

Lower Duwamish Waterway Group

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

DATA REPORT: SURVEY AND SAMPLING OF LOWER DUWAMISH WATERWAY SEEPS FINAL

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Region 10

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Acronyms

Acronym	Definition
ARI	Analytical Resources, Inc.
BEHP	bis(2-ethylhexyl)phthalate
DOC	dissolved organic carbon
DQI	data quality indicator
Ecology	Washington State Department of Ecology
EPA	US Environmental Protection Agency
Frontier	Frontier Geosciences, Inc.
GPS	global positioning system

Acronym	Definition
LCS	laboratory control standard
LCSD	laboratory control standard duplicate
LDW	Lower Duwamish Waterway
LDWG	Lower Duwamish Waterway Group
MHHW	mean higher high water
MLLW	mean lower low water
MS	matrix spike
MSD	matrix spike duplicate
NAPL	non-aqueous phase liquid
NTU	nephelometric turbidity unit
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PCL	practical quantitation limit
QA/QC	quality assurance/quality control
QAPP	Quality Assurance Project Plan
RI	Remedial Investigation
RM	river mile
RPD	relative percent difference
SQS	Sediment Quality Standards
SVOC	semivolatile organic compound
TOC	total organic carbon
TPH	total petroleum hydrocarbons
TPH-D	diesel-range total petroleum hydrocarbons
TPH-G	gasoline-range total petroleum hydrocarbons
TPH-MO	motor oil-range total petroleum hydrocarbons
TSS	total suspended solids
VOC	volatile organic compound
WQC	Washington State water quality criteria

1.0 Introduction

This report summarizes the results of the seep survey and sampling conducted as part of the Phase 2 Remedial Investigation (RI) for the Lower Duwamish Waterway (LDW). This study was designed to conduct a reconnaissance survey of all LDW seeps and to collect seep water from a subset of these seeps for chemical analysis. Data from this study will be used for the following purposes:

- ◆ evaluate whether seep discharges below mean higher high water (MHHW)¹ and above mean lower low water (MLLW) may significantly contribute to chemical inputs to the LDW, either through dissolved phase, colloidal phase, or product phase inputs
- ◆ determine if additional seeps should be selected for sampling in the future either as part of the Phase 2 RI, site-specific source evaluations, or as part of the source control work being conducted by the Lower Duwamish Source Control Work Group
- ◆ determine if additional surface sediment samples are needed from seep areas

Two field events were conducted to meet the objectives of this study. The first field event, conducted on May 5 to May 10, 2004, was a reconnaissance survey to identify seeps, make visual observations of seep characteristics, and measure conventional water quality parameters in the field. The second field event, conducted on June 29 to July 3, 2004, involved the collection of seep water samples for chemical analysis from a subset of seeps that were selected based on the results of the reconnaissance survey, existing data, and potential source information.² Section 2.0 summarizes the methods and results of the reconnaissance survey and Section 3.0 summarizes the methods and results of the seep water sampling for chemical analyses. The text is supported by the following appendices:

- ◆ Appendix A – reconnaissance survey data tables
- ◆ Appendix B – rainfall data and associated seasonal changes in groundwater elevations
- ◆ Appendix C – chain of custody forms
- ◆ Appendix D – field forms and field notes
- ◆ Appendix E – data validation report
- ◆ Appendix F – seep water analytical data tables

¹ The Source Control Work Group is responsible for implementation of plans for source characterization above MHHW.

² As described in Section 2.4, the subset of seeps to be sampled was selected at a meeting with EPA and Ecology on May 25, 2004. A portion of this meeting included input from stakeholders on seep selection.

- ◆ Appendix G – raw analytical laboratory data
- ◆ Appendix H – data management

2.0 Reconnaissance Survey

The objective of the reconnaissance survey was to identify seeps along the LDW, record observations, and collect field measurements of conventional water quality parameters at as many seeps as possible during the survey period, including at least one major seep per area with high seepage. Data from the reconnaissance survey in combination with potential source information and existing data were used to identify a subset of seeps for chemical analysis. Additional details on study design, rationale, and methods for the reconnaissance survey are presented in the Quality Assurance Project Plan (QAPP) for Survey and Sampling of Lower Duwamish Waterway Seeps (Windward 2004).³

The reconnaissance survey was conducted on May 5, 6, 7, and 10, 2004. These survey dates were selected because tides as low as -3.3 ft MLLW occurred during that period. The survey area included all shoreline areas accessible by boat along the LDW from River Mile⁴ (RM) 0.0 to RM 5.0.⁵

The following sections present the seep identification process; seep observations and water quality measurements; deviations from the QAPP; and the subset of seeps that were selected for chemical analysis. Data collected during the reconnaissance survey and identified seep locations are presented in Appendix A. A full set of photographs documenting the survey can be viewed on the Lower Duwamish Waterway Group (LDWG) website; go to <http://www.ldwg.org>, click on *documents*, and scroll to the Seep Survey Photo Album. Photographs will also be submitted to EPA and Ecology on a CD.

2.1 SEEP IDENTIFICATION

The shoreline was accessed by boat during the reconnaissance survey. Two boats were used to maximize efficiency of the survey during the limited low tide period with water levels below +1 ft MLLW. The field crew in the first boat identified and staked the seeps. The field crew in the second boat recorded seep observations and water quality measurements at staked seeps.

Information was collected at as many seeps as possible during the reconnaissance survey. At locations where multiple seeps were flowing, one seep was selected that

³ This document is referred to as the QAPP in the remainder of this report.

⁴ River mile as measured from the southern tip of Harbor Island.

