FINAL

Appendix A
Updated Analytical Methods and Requirement Tables

Analytical tables presented in this appendix have been updated to include revisions from the Washington State Department of Ecology's Sediment Cleanup User's Manual (Ecology 2021), including the revised temperature for frozen samples (-18°C) and revised holding times for total organic carbon (TOC), metals and mercury. In addition, Analytical Resources, LLC (ARL) has updated the analytical method for metals from US Environmental Protection Agency (EPA) method 6020A to 6020B and revised the required quality control (QC) samples for metals and mercury.

TABLES

Table A-1
Analytical Methods, Containers, and Sample Handling Requirements for Sediment and Bank Samples

Parameter[1]	Method	Reference[1]	Extraction Solvent	Cleanup	Laboratory	Container	Preservative	Sample Holding Time
TOC	high-temperature combustion	EPA 9060A	na	na	ARL	4-oz glass jar	cool to ≤ 6°C; freeze to ≤ -18°C	28 days 6 months if frozen
Percent solids	drying oven	SM 2540G	na	na	ARL		cool to 4 ± 2°C	6 months
Metals	ICP-MS	EPA 3050B EPA 6020B UCT-KED	na	na	ARL	4-oz glass jar	cool to ≤ 6°C; freeze to ≤ -18°C	6 months 2 years if frozen
Mercury	cold vapor-atomic fluorescence spectroscopy	EPA 7471B	na	na	ARL			28 days 1 year if frozen
cPAHs[2,3]	GC/MS-SIM	EPA 3546/ EPA 8270E-SIM	dichloromethane / acetone	Silica gel	ARL	16-oz glass jar	cool to 0–6°C; freeze to ≤ -18°C	1 year to extraction if frozen; 14 days to extraction if refrigerated; when thawed, 40 days after extraction; store extracts at ≤ 6°C and in the dark
PAHs[4]/SVOCs	GC/MS	EPA 3546/ EPA 8270E/EPA 8270E-SIM	dichloromethane / acetone	GPC (optional)	ARL		cool to 0–6°C; freeze to ≤ -18°C	1 year to extraction if frozen; 14 days to extraction if refrigerated; when thawed, 40 days after extraction; store extracts at ≤ 6°C and in the dark

Parameter[1]	Method	Reference[1]	Extraction Solvent	Cleanup	Laboratory	Container	Preservative	Sample Holding Time
PCB Aroclors	gas chromatography/electron capture detection	EPA 3546 Mod EPA 8082A	Hexane/ acetone	Silica gel, sulfuric acid/ permanganate sulfur, or acid/ base partition (optional)	ARL		cool to 0–6°C; freeze to ≤ -18°C	1 year to extraction if frozen; 14 days to extraction if refrigerated; when thawed, 40 days after extraction; store extracts at ≤ 6°C and in the dark
Dioxins/furans	HRGC/HRMS	EPA 1613b	Toluene	Florisil, silica gel, sulfuric acid	ARL	8-oz amber glass jar	cool to ≤ 4°C; freeze to ≤ -18°C	1 year until extraction and 1 year after extraction if stored in the dark at ≤ -18°C

Notes:

1. Laboratory SOPs are confidential and are available upon EPA request.
2. Per the ROD (EPA 2014), cPAHs consist of a subset of seven PAHs that EPA has classified as probable human carcinogens: benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene.
3. cPAHs will be analyzed by 8270E-SIM in samples that require only cPAH analysis (i.e., 0- to 45-cm samples in Recovery Category 2/3) and not the full SVOC list.

ARL: Analytical Resources, LLC
cPAH: carcinogenic polycyclic aromatic hydrocarbon
EPA: US Environmental Protection Agency
GC: gas chromatography
GPC: gel permeation chromatography
HDPE: high-density polyethylene
HRGC/HRMS: high-resolution gas chromatography/high-resolution mass spectrometry
ICP: inductively coupled plasma
MS: mass spectrometry
na: not applicable or not available
PAH: polycyclic aromatic hydrocarbon
PCB: polychlorinated biphenyl
ROD: Record of Decision
SIM: selected ion monitoring
SM: Standard Method

SOP: standard operating procedure
SVOC: semivolatile organic compound
TOC: total organic carbon
UCT-KED: universal cell technology-kinetic energy discrimination

The updated laboratory method detection limit (MDL) and reporting limit (RL) goals for each analytical method are compared to their respective minimum sediment remedial action levels (RALs) in Table A-2. All the analytical methods are sufficiently sensitive.

