1	2.0
PCB-187	0.1	2.0
PCB-188	0.1	2.0
PCB-189	0.1	2.0
PCB-190	0.1	2.0
PCB-191	0.1	2.0
PCB-192	0.1	2.0
PCB-194	0.1	2.0
PCB-195	0.1	2.0

Table C-3. EDL and LMCL values for PCB congeners

Analyte	EPA Method 1668C	
	Tissue (ng/kg ww) based on 10-g sample	
	EDL[a]	LMCL[b]
PCB-196	0.1	2.0
PCB-197/200	0.1	2.0
PCB-198/199	0.1	2.0
PCB-201	0.1	2.0
PCB-202	0.1	2.0
PCB-203	0.1	2.0
PCB-204	0.1	2.0
PCB-205	0.1	2.0
PCB-206	0.1	2.0
PCB-207	0.1	2.0
PCB-208	0.1	2.0
PCB-209	0.1	2.0

[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 sample mass of each sample.

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

Table C-4. Method detection limits and reporting limits for cPAHS and conventionals in sediment

Analyte	Method	Unit	MDL	RL
cPAHs (based on 10-g dw sample)				
Benzo(a)anthracene	EPA 8270D-SIM	µg/kg dw	0.537	5.00
Benzo(a)pyrene	EPA 8270D-SIM	µg/kg dw	0.915	5.00
Benzo(b)fluoranthene	EPA 8270D-SIM	µg/kg dw	1.37	5.00
Benzo(k)fluoranthene	EPA 8270D-SIM	µg/kg dw	0.760	5.00
Chrysene	EPA 8270D-SIM	µg/kg dw	0.488	5.00
Dibenzo(a,h)anthracene	EPA 8270D-SIM	µg/kg dw	1.53	5.00
Indeno(1,2,3-cd)pyrene	EPA 8270D-SIM	µg/kg dw	0.575	5.00
Conventionals				
Percent solids	SM 2540G	% dw	na	0.040
TOC (based on 1-g dw sample)	EPA 9060	% dw	0.018	0.02
Black carbon (based on 10-g dw sample)	Gustafsson, 2001 - CTO Pretreatment / Combustion (950°C) / IR detect	wt%	0.2	0.6

cPAH – carcinogenic polycyclic aromatic hydrocarbon
dw – dry weight
EPA – US Environmental Protection Agency
MDL – method detection limit
na – not available
PSEP - Puget Sound Estuary Program
RL – reporting limit
SIM – selective ion monitoring
ww – wet weight

Table C-5. EDLs and LMCLs for cPAHs in passive samplers and estimated detection limits in porewater

Analyte	EPA Method 8270 Modified		Estimated porewater DL (ng/L)[c]
	Passive Sampler (ng/g) Based on 1-g PE sample		
	EDL[a]	LMCL[b]	
Benzo(a)anthracene	5	25	0.138
Benzo(a)pyrene	5	25	0.035
Benzo(b)fluoranthene	5	25	0.035
Benzo(j/k)fluoranthene	5	25	0.035
Chrysene	5	25	0.138
Dibenzo(a,h)anthracene	10	25	0.005
Indeno(1,2,3-cd)pyrene	10	25	0.004

[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 sample mass of each sample.

[c] Assuming 0.1 g of PE and that full equilibrium is reached. Note that full equilibrium may not be achieved for all PAHs.

Axys – Axys Analytical Services Ltd.
DL – detection limit
EPA – US Environmental Protection Agency
EDL – estimated detection limit
J – estimated concentration
LMCL – lower method calibration limit
RL – reporting limit
ww – wet weight

APPENDIX D. PASSIVE SAMPLER STANDARD OPERATING PROCEDURES

STANDARD OPERATING PROCEDURE (SOP) LB-17

EX SITU DETERMINATION OF POREWATER POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) USING POLYETHYLENE PASSIVE SAMPLERS

Note: This SOP is based upon guidance for the use of passive sampling in the evaluation of contaminated sediments (EPA et al, 2017).