⁵ Seeps within the Terminal 117 early action area, between RM 3.5 and 3.7 on the west side of the LDW, were not staked or assessed during the reconnaissance survey because seep water samples were recently collected within that area prior to this sampling event and a full data validation was conducted (Windward et al. 2004).

was considered representative of conditions in the area. Some areas with low broad areas of seepage were not identified during the survey because the low flow rates would not allow for sample collection. In addition, some areas with barges or piers resulted in restricted access and could not be surveyed. Locations of areas with broad seepage and restricted access are identified on a qualitative basis on Figure A-1 in Appendix A. A total of 82 seeps were staked by the field crew in the first boat. Seeps 1 to 26 were staked on May 5, Seeps 27 to 56 were staked on May 6, and Seeps 57 to 82 were staked on May 7. These seeps are shown in Figure 2-1.

Selected seep location coordinates were recorded with a global positioning system (GPS) and marked with stakes. In addition, compass bearings on fixed objects were recorded and a rough schematic diagram was drawn for each seep location. Each seep staked during the survey was assigned a unique alphanumeric location ID number. The first three characters of the location ID are "LDW" to identify the Lower Duwamish Waterway project area. The next two characters are "SP" to identify the type of medium (i.e., seep) observed, followed by consecutive numbers, beginning with 01, to identify the specific location within the LDW area. For example, the location ID of the first seep staked was LDW-SP-01. The sample ID number for the water quality parameter data was the location ID followed by the letter "R" to signify the reconnaissance survey, and then the letter "a" or "b" to designate the duplicate measure. For example, the sample ID for the first water quality measurement at the first seep was LDW-SP-01-R-a.

2.2 SEEP WATER QUALITY MEASUREMENTS AND OBSERVATIONS

Seep water was collected at each staked seep for measurement of conventional water quality parameters. Seep water was collected by placing a container directly under the flow, or by directing the flow into a container using a funnel with attached tubing. A Hydrolab probe was placed into the container of seep water to measure conductivity, temperature, dissolved oxygen, pH, and oxidation-reduction potential. Water quality measurements of LDW water were also made at approximately one location per river mile by lowering the Hydrolab probe into the LDW and recording measurements at both the surface and at 1 m below the surface.

Seep water quality data were collected by the field crew in the second boat at each of the 82 staked seeps. Most water quality measurements were made on the same day that the seeps were staked by the field crew in the first boat. However, some measurements were made on subsequent days because rising water levels caused some seeps to become submerged by the time the second boat arrived at the seep. Seep water quality data are presented in Table A-1 of Appendix A. Measurements were also made of LDW water quality at locations within the LDW adjacent to or directly offshore from five seeps (Seeps 19, 26, 56, 62, and 73). LDW water quality data are presented in Table A-2. These measurements were taken at 1-m depth below the LDW water surface, and were taken as close to the shore as possible; distances from the waterline at the time of sampling were as follows:

- ◆ Seep 19: 10 m
- ◆ Seep 26: 15 m
- ◆ Seep 56: adjacent to seep
- ◆ Seep 62: 40 m
- ◆ Seep 73: 21 m

At each staked seep location, observations were made of seep characteristics such as staining or discoloration, oily or other sheen, bacterial slime, odor, colored or milky discharge, formation of precipitates, vegetation, or the presence of waste material. In addition, descriptions of the seep substrate, the embankment substrate, and the seep location relative to vertical changes in the embankment or beach substrate were recorded. Qualitative flow rate estimates were made at each seep; estimates were described as either high flow (e.g., active flow), medium flow (e.g., smaller stream), or low flow (e.g., trickle). Notes on these observations are presented in Table A-2 of Appendix A.

2.3 FIELD DEVIATIONS FROM THE QAPP

Several QAPP deviations were necessary in the field because of time constraints associated with sampling during low tide levels. These deviations are noted as follows:

- ◆ Duplicate Hydrolab measurements were made only at the first two locations on the first two days instead of at all seep locations.
- ◆ The survey was conducted in some areas (Seeps 24, 25, 26, 51, 55, 56, 76, 79, 80, 81, and 82) when water level was +1 ft MLLW.
- ◆ One additional field day (May 10, 2004) was added to the survey to collect water quality measurements at Seeps 72, 75, 77, and 78.

2.4 SELECTION OF SEEPS FOR CHEMICAL ANALYSIS

Information collected during the reconnaissance survey was submitted to the US Environmental Protection Agency (EPA) and the Washington State Department of Ecology (Ecology) on May 18, 2004. A meeting was held on May 25, 2004 with EPA and Ecology to select a subset of seeps for chemical analysis. Input from stakeholders was also received at this meeting and was considered in seep selection. These seeps were selected based on a weight-of-evidence approach, which included potential source information and existing sediment, groundwater, and seep data, in addition to information gathered during the reconnaissance survey. Additional details on potential sources and existing sediment, groundwater, and seep data are discussed in more detail in the QAPP (Windward 2004).

Eighteen seeps⁶ were selected at the May 25, 2004 meeting for collection of seep water for chemical analyses. Seep locations are presented in Figure 2-1. A summary of the rationale for selecting each seep is presented in Table 2-1. Key considerations were proximity to potential sources, existing sediment data, and observations made during the reconnaissance survey. Properties listed in Table 2-1 were considered potential sources based on information from the following: 1) Appendix G of the Phase 1 remedial investigation (Windward 2003), 2) the Source Control Work Group's source matrix (Flint 2003), and 3) input from EPA, Ecology, and stakeholders at a meeting held on May 25, 2004.