Table A-2
RAO 3 COCs and Associated RL Goals and RALs for Individual 0–10-cm Sediment Samples

COC	Method	RL	Lowest RAL (Benthic SCO)
Metals (mg/kg dw)			
Arsenic	EPA 6020B	0.2	57
Lead	EPA 6020B	0.1	450
Mercury	EPA 7471B	0.025	0.41
PAHs and SVOCs (µg/kg dw)			
Benzo(a)anthracene	EPA 8270E	20.0	2,200[1]
Benzo(a)pyrene	EPA 8270E	20.0	1,980[1]
Total benzofluoranthenes	EPA 8270E	40.0	4,600[1]
Chrysene	EPA 8270E	20.0	2,200[1]
Dibenzo(a,h)anthracene	EPA 8270E	20.0	240[1]
Indeno(1,2,3-cd)pyrene	EPA 8270E	20.0	680[1]
Anthracene	EPA 8270E	20.0	4,400[1]
Acenaphthene	EPA 8270E	20.0	320[1]
Acenapthylene	EPA 8270E	20.0	1,320[1]
Benzo(g,h,i)perylene	EPA 8270E	20.0	620[1]
Fluoranthene	EPA 8270E	20.0	3,200[1]
Fluorene	EPA 8270E	20.0	460[1]
Naphthalene	EPA 8270E	20.0	1,980[1]
Phenanthrene	EPA 8270E	20.0	2,000[1]
Pyrene	EPA 8270E	20.0	20,000[1]
Total HPAHs[2]	EPA 8270E	40.0	19,200[1]
Total LPAHs[3]	EPA 8270E	20.0	7,400[1]
4-methylphenol	EPA 8270E	20.0	670
Bis(2-ethylhexyl)phthalate	EPA 8270E	50.0	940[1]
Butyl benzyl phthalate	EPA 8270E	20.0	98[1]
Phenol	EPA 8270E	20.0	420
PCBs (µg/kg dw)			
PCBs	EPA 8082A (Aroclors)	4.0	240[1]

Notes:

1. OC-normalized RAL was converted to dry weight value for this table using 2% TOC (average LDW sediment TOC). This value, which is less than the dry weight AETs in Table 8-1 of SCUM (Ecology 2021), is presented herein as a dry weight value only for the purpose of comparison to RLs.
2. HPAH compounds include fluoranthene, pyrene, benzo(a)anthracene, chrysene, total benzofluoranthenes, benzo(a)pyrene, indeno(1,2,3 cd)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene.
3. LPAH compounds include naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, and 2-methylnaphthalene.
AET: apparent effects threshold
COC: contaminant of concern
dw: dry weight
EPA: US Environmental Protection Agency
HPAH: high-molecular-weight polycyclic aromatic hydrocarbon
LDW: Lower Duwamish Waterway
LPAH: low-molecular-weight polycyclic aromatic hydrocarbon
OC: organic carbon
PAH: polycyclic aromatic hydrocarbon
PCB: polychlorinated biphenyl
RAL: remedial action level
RAO: remedial action objective
RL: reporting limit
SCO: sediment cleanup objective
SCUM: Sediment Cleanup User's Manual
SVOC: semivolatile organic compound
TOC: total organic carbon