METHOD DESCRIPTION

This SOP provides instruction on the use of polyethylene (PE) passives samplers in the laboratory for the determination of PAH porewater concentrations in sediments. PE samplers will be equilibrated with sediments for 1 month using an orbital shaker, ensuring that there is sufficient mass of PE sampler to detect PAHs, and utilizing sufficient mass of sediment in each exposure so the addition of the PE sampler causes negligible depletion (i.e. < 1% by mass) of each analyte in the sediment system.

Pre-cleaned and performance reference compound (PRC) impregnated PE sheets will be prepared by SGS AXYS Analytical Services Ltd. (AXYS) using procedures described in Gschwend et al 2012. The PE sheets will then be transported to Analytical Resources, Inc. (ARI) on ice as detailed in the accompanying Lower Duwamish Waterway Clam Tissue Quality Assurance Project Plan (QAPP), and stored in a freezer until the aqueous equilibrium exposures are started.

Sediment samples will be collected, transported and stored at ARI as detailed in the accompanying QAPP. Before starting the aqueous equilibrium exposures, a small sub-sample of each stored sediment sample will be taken to determine moisture content. This information will be used to determine the volume of sodium azide (biocide) solution to be added to the exposures to achieve a well-formed slurry (80% water content).

PAH analysis of the samplers will be conducted by AXYS following methods described in the accompanying QAPP.

EQUIPMENT

- Drying Oven: Capable of maintaining a temperature of 105 ±2°C
- Aluminum Weighing Boats
- Top loading balance (readability = 0.01 g, capacity = 4000 g)
- Desiccator
- Laboratory grade deionized water
- Sodium azide
- Top loading balance (readability = 0.0001 g, capacity = 200 g)
- Pre-cleaned, PRC impregnated PE sheets
- Orbital shaker (capacity = > 20 kg)
- Stainless steel scissors
- Methanol

PERSONAL PROTECTIVE EQUIPMENT (PPE)

The analyst will be attired in the following PPE:

- Safety glasses
- Lab coat
- Nitrile gloves
- Long pants
- Closed-toe shoes

MOISTURE CONTENT

Calibration

1. Verify the balance was calibrated by the laboratory prior to use.

Sample Preparation

1. Initiate a Percent Moisture Benchsheet and complete the required information.
2. Record the Analyst, Oven ID, Thermometer ID, and Balance ID on the Percent Moisture Benchsheet.

3. Label an aluminum dish with a unique numerical ID (1, 2, 3…) for each sample.
4. Weigh the aluminum dish using a calibrated analytical balance and record the weight measurement on the benchsheet to the nearest 0.01 g in the "Tare" column.
5. Thoroughly mix the sample then measure 5-10 g of sample into the pre-weighed, pre-labeled aluminum dish. Weigh to the nearest 0.01 g and record the weight measurement onto the benchsheet in the "Wet Wt." column.
6. Place the dish in the drying oven maintained at a temperature of 105 ±2°C. Record the date and the time the samples were placed in the oven.
7. Dry the sample for a minimum of 12 hours but do not exceed 24 hours. After this time has elapsed, remove the samples from the oven and allow them to cool in a desiccator before weighing.
8. Reweigh the samples and record the weight measurements in the "Tare+Dry Wt." column of the benchsheet.
9. Record the oven temperature and time out of the oven on the benchsheet.
10. Calculate sediment moisture content using formula below and record on the benchsheet.

Calculations

$$\text{Percent Moisture} = 100 - \left(\frac{[(Tare+Dry\ Wt.)-(Tare)]}{(Wet\ Wt.)}\ x\ 100\right)$$

AQUEOUS EQUILIBRIUM EXPOSURES

Passive Sampler Preparation

1. Prior to starting the equilibrium exposures, remove PE sheets from the freezer.
2. Cut PE sheets into 0.1g PE strips using methanol wiped stainless steel scissors. Always handle the PE sheets and strips wearing nitrile gloves.
3. Wrap all PE strips in aluminum foil and store at 4ºC ± 2°C until all sediment slurries are ready as described below.

Exposure Preparation

1. Initiate an Exposure Setup Benchsheet and complete the required information.
2. Label 1 L wide mouth glass jars, with Teflon-lined caps, with unique sediment sample IDs.