Table 2-1. Summary of rationale for selecting seeps to sample for chemical analysis

SEEP	RATIONALE
10	possible historical source; sediment CSL/ML exceedances
12	adjacent to Crowley; sediment CSL/ML exceedances
20	adjacent to Jorgensen; light sheen observed in LDW water along Jorgensen property during reconnaissance survey – no sheen observed in seep or its intertidal vicinity
24	adjacent to Boeing Development Center; potential historical source from former hazardous waste site and scrap facility; sediment CSL/ML exceedances
39	adjacent to Delta Marine; potential upland dredge spoils; high seep flow
41	light sheen observed in the vicinity of the seep during reconnaissance survey
48	adjacent to Long Painting; public access area
53	adjacent to Swan Bay Holdings; black ooze at seep and petroleum odor observed during reconnaissance survey
54	adjacent to Swan Bay Holdings; grey foamy seep water and construction and metal debris observed along the bank during reconnaissance survey
61	adjacent to Glacier NW (near former Reichhold plant); discolored seep water and sulfide odor observed during reconnaissance survey
62	adjacent to Glacier NW (near former Reichhold plant); dioxins/furans detected in sediment
64	sheen in vicinity of seep and discolored seep water observed during reconnaissance survey
69	near Central Painting, McFarland Property, and Birmingham Steel; restoration site; public access; sediment SQS/SL exceedances
71	near Birmingham Steel; public access area
75	near T-108/Chiyoda property; potential historical source of PCBs, PAHs, and metals: gasoline detected in upland groundwater; discolored seep water observed during reconnaissance survey; restoration area
76	sediment CSL/ML exceedances; discolored seep water observed during reconnaissance survey
80	adjacent to James Hardie Gypsum; downgradient from Philip Services; sediment CSL/ML exceedances
82	adjacent to Lone Star; adjacent to historical hazardous waste disposal area and junkyard; downgradient from Philip Services

CSL/ML – Washington State Sediment Management Standards Cleanup Screening Level or the Maximum Level in the Dredged Material Management Program

⁶ Samples were subsequently collected at 16 of the 18 selected seeps because two of the seeps (Seep 24 and Seep 53) were dry at the time of sampling.

3.0 Seep Water Sampling and Analyses

This section discusses the methods and results of sampling and chemical analyses of seep water samples.

3.1 METHODS

Seep water sampling for chemical analyses was conducted over a period of five days from June 29 to July 3, 2004. These sampling dates were selected because tides as low as -4.0 ft MLLW occurred during that period. This section discusses the methods used to collect seep water and measure field water quality parameters, and summarizes the chemical analysis methods. A detailed description of methods is presented in Section 3.2.2 of the QAPP (Windward 2004).

3.1.1 Sampling methods

All seeps identified for seep water sampling were located by the GPS coordinates and the stakes placed during the reconnaissance survey.

3.1.1.1 Seep water collection methods

This section describes the seep water collection methods for analysis of the following chemicals:

- ◆ metals
- ◆ mercury
- ◆ semi-volatile organic compounds (SVOCs)
- ◆ volatile organic compounds (VOCs)
- ◆ polychlorinated biphenyls (PCBs) as Aroclors
- ◆ organochlorine pesticides
- ◆ diesel-range total petroleum hydrocarbons (TPH-D)⁷
- ◆ gasoline-range TPH (TPH-G)
- ◆ total organic carbon (TOC)
- ◆ dissolved organic carbon (DOC)
- ◆ total suspended solids (TSS)

Seep water samples were collected using stainless steel PushPoint mini-piezometers developed and sold by MHE Products. A peristaltic pump was used to withdraw seep water from the mini-piezometer through a 2 to 3-ft length piece of Masterflex tubing.

⁷ TPH-D analysis included reporting of motor oil-range TPH (TPH-MO).

The mini-piezometers were generally placed in the sediment to a depth of about 4 to 6 inches. Once the seep water ran clear (i.e., usually after about 50 mL of flow or 30 seconds of pumping), a turbidity measurement was taken.

If the turbidity was less than or equal to 5 nephelometric turbidity units (NTU), mini-piezometers were used to sample the seep if a sufficient volume of sample could be collected with the mini-piezometers. Table 3-1 summarizes the sample collection methods used at each seep. Seeps were identified as potential non-aqueous phase liquid (NAPL) seeps if a sheen or petroleum odor was observed in the immediate vicinity of the seep during the reconnaissance survey or during the seep water sampling event. TPH was analyzed in seep water collected from potential NAPL seeps.

At Seeps 10 and 62, sufficient seep water could not be collected using the mini-piezometer, so seep water was collected by placing a glass funnel with attached tubing into the flowing seep water channel and directing the flow into the sampling container (Table 3-1). At Seep 64, turbidity was less than 5 NTU on July 2, but only filtered samples and a portion of the unfiltered samples (SVOCs and PCBs) could be collected before the tide rose and covered the seep. Upon returning to the seep on July 3, the turbidity remained greater than 5 NTU using either the mini-piezometer method (after pumping for 15 minutes) or the funnel method to collect surface seep water flow. Therefore, the remaining unfiltered samples were not collected. Two seep locations, 24 and 53, could not be sampled. At the intended time of sampling at Seep 24, there was no visible flow and the sediment was dry. Seep 53 was submerged because of the discharge from an upgradient outfall on June 30 and July 2. On July 3, Seep 53 was exposed, but no flow was emerging from the seep and the sediment in the vicinity of the seep was dry.