Table A-3
Laboratory QC Sample Analysis Summary

Analysis Type	Method	Initial Calibration	Initial Calibration Verification (2nd source) and Calibration Blank	Continuing Calibration Verification and Calibration Blank	CRM or LCS[1]	Laboratory Replicates	MS	MSD	Method Blanks	Internal Standards/ Surrogate Spikes
TOC	EPA 9060A	Prior to analysis	After initial calibration	Every 10 samples	1 per 20 samples or per batch	1 per 20 samples or per batch	1 per 20 samples or per batch	na	1 per 20 samples or per batch	na
Percent solids	SM 2540G	na	na	na	na	1 per 20 samples or per batch	na	na	na	na
Metals	EPA 6020BUCT 6020B UCT-KED	Daily, prior to analysis	After initial calibration; interference check standard and spectral interference check at beginning of analytical run; spectral interference check every 12 hours	Every 10 samples and at end of analytical sequence	1 per prep batch	1 per batch or SDG	1 per batch or SDG	na	1 per prep batch	Each sample (internal standard only)
Mercury	EPA 7471B	Prior to analysis	After initial calibration	Every 10 samples and at end of analytical sequence	1 per prep batch	1 per batch or SDG	1 per batch or SDG	na	1 per prep batch	na
PAHs/cPAHs	EPA 8270E/ EPA 8270E-SIM	Prior to analysis	After initial calibration	Before and after sample analysis, and every 12 hours	1 per prep batch[2]	na	1 per batch or SDG	1 per batch or SDG	1 per prep batch	Each sample
PCB Aroclors	Mod EPA 8082A	Prior to analysis	After initial calibration	Before and after sample analysis, every 10–20 analyses or 12 hours	1 per prep batch[3]	na	1 per batch or SDG	1 per batch or SDG	1 per prep batch	Each sample

Analysis Type	Method	Initial Calibration	Initial Calibration Verification (2nd source) and Calibration Blank	Continuing Calibration Verification and Calibration Blank	CRM or LCS[1]	Laboratory Replicates	MS	MSD	Method Blanks	Internal Standards/ Surrogate Spikes
SVOCs	EPA 8270E/ EPA 8270E-SIM	Prior to analysis	After initial calibration	Before and after sample analysis and every 12 hours	1 per prep batch	na	1 per batch or SDG	1 per batch or SDG	1 per prep batch	Each sample
Dioxins/ furans	EPA 1613b	Prior to analysis	After initial calibration	Before and after sample analysis and every 12 hours	1 CRM and LCS/ LCSD per prep batch[3]	na	na	na	1 per prep batch	Each sample

Notes:

A batch is a group of samples of the same matrix analyzed or prepared at the same time, not exceeding 20 samples.
1. An LCS may be used to assess accuracy when CRM is unavailable.
2. Sigma-Aldrich SQC017-40G and CRM 143 BNA will be used to assess accuracy for cPAHs and PAHs.
3. Puget Sound sediment reference material will be used to assess accuracy for PCB Aroclors and dioxins/furans.
cPAH: carcinogenic polycyclic aromatic hydrocarbon
CRM: certified reference material
EPA: US Environmental Protection Agency
LCS: laboratory control sample
LCSD: laboratory control sample duplicate
MS: matrix spike
MSD: matrix spike duplicate
na: not applicable or not available
PAH: polycyclic aromatic hydrocarbon
PCB: polychlorinated biphenyl
QC: quality control
SDG: sample delivery group
SIM: selected ion monitoring
SM: Standard Method
SVOC: semivolatile organic compound
TOC: total organic carbon
UCT-KED: universal cell technology-kinetic energy discrimination

Table A-4
Acceptance Limits and Corrective Actions for Laboratory Analyses

Parameter	QC Sample	Acceptance Limits	Corrective Action
TOC	Method blank	Less than ½ the LOQ or greater than 1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater	Reprocess affected samples in batch. If insufficient sample volume remains for reprocessing or if holding times have been exceeded, report the results with B-flags.
	CRM	+/- 25%	Rerun CRM to confirm outlying condition. Verify operating conditions on a Corrective Action Form. As the CRM is received dry, no batch sample control is based on recovery values.
	Laboratory replicate	+/- 20%	Review data for errors. Matrix QC control limits are advisory as they are an indication of sample characteristics. Flag outliers.
	MS/MSD	+/- 25% recovery, +/-20% RPD	Review data for errors. Matrix QC control limits are advisory as they are an indication of sample characteristics. Flag outliers.
Percent Solids	Laboratory replicate	+/- 20%	Review data for errors and notes for indications of sample appearance (rocks, wood chips, etc.). Flag outliers.
Metals	Method blank	Less than ½ the LOQ or greater than 1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater	Reprocess affected samples in batch. If insufficient sample volume remains for reprocessing or if holding times have been exceeded, report the results with appropriate data qualifiers.
	LCS	+/- 20%	Correct problem; then, if necessary, re-prep and reanalyze the LCS and all samples for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, explain in the Case Narrative.
	Laboratory replicate	+/- 20%	Review data for errors. Matrix QC control limits are advisory as they are an indication of sample characteristics. Flag outliers.
	MS	+/- 25%	Review data for errors. For matrix evaluation only; no corrective action required.
	Internal standards	30–120% if IS in the ICAL Blank	If recoveries area is acceptable for QC samples but not field samples, the field samples may be considered to suffer from matrix effect.