3. Thoroughly homogenize the sediment samples, and place approximately 1 kg wet weight of each sample into its corresponding labeled jar.
4. Record the weight of sediment in each jar in the Exposure Setup Benchsheet to the nearest 0.1 g.
5. Add sufficient volume of 2 g/L sodium azide solution to each glass jar to achieve a sediment slurry of 80% moisture content. Record the volume of solution added to each jar in the Exposure Setup Benchsheet to the nearest ml.
6. Add a pre-weighed 0.1 g PE strip to each jar. Record the weight of each strip to 4 decimal points in the Exposure Setup Benchsheet.
7. Tightly seal the lid of each jar, and securely load all jars onto the orbital shaker. Jars should be positioned securely, ensuring they will be able to safely withstand 1 month of agitation without breakage.
8. Turn on the orbital shaker and gradually increase the shaking speed to around 100 rpm.
9. Monitor jars for the first hour to ensure jars remain securely in place during shaking, and make any packing adjustments if necessary.
10. Initiate a Daily Conditions Benchsheet and complete the required information.
11. Monitor temperature, shakers, and jars daily for 1 month, and record observations on the Daily Conditions Benchsheet.

Exposure Termination

1. After 1 month, stop the orbital shaker and remove all glass jars.
2. Gradually empty the contents of each jar into a beaker to recover each PE strip.
3. Rinse each PE strip with laboratory grade deionized water to remove all attached sediment.
4. Wipe each PE strip with clean laboratory wipes to remove any remaining sediment and water.
5. Wrap each PE strip in a clean labeled aluminum foil envelope. Insert each envelope in a resealable plastic bag with corresponding sample ID label.
6. Insert all resealable plastic bags into a larger resealable plastic bag, and place the large bag on ice in a cooler for transport to AXYS for analysis. Sample packing, transport information, and sample custody procedures are described in accompanying QAPP.

QUALITY ASSURANCE AND QUALITY CONTROL SAMPLES

The following quality assurance and quality control samples will be included to support data validation and usability determination:

- Laboratory blank (5 percent frequency, or 1 per maximum 20 samples). For the laboratory blank, 900 ml laboratory grade deionized water and 100 ml of 2 g/L sodium azide solution will be added to a wide mouth glass jar. A pre-weighed 0.1g PRC impregnated PE strip will be added to this jar, and the jar will be treated in the same way as jars containing sediment samples.

- Duplicate samples (5 percent frequency, or 1 per maximum 20 samples). Prepare duplicate aqueous equilibrium exposures for select samples.

DATA MANAGEMENT

All data will be recorded immediately, legibly and in ink on the appropriate benchsheets. Any recording mistakes will be struck out with a single line and initialed and dated by the analyst. Hard copies of completed forms will be compiled and stored. Forms will also be scanned electronically, and these electronic copies will be submitted to EPA as part of the Data Report.

WASTE DISPOSAL

The analyst will perform this analysis with the intent of obtaining the best quality analytical results while generating the minimum amount of waste.

Waste generated during this analysis will include the sediment from all aqueous equilibrium exposures. This waste will be composited and disposed appropriately per laboratory procedures.

REFERENCES

EPA, SERDP, ESTCP. 2017. Laboratory, field, and analytical procedures for using passive sampling in the evaluation of contaminated sediments: user's manual. EPA/600/R- 16/357. February 2017 final web version (1.0). US Environmental Protection Agency, US Department of Defense, Strategic Environmental Research and Development Program, and Environmental Security Technology Certification Program.

Gschwend P, MacFarlane J, Palaia K, Reichenbacher S, Gouveia D. 2012. Passive PE sampling in support of in situ remediation of contaminated sediments (standard operating procedure for the preparation of polyethylene devices). ESTCP Project ER-200915. SERDP/ESTCP