Table 3-1. Seep characteristics and sample collection methods

SEEP NUMBER	DATE COLLECTED	LOCATION COORDINATES ^a	POTENTIAL NAPL SEEP	TURBIDITY (NTU)	SAMPLE COLLECTION METHOD	TIME COLLECTED	APPROX. WATER LEVEL AT TIME OF COLLECTION (ft MLLW)
Seep 10	7/1/04 ^b	X: 1273441 Y: 198968	no	>5	S	8:45	-1.1
Seep 12	7/1/04	X: 1272645 Y: 198679	no	≤5	MP	9:15	-2.2
Seep 20	7/1/04	X: 1276012 Y: 195160	no	≤5	MP	10:45	-3.6
Seep 24	ns ^c	na na	no	ns	ns	ns	ns
Seep 39	7/1/04	X: 1276275 Y: 192164	no	≤5	MP	13:30	+1.8
Seep 41	7/1/04	X: 1275885 Y: 193497	yes ^d	≤5	MP	12:00	-2.2

SEEP NUMBER	DATE COLLECTED	LOCATION COORDINATES ^a	POTENTIAL NAPL SEEP	TURBIDITY (NTU)	SAMPLE COLLECTION METHOD	TIME COLLECTED	APPROX. WATER LEVEL AT TIME OF COLLECTION (ft MLLW)
Seep 48	6/30/04	X: 1273279 Y: 197420	no	≤5	MP	7:30	0.7
Seep 53	ns ^e	na na	yes ^f	ns	ns	ns	ns
Seep 54	6/30/04	X: 1269884 Y: 200289	yes ^d	≤5	MP	9:45	-2.7
Seep 61	7/2/04	X: 1267783 Y: 203778	no	≤5	MP	11:00	-3.9
Seep 62	7/2/04 ^b	X: 1267939 Y: 204000	no	>5	S	10:30	-3.4
Seep 64	7/2/04	X: 1266958 Y: 206202	yes ^g	≤5 ^h	MP	12:20	-3.4
Seep 69	6/29/04	X: 1265842 Y: 208291	yes ⁱ	≤5	MP	13:00	5.6
Seep 71	6/29/04	X: 1265941 Y: 210357	no	≤5	MP	8:40	-1.4
Seep 75	7/3/04	X: 1267543 Y: 207510	no	≤5	MP	10:30	-1.7
Seep 76	6/29/04	X: 1268560 Y: 206456	no	≤5	MP	10:30	-0.3
Seep 80	7/1/04	X: 1268821 Y: 203600	yes ⁱ	≤5	MP	13:00	5.6
Seep 82	6/30/04	X: 1269372 Y: 202731	no	≤5	MP	7:00	4.1

ns – location was not sampled

na – not available

MP – mini-piezometer method

NAPL – non-aqueous phase liquid

NTU – nephelometric turbidity unit

S – surface collection method using funnel and tubing

^a NAD 1983 State Plane Washington North

^b VOCs were resampled on July 30, 2004 because the original VOC samples from these seeps were inadvertently discarded by the laboratory because of a miscommunication

^c Seep 24 was not sampled because it was dry

^d Sheen observed at seep during reconnaissance survey and again during sample collection event

^e Seep 53 was not sampled because it was either dry or submerged in flow from a nearby outfall

^f Black liquid and petroleum odor associated with seep in reconnaissance survey; black liquid not observed during sample collection event although petroleum odor was associated with sediment in general area

^g Sheen observed in the LDW near the seep (no apparent association with the seep itself) during reconnaissance survey and again during sample collection event

^h Turbidity was ≤5 NTU on July 2 before collection of unfiltered samples was completed, but >5 NTU on July 3.

ⁱ Added as a NAPL site during seep water chemistry sampling event because sheen was observed at seep at the time of sampling

Because of the large quantity of sample volume required for analysis, two mini-piezometers attached to separate peristaltic pumps were used at each seep location. The first chemistry sample collected was the mercury sample, using the detailed steps described in the QAPP to minimize sample contamination. Following the sampling for mercury, seep water samples were collected for metals,⁸ PCBs, organochlorine pesticides, SVOCs, TPH-D, TSS, TOC, and DOC analyses. Samples for metals analyses were filtered in the field using an in-line disposable filter cartridge containing a 0.45- μm nitrocellulose filter. Mercury and DOC samples were not filtered in the field, but were instead filtered in the laboratory on the day they were received. A third mini-piezometer at each seep was used for sampling VOCs and gasoline-range TPH (TPH-G). These volatile samples were collected using a 50-mL syringe designed by MHE Products specifically for use with the PushPoint mini-piezometers.

For sample bottles requiring acidification, the preservative was added to the sample bottles prior to field collection, with the exception of mercury and DOC bottles. Mercury and DOC samples were acidified after they were filtered in the laboratory.

Turbidity was measured at each seep to determine whether the seep water sample should be filtered prior to chemical analyses.⁹ If the turbidity of the seep sample was less than or equal to 5 NTU, both unfiltered and filtered samples were collected and analyzed to determine what particle size fraction was associated with the chemicals, with the exception of VOC samples, which were never filtered. If the turbidity was greater than 5 NTU (i.e., Seeps 10 and 62), then only filtered samples were collected and analyzed because there was reason to believe that the sampling method entrained sediment that was not present in the undisturbed seep flow. For samples collected from locations with the potential presence of NAPL, both the unfiltered and filtered samples were analyzed for TPH-D. For these locations, the TPH-G sample was not filtered because the volatile components would likely be lost during the filtering process. Table 3-2 summarizes the seep water chemistry samples collected at each seep, based on the turbidity results and the potential NAPL presence.

Samples for SVOCs, PCBs, and organochlorine pesticide analyses were filtered in the laboratory through a 1- μm glass fiber filter and samples for mercury were filtered in the laboratory through a 1- μm polyethylsulfone filter. These filter sizes were chosen to remove non-colloidal particles greater than 1 μm that may have been introduced into the seep water by the sampling method. Samples for metals (except mercury) analyses were filtered through a 0.45- μm nitrocellulose filter to represent the dissolved fraction for comparison to Washington State dissolved water quality criteria (WQC).

⁸ Arsenic analyses were conducted on aliquots taken from the metals bottle.