Parameter	QC Sample	Acceptance Limits	Corrective Action
Mercury	Method Blank	Less than ½ the LOQ or greater than 1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater	Reprocess affected samples in batch. If insufficient sample volume remains for reprocessing or if holding times have been exceeded, the results shall be reported with the appropriate data qualifiers.
	LCS	+/- 20%	Correct problem; then, if necessary, re-prep and reanalyze the LCS and all samples for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, explain in the Case Narrative.
	Laboratory replicate	+/- 20%	Review data for errors. Matrix QC control limits are advisory as they are an indication of sample characteristics. Flag outliers.
	MS	+/- 25%	Review data for errors. For matrix evaluation only; no corrective action required.

Parameter	QC Sample	Acceptance Limits	Corrective Action
PAHs	Method blank	Less than ½ the LOQ or greater than 1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater	Reprocess affected samples in batch. If insufficient sample volume remains for reprocessing or if holding times have been exceeded, the results shall be reported with the appropriate data qualifiers.
	LCS	Laboratory acceptance criteria (see Table 4-6 for limits) or 50–150% until sufficient data have been generated for in-house limits	Correct problem; then, if necessary, re-prep and reanalyze the method blank, LCS, and all samples in the batch (including matrix QC) for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, data must be explained in the Case Narrative.
	CRM	See reference material certification for windows	Review data for errors. Flag outliers on summary sheet. If all laboratory QC and field samples have surrogates within limits, narrate the outliers in the Case Narrative.
	MS/MSD	Use LCS limits as advisory limits	Review data for errors. For matrix evaluation only; no corrective action required.
	Internal standards	50–200% of ICAL Midpoint standard	Inspect instrument for malfunctions, correct problem, and reanalyze extracts. Review data for possible matrix effect and rerun samples at dilution to bring internal standards into control. If corrective action fails, explain in Case Narrative.
	Surrogates	Laboratory acceptance criteria 21–134% or 50–150% until sufficient data have been generated for in-house limits	Correct problem; then, if necessary, re-prep and reanalyze failed samples for surrogates in the batch if sufficient material is available. If obvious chromatographic interference is present, reanalysis may not be necessary, but the client must be notified prior to reporting data, and failures must be discussed in the Case Narrative.

Parameter	QC Sample	Acceptance Limits	Corrective Action
PCB Aroclors	Method blank	Less than ½ the LOQ or less than 1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater	Reprocess affected samples in batch. If insufficient sample volume remains for reprocessing or if holding times have been exceeded, the results shall be reported with the appropriate data qualifiers.
	RM (Puget Sound Reference Material)	See Table 4-6 for limits	Review data for errors. Flag outliers on summary sheet. If all laboratory QC and field samples have surrogates within limits, narrate the outliers in the Case Narrative.
	LCS	Laboratory acceptance criteria (see Table 4-6 for limits) or 50-150% until sufficient data have been generated for in-house limits	Correct problem; then, if necessary, re-prep and reanalyze the method blank, LCS, and all samples in the batch (including matrix QC) for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, data must be explained in the Case Narrative.
	MS/MSD	Use LCS limits as advisory limits	Review data for errors. For matrix evaluation only; no corrective action required.
	Internal standards	50–200% of ICAL Midpoint standard	Inspect instrument for malfunctions, correct problem, and reanalyze extracts. Review data for possible matrix effect and rerun samples at dilution to bring internal standards into control. If corrective action fails, explain in Case Narrative.
	Surrogates	Laboratory acceptance criteria 44–126% or 50–150% until sufficient data have been generated for in-house limits	Correct problem; then, if necessary, re-prep and reanalyze failed samples for surrogates in the batch if sufficient material is available. If obvious chromatographic interference is present, reanalysis may not be necessary, but the client must be notified prior to reporting data, and failures must be discussed in the Case Narrative.