Table D1. Physicochemical Properties of PAHs

Constituent of Interest	log K_{ow} [a]	log K_{PEW} (L_W/kg_{PE}) [a]	log D_{PE} (cm^2/s) [a]
Naphthalene	3.40	2.86	-7.92
Acenaphthylene	3.90	3.46	-8.17
Acenaphthene	4.00	3.56	-8.13
Fluorene	4.10	3.86	-8.36
Phenanthrene	4.50	4.16	-8.44
Anthracene	4.60	4.16	-8.42
Fluoranthene	5.00	4.86	-8.96
Pyrene	5.00	4.86	-8.76
Benz(a)anthracene	5.80	5.56	-8.96
Chrysene	5.70	5.56	-8.94
Benzo(b)fluoranthene	5.90	6.16	-9.45
Benzo(j/k)fluoranthenes	5.90	6.16	-9.45
Benzo(a)pyrene	6.10	6.16	-9.28
Dibenzo(ah)anthracene	7.39	7.28	-9.64
Indeno(1,2,3-cd)pyrene	7.09	7.36	-9.78
Benzo(ghi)perylene	7.04	7.23	-9.64

Notes:

DL = Detection Limit

D_{PE} = Polyethylene Diffusivity

K_{OW} = Octanol to Water Partition Constant

K_{PEW} = Polyethylene to Water Partition Constant

PAH = polycyclic aromatic hydrocarbon

SDL = Sample Detection Limit

[a] Default values in PRC calculator. Default K_{PEW} values were obtained from Lohmann, R., 2011. Critical review of low-density polyethylene's partitioning and diffusion coefficients for trace organic contaminants and implications for its use as a passive sampler. Environmental science & technology, 46(2), pp.606-618.

[b] Provided by AXYS assuming final extract volume of 500µl

[c] Assuming 0.1 gram of PE and that full equilibrium is reached. Note that full equilibrium may not be achieved for all PAHs.

Attachment D-1

GUIDANCE DOCUMENT

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

ESTCP Project ER-200915

December 2012

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14. ABSTRACT

The purpose of this Standard Operating Procedure (SOP) is to provide a description of the methods used in the deployment and retrieval of polyethylene devices (PEDs) in sediment-pore water environments for the sampling of hydrophobic organic compounds (HOCs) such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). The overall objective of PED sampling is to determine the horizontal and vertical distributions of HOCs in pore waters of bed sediments. This SOP does not discuss deployment of PEDs in atmospheric or aqueous systems. This SOP should be used in conjunction with companion SOPs for Preparation of Polyethylene (PE) Media and Extraction Procedures for PE Media.

15. SUBJECT TERMS

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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.

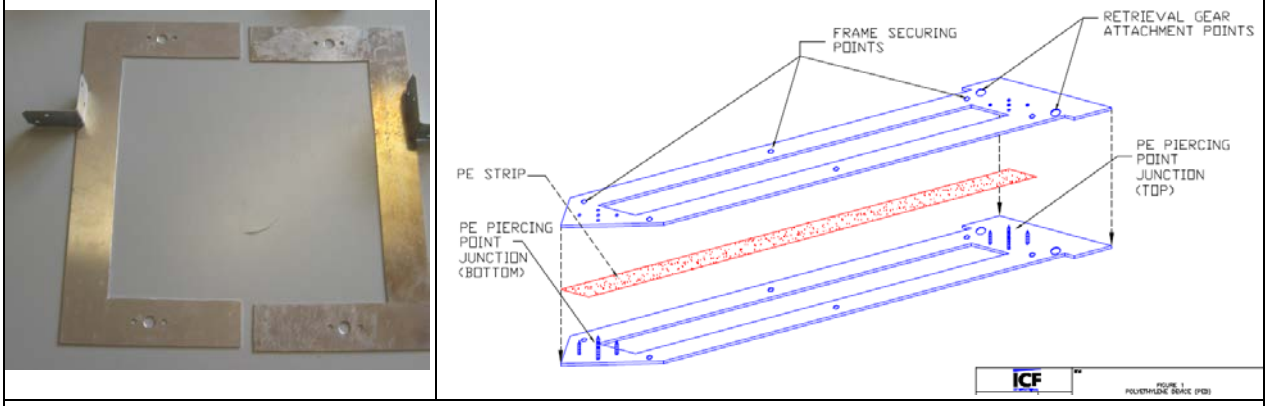

Figure 1.
(left panel) Aluminum sheet cut into two "C-shaped" pieces allowing the investigator to mount and hold ~25 cm strips of PE an open window when the two pieces are overlapped and bolted together.
(right panel) Drawing of two aluminum sheet pieces cut so as to sandwich a strip of PE and expose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