⁹ VOC samples were not filtered prior to analysis.

Table 3-2. Seep water chemistry samples collected

SEEP NUMBER	UNFILTERED FRACTION										FILTERED FRACTION						
	VOCs	METALS	MERCURY	SVOCs	PCBs	ORGANOCHLORINE PESTICIDES	TOC	TSS	TPH-D	TPH-G	METALS	MERCURY	SVOCs	PCBs	ORGANOCHLORINE PESTICIDES	DOC	TPH-D
Seep 10	X										X	X	X	X	X	X	
Seep 12	X	X	X	X	X	X	X	X			X	X	X	X	X	X	
Seep 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X	
Seep 39	X	X	X	X	X	X	X	X			X	X	X	X	X	X	
Seep 41	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Seep 48	X	X	X	X	X	X	X	X			X	X	X	X	X	X	
Seep 54	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Seep 61	X	X	X	X	X	X	X	X			X	X	X	X	X	X	
Seep 62	X										X	X	X	X	X	X	
Seep 64	X			X	X		X		X	X	X	X		X	X	X	
Seep 69	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Seep 71	X	X	X	X	X	X	X	X			X	X	X	X	X	X	
Seep 75	X	X	X	X	X	X	X	X			X	X	X	X	X	X	
Seep 76	X	X	X	X	X	X	X	X			X	X	X	X	X	X	
Seep 80	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Seep 82	X	X	X	X	X	X	X	X			X	X	X	X	X	X	

3.1.1.2 Field quality control samples

Four types of field quality control (QC) samples were collected. These samples included: 1) rinsate blanks for the sampling equipment, 2) field replicate samples, 3) trip blanks for VOCs, and 4) atmospheric field blanks for mercury. Each of these types of samples is described below.

Rinsate blank samples were created by rinsing the sample collection device (i.e., mini-piezometer with attached tubing and in-line filter, or glass funnel with attached tubing) with laboratory reverse-osmosis water. Using the mini-piezometer with attached tubing, two rinsate blanks were collected for unfiltered mercury analysis, and one rinsate blank was collected for unfiltered metals, PCBs, organochlorine pesticides, and diesel-range TPH. Using the glass funnel with attached tubing, one rinsate blank was collected for unfiltered mercury, metals, PCBs, organochlorine pesticides, and diesel-range TPH.

One field replicate sample was collected at Seep 82 and analyzed for all filtered and unfiltered parameters except TPH. One field replicate sample was collected at Seep 80 and analyzed for filtered TPH-D, and unfiltered TPH-G and TPH-D.

Each cooler with VOC samples included a trip blank sample, which was analyzed for VOCs. The trip blanks consisted of reverse osmosis water sealed in a VOC sample container by the laboratory. These blank samples were transported from the laboratory to the field and then returned to the laboratory, unopened, with the field samples.

Six atmospheric blank samples were collected. These field blanks consisted of a sample bottle filled with reverse osmosis water. At the initiation of seep water sample collection, the sample bottle lid was removed, and was then replaced immediately after the mercury sample was collected. One atmospheric blank was collected for each group of seep water samples collected within a 2-mi river section on the day those samples were collected. The sample groups and collection dates associated with each atmospheric blank are as follows:

- ◆ Seeps 69, 71, and 76 on June 29
- ◆ Seeps 48, 54, and 82 on June 30
- ◆ Seeps 20, 39, and 41 on July 1
- ◆ Seeps 10, 12, and 80 on July 1
- ◆ Seeps 61, 62, and 64 on July 2
- ◆ Seep 75 on July 3

3.1.1.3 Field measurements

Conventional water quality parameters were measured in the field using a Hydrolab probe, which was immersed in a container of seep water. The probe was allowed to equilibrate before taking measurements of conductivity, temperature, dissolved oxygen, pH, and oxidation-reduction potential. Duplicate measurements with two different Hydrolab instruments were taken at all seep locations. The results of these measurements are presented in Table F-1 in Appendix F.

Seep flow rate was calculated using one of two methods: 1) measuring the time for diverted seep flow to fill a container of known volume, or 2) measuring the width, depth, and velocity of the channel; velocity was obtained by measuring the time for a styrofoam float to cover a known distance. Flow rate data for each of the seeps sampled in the second field event are presented in Table F-2 in Appendix F.

3.1.1.4 Sample identification

Location IDs for each seep were assigned during the reconnaissance survey, as described in Section 2.1. The sample ID consisted of the location ID followed by the letter "C" to signify chemical sampling, rather than the letter "R" as used for the reconnaissance survey water quality samples. The sample ID was then followed by the letter "U" to designate an unfiltered sample, or by the letter "F" to designate a filtered sample. For example, the filtered seep water sample collected at seep location 12 was

LDW-SP-12-C-F. Field quality assurance/quality control (QA/QC) samples were assigned modified sample IDs as described below:

- ◆ Field replicate samples were assigned the same sample ID as the sample collected at that seep, followed by "FD." For example, the filtered field replicate sample collected from seep location 82 was LDW-SP-82--C-FD-F.
- ◆ Rinsate blanks were assigned the same sample ID as the sample collected at that seep, followed by "RB." For example, the rinsate blank collected at seep location 64 was LDW-SP-64-C-RB.
- ◆ Identifiers for VOC trip blanks contained the prefix "LDW-SP" followed by a unique numeric identifier, the letter "C," and the letters "TB" to designate trip blank. For example, the first trip blank submitted to the laboratory was LDW-SP-C-TB-01.
- ◆ Atmospheric blanks (primarily to account for potential atmospheric mercury contamination) were assigned the same sample ID as the sample collected at that seep, followed by "AB." For example, an atmospheric blank collected at seep location 64 was LDW-SP-64-C-AB.