Parameter	QC Sample	Acceptance Limits	Corrective Action
SVOCs	Method blank	Less than ½ the LOQ or greater than 1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater. Common contaminants must not be detected > LOQ	Correct problem. Reprocess affected samples in batch. If insufficient sample volume remains for reprocessing or if holding times have been exceeded, the results shall be reported with the appropriate data qualifiers.
	LCS	Laboratory acceptance criteria (see Table 4-6 for limits) or 50–150% until sufficient data have been generated for in-house limits	Correct problem; then, if necessary, re-prep and reanalyze the method blank, LCS, and all samples in the batch (including matrix QC) for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, data must be explained in the Case Narrative.
	MS/MSD	Use LCS limits as advisory limits	Review data for errors. For matrix evaluation only; no corrective action required.
	Internal standards	50–200% of ICAL Midpoint standard	Inspect instrument for malfunctions, correct problem, and reanalyze extracts. Review data for possible matrix effect and rerun samples at dilution to bring internal standards into control. If corrective action fails, explain in Case Narrative.
	Surrogates	Laboratory acceptance criteria 24–134% or 50–150% until sufficient data have been generated for in-house limits	Correct problem, then re-prep and reanalyze failed samples for surrogates in the batch if sufficient material is available. If obvious chromatographic interference is present, reanalysis may not be necessary, but the client must be notified prior to reporting data, and failures must be discussed in the Case Narrative.

Parameter	QC Sample	Acceptance Limits	Corrective Action
Dioxin/Furans	Method blank	Less than ½ the LOQ, except OCDF and OCDD, which should be less than three times the LOQ, or less than 1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater	Confirm results by reanalyzing method blank. Re-extract and reprocess all associated samples if attributed to processing. Qualify data with B-flags as appropriate.
	Internal standards	25–150% of the continuing calibration verification	Correct problem, then reanalyze the sample(s) with failed internal standards. If corrective action fails in field samples with passing internal standards in laboratory QC, data must be explained in the Case Narrative.
	RM (Puget Sound Reference Material)	See Table 4-6	Review data for errors. If labels are in control for all samples and targets are in control for LCS, describe the issue in the case narrative.
	Extraction (cleanup) standard	35–197%	Review data for matrix effect. Rerun at dilution to prove matrix effect. Re-extract affected sample if attributed to processing error. If insufficient sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifiers and narrated.
	Labeled compounds	See Table 4-6	If matrix affects are noted from perfluorkerosene dropouts, rerun samples at dilution to bring labels into control. If not attributed to matrix effect, re-extract and reanalyze affected sample.
	Laboratory replicate	+/- 25%	For matrix evaluation only. Review data for errors. Flag outliers on summary sheet.

Notes:
Acceptance limits and corrective actions were provided by ARL based on its standard analytical protocols.

ARL: Analytical Resources LLC
CRM: certified reference material
ICAL: initial calibration
LCS: laboratory control sample
LOQ: limit of quantitation
MS: matrix spike
MSD: matrix spike duplicate
OCDD: octachlorodibenzo-*p*-dioxin
OCDF: octachlorodibenzofuran
PAH: polycyclic aromatic hydrocarbon
PCB: polychlorinated biphenyl
QC: quality control
RM: reference material

RPD: relative percent difference
SVOC: semivolatile organic compound
TOC: total organic carbon

References

Ecology. 2021. Sediment cleanup user's manual. Guidance for implementing the cleanup provisions of the sediment management standards, Chapter 173-204 WAC. Third revision December 2021. Pub. No. 12-09-057. Toxics Cleanup Program, Washington State Department of Ecology, Olympia, WA.

EPA. 2014. Record of Decision, Lower Duwamish Waterway Superfund Site. Part 3. Responsiveness summary. US Environmental Protection Agency, Region 10, Seattle, WA.