3.1.1.5 Field deviations from the QAPP

Several deviations to the QAPP were made during field sampling, as described in the following paragraphs.

Seep 64 was sampled over two days because of time constraints related to the tide. Turbidity was less than 5 NTU on July 2, but only filtered samples and a portion of the unfiltered samples (SVOCs and PCBs) could be collected before the tide rose and covered the seep. Upon returning to the seep on July 3, the turbidity remained greater than 5 NTU using either the mini-piezometer method (after pumping for 15 minutes) or the funnel method to collect surface seep water flow. Therefore, the remaining unfiltered samples were not collected (metals, mercury, organochlorine pesticides,¹⁰ and TSS).

All the sampling could not be completed by July 2, 2004 because of tidal constraints, so an additional day was needed to complete the sampling. To complete the sampling, Seep 75 was sampled and rinsate blank samples were collected on July 3, 2004.

Two locations (Seeps 24 and 53) could not be sampled. At the intended time of sampling at Seep 24, there was no visible flow and the sediment was dry. Seep 53 was submerged by flow from an upgradient outfall on June 30 and July 2. On July 3, Seep

¹⁰ Although an unfiltered sample from Seep 64 was analyzed for PCBs, and PCBs and pesticides were analyzed in the same extract, pesticide data are not available for this sample because the pesticide standards were not analyzed. The standards were not analyzed because pesticides were not requested for this sample because the intent was to collect this sample the following day, as discussed above. Also, sufficient volume was not available for this sample to obtain relevant pesticide detection limits.

53 was exposed, but no flow was emerging from the seep and the sediment in the vicinity of the seep was dry.

An additional method that was not specified in the QAPP was used to measure flow rates at some seeps as a time-saving measure. This method involved measuring the width, depth, and velocity of the channel. The velocity was obtained by measuring the time for a styrofoam float to cover a known distance. The accuracy of this method is not expected to be substantially different than that of the method specified in the QAPP.¹¹

The QAPP specified that one field replicate sample would be collected for every 10 samples analyzed for mercury. However, as a result of an oversight in the field, only one field replicate sample was collected for the 13 unfiltered samples analyzed for mercury and only one field replicate sample was collected for the 16 filtered samples analyzed for mercury.

3.1.2 Laboratory methods

The methods and procedures used to analyze the seep water samples are briefly summarized below and described in detail in the QAPP (Windward 2004).

3.1.2.1 Analytical methods

The methods used for chemical analysis of seep water samples as well as the analytical laboratory that conducted the analyses are identified in Table 3-3.

Table 3-3. Laboratory preparation and analytical methods

PARAMETER	SAMPLE PREPARATION METHOD	CLEANUP METHOD	ANALYTICAL METHOD	LABORATORY
VOCs	EPA SW5030	none	GC/MS (EPA 8260B)	ARI
Mercury	EPA 1631E	EPA 1631E	CVAF (EPA 1631E)	Frontier
Arsenic	SM 3114C	none	HG-AFS (SM 3114C)	Frontier
Metals	1% HNO ₃ closed vessel oven digest	none	ICP-MS (EPA 200.8)	Frontier
SVOCs	EPA 3510C or EPA 3520C	none	GC/MS (EPA 8270C)	ARI
PCBs as Aroclors	Manchester Method (Modified EPA 3510)	EPA 3660B (sulfur) optional ^a ; EPA 3630B (silica gel) optional ^a	GC/ECD (EPA 8080)	ARI
Organochlorine pesticides	Manchester Method (Modified EPA 3510)	EPA 3660B (sulfur) optional ^a ; EPA 3630B (silica gel) optional ^a	GC/ECD (EPA 8080)	ARI

¹¹ The flow rate method in the QAPP involved measuring the rate at which seep water flowing over a defined area filled a container of known volume.

PARAMETER	SAMPLE PREPARATION METHOD	CLEANUP METHOD	ANALYTICAL METHOD	LABORATORY
Total organic carbon	EPA 415.1	none	Non-dispersive infrared combustion (EPA 415.1)	ARI
Dissolved organic carbon	EPA 415.1	none	Direct combustion (EPA 415.1)	ARI
Total suspended solids	EPA 160.2	none	EPA 160.2	ARI
Total petroleum hydrocarbons – gasoline range	SW 5030	none	WDOE NWTPH-G	ARI
Total petroleum hydrocarbons – diesel extended range	SW 3510C	none	WDOE NWTPH-Dx	ARI

ARI – Analytical Resources, Inc.

CVAF – cold vapor atomic fluorescence

Dx – diesel extended range

Frontier – Frontier Geosciences, Inc.

G – gasoline

GC/ECD – gas chromatography/electron capture detection

GC/MS – gas chromatography/mass spectrometry

HG-AFS – hydride generation atomic fluorescence spectroscopy

ICP-MS – inductively coupled plasma mass spectrometry

NWTPH – Northwest total petroleum hydrocarbon

WDOE – Washington Department of Ecology

^a The need for cleanup and the type of cleanup was based on screens and the color of the extracts.

3.1.2.2 Laboratory deviations from the QAPP

Several deviations from the QAPP were made related to laboratory analysis of samples, as described in the following paragraphs.

The original VOC samples for Seeps 10 and 62 were inadvertently discarded by the laboratory prior to analysis because of a discrepancy in the chain-of-custody form. Seeps 10 and 62 were re-sampled for VOCs during a low tide on July 30, 2004.

The filtered fraction of Seep 64 was collected but not analyzed for SVOCs or TPH-D. This oversight was not discovered before holding times were exceeded for these samples. As a result, there are no SVOC or TPH-D data for filtered samples from Seep 64. However, all SVOCs and TPH-D results were undetected in unfiltered samples from Seep 64, indicating that detected results would not have been expected in the filtered samples.

Preservative was not added to the metals bottles prior to field collection on June 29, 2004. Thus, filtered and unfiltered metals samples for Seeps 69, 71, and 76 were preserved upon receipt in the laboratory on June 29, 2004. Preservation of samples in the laboratory rather than at the time of field collection is not a method deviation, and did not require the addition of data qualifiers to the results for these samples.

Samples LDW-SP-39-C-F and LDW-SP-39-C-U for metals and mercury analysis were delivered to Analytical Resources, Inc. (ARI) rather than Frontier Geosciences, Inc.

(Frontier) on July 1, 2004, so samples were delivered to Frontier on the following day, July 2. As a result, the mercury samples were filtered and preserved one day later than specified in the QAPP. Because filtration and preservation one day after sampling is not a method deviation, data qualifiers were not added to the results for these samples.

EPA method 8080 was used for analysis of both PCBs and pesticides, rather than EPA method 8082 for PCBs and EPA method 8081 for pesticides, to ensure that the lowest possible detection limits were obtained.

Although not specified in the QAPP, water samples from Seeps 69 and 80 were analyzed for TPH-D and TPH-G because a sheen was observed in the immediate vicinity of those seeps at the time of sampling.

3.2 RESULTS

Results of the seep water chemical analyses are summarized in this section and compared to WQC. Complete data tables and raw laboratory data can be found in Appendices F and G, respectively. A detailed discussion of the approach used in averaging laboratory replicates and methods for calculating total concentrations for PCBs and DDTs are presented in Appendix H.

Data validation results are also presented in this section. Quality assurance review of the chemistry data was conducted in accordance with the QA/QC requirements and technical specifications of the methods, and the National Functional Guidelines for Organic and Inorganic Data Review (EPA 1999, 2002). Saylor Data Solutions, Inc. conducted a full data validation of the analytical results. The results of the data validation are summarized in Section 3.2.2 and presented in full in Appendix E.

3.2.1 Seep water sampling results

In this section, chemical concentrations measured in seep water samples are compared to acute and chronic marine WQC for the surface waters of the State of Washington (WAC 173-201). Acute and chronic WQC for metals, with the exception of the chronic WQC for mercury, represent dissolved concentrations, so comparisons are made to filtered samples. Acute and chronic WQC for organic compounds and the chronic WQC for mercury represent total concentrations, so comparisons for these chemicals are made to unfiltered samples. Acute WQC represent instantaneous concentrations not to be exceeded at any time for organochlorine pesticides, and 1-hour average concentrations not to be exceeded more than once every three years on the average for metals and pentachlorophenol (PCP). Chronic WQC represent 24-hour average concentrations not to be exceeded at any time for organochlorine pesticides, and 4-day average concentrations not to be exceeded more than once every three years on the average for metals and PCP. Interpretation of the relevance and applicability of acute and chronic WQC to seep water data will be discussed in the Phase 2 risk assessments and RI. For example, these assessments will discuss how the tidal cycle in the LDW

would affect exposure duration and dilution (e.g., chronic exposure conditions are implausible) as well as the exposure potential for the set of organisms used to determine WQC for specific chemicals. In addition, the RI will summarize groundwater and surface water data available for the LDW, which may be useful in interpreting concentrations of some chemicals in seeps (e.g., copper). These seep data will also be reviewed to determine the need for adjacent surface sediment samples in the surface sediment QAPP.

3.2.1.1 Metals

Table 3-4 presents a summary of the metals detected in seep water samples, including the number of detections, the range of detected metals concentrations, and the range of detection limits. Results for all metals analyzed in seep water are presented in Table 3-5, and compared to marine chronic and acute WQC. Concentrations in bold in Table 3-5 are greater than their respective WQC.

Table 3-4. Summary of metals detected in seep samples

ANALYTE	DETECTION FREQUENCY ^a	MINIMUM DETECTED CONCENTRATION (µg/L)	MAXIMUM DETECTED CONCENTRATION (µg/L)	MINIMUM REPORTING LIMIT (µg/L)	MAXIMUM REPORTING LIMIT (µg/L)
Arsenic (filtered)	17/17	0.054	253	na	na
Arsenic (unfiltered)	14/14	0.058	287	na	na
Cadmium (filtered)	17/17	0.009	0.513	na	na
Cadmium (unfiltered)	14/14	0.021	0.710	na	na
Chromium (filtered)	0/17	nd	nd	1.51	9.74
Chromium (unfiltered)	1/14	74.9	74.9	2.91	11.4
Copper (filtered)	8/17	8.16	22.8	3.28	7.77
Copper (unfiltered)	11/14	8.06	50.9	4.77	6.47
Lead (filtered)	17/17	0.036	3.00	na	na
Lead (unfiltered)	14/14	0.080	296	na	na
Mercury (filtered)	17/17	0.00062	0.0153	na	na
Mercury (unfiltered)	14/14	0.00061	0.582	na	na
Nickel (filtered)	13/17	0.84	5.25	0.040	0.040
Nickel (unfiltered)	13/14	2.80	8.83	0.040	0.040
Silver (filtered)	15/17	0.012	0.113	0.015	0.015
Silver (unfiltered)	12/14	0.026	0.126	0.015	0.015
Zinc (filtered)	17/17	3.29	164	na	na
Zinc (unfiltered)	14/14	3.49	322	na	na

na – not applicable

nd– not detected

^a Including the field replicate sample, 17 filtered samples and 14 unfiltered samples were analyzed for all metals.

Table 3-5. Concentrations of metals in filtered and unfiltered seep water samples and marine WQC (for comparison to the unfiltered concentrations for mercury and filtered concentrations for all other metals)

ANALYTE (µg/L)	SEEP 10	SEEP 12	SEEP 20	SEEP 39	SEEP 41	SEEP 48	SEEP 54	SEEP 61	SEEP 62	CHRONIC WQC	ACUTE WQC
Arsenic (filtered)	0.841	0.771	1.35	0.054	0.235	0.422	0.404	72.4^a	6.84	36	69
Arsenic (unfiltered)	na	1.13	1.58	0.058	0.230 ^b	0.618	1.30	67.2	na		
Cadmium (filtered)	0.085	0.107	0.111	0.206	0.133	0.101	0.012	0.009	0.110	9.3	42
Cadmium (unfiltered)	na	0.133	0.114	0.272	0.158	0.127 ^b	0.710	0.022 ^b	na		
Chromium (filtered)	6.31 U	7.06 U	8.80 U	4.36 U	6.95 U	7.58 U	4.02 U	1.83 U	7.73 U	50	1,100
Chromium (unfiltered)	na	6.34 U	11.4 U	6.01 U	3.68 U	4.58 U ^b	74.9	0.07 U ^b	na		
Copper (filtered)	8.69 J^a	12.5 J^a	8.16 J^a	10.1 J^a	5.24 U^a	10.1 J^a	4.53 U	4.72 U	7.77 U^a	3.1	4.8
Copper (unfiltered)	na	15.8 J	10.2 J	12.2 J	5.96 U	11.1 J ^b	6.47 U	4.75 U ^b	na		
Lead (filtered)	0.252	0.129	0.096	0.051	0.036	0.154 J	0.703	0.088	0.100	8.1	210
Lead (unfiltered)	na	0.823	1.44	0.161	0.080	1.06 ^b	296	0.240 ^b	na		
Mercury (filtered)	0.00092	0.00074	0.00062	0.00087	0.00062	0.00132	0.0132	0.00099 J	0.00256		
Mercury (unfiltered)	na	0.00518	0.00061	0.00094 ^b	0.00112	0.00109	0.582	0.00216 ^b	na	0.025	1.8
Nickel (filtered)	1.32	4.24	5.25	2.78	2.23	1.56	0.84	0.04U	0.04 U	8.2	74
Nickel (unfiltered)	na	8.03	8.83	6.43	4.71	3.23 ^b	3.92	0.04U ^b	na		
Silver (filtered)	0.021	0.053	0.112	0.028	0.036	0.053	0.015 U	0.027	0.044	1.9	1.9
Silver (unfiltered)	na	0.033	0.086	0.025	0.026	0.054 ^b	0.015 U	0.030 ^b	na		
Zinc (filtered)	11.97	14.1	8.08	8.30	6.07	15.8	5.45	3.29	12.2	81	90
Zinc (unfiltered)	na	16.1	10.8	9.90	7.14	17.7 ^b	322	3.49 ^b	na		

Table 3-5, continued

PARAMETER	SEEP 64	SEEP 69	SEEP 71	SEEP 75	SEEP 76	SEEP 80	SEEP 82	SEEP 82 (FD)	CHRONIC WQS	ACUTE WQS
Arsenic (filtered)	1.28	1.47	1.02	2.20	253	0.590	1.20	1.14	36	69
Arsenic (unfiltered)	na	1.64	1.91	2.49	287	0.855	1.46	2.20		
Cadmium (filtered)	0.045	0.016	0.023	0.021	0.091	0.011	0.513	0.503	9.3	42
Cadmium (unfiltered)	na	0.112	0.078	0.031 ^b	0.204	0.037	0.569	0.606		
Chromium (filtered)	1.51 U	3.10 U	2.03 U	9.74 U	7.04 UJ	6.70 U	3.25 U	3.51 U	50	1,100
Chromium (unfiltered)	na	2.91 U	4.24 U	5.37 U ^b	5.67 U	4.61 U	5.65 U	5.81 U		
Copper (filtered)	6.99 U^a	4.63 U	6.07 U^a	6.79 U^a	3.28 UJ	22.8^a	8.22 J^a	8.27 J^a	3.1	4.8
Copper (unfiltered)	na	8.06 J	12.1 J	8.43 J ^b	50.9	21.4	10.9 J	13.4 J		
Lead (filtered)	0.193	0.066	0.175	0.056	3.00	0.078	0.206	0.201	8.1	210
Lead (unfiltered)	na	0.356	15.2	0.650 ^b	56.4	0.277	2.31	8.29		
Mercury (filtered)	0.00126 J	0.00349	0.00201	0.00077	0.0153	0.00869	0.00380	0.00295		
Mercury (unfiltered)	na	0.0127 ^b	0.0322	0.00171	0.0616	0.00646	0.0168	0.0117	0.025	1.8
Nickel (filtered)	0.04 U	3.22	1.95	1.42	2.37 J	0.04 U	3.56	3.36	8.2	74
Nickel (unfiltered)	na	4.52	3.44	3.48 ^b	3.79	2.80	5.83	6.12		
Silver (filtered)	0.049	0.053	0.070	0.081	0.012	0.015 U	0.113	0.084	1.9	1.9
Silver (unfiltered)	na	0.053	0.068	0.068 ^b	0.077	0.015 U	0.088	0.126		
Zinc (filtered)	3.86	3.95	10.2	5.35	138 J^a	16.8	164^a	158^a	81	90
Zinc (unfiltered)	na	45.6	26.9	8.36 ^b	309	14.1	186	201		

na – not analyzed

FD – field duplicate sample

Data qualifiers: U = not detected at reporting limit shown; J = estimated concentration; UJ = not detected at estimated reporting limit shown

Concentrations or reporting limits in BOLD are greater than their respective marine chronic WQC

^a Concentration is greater than the marine acute WQC

^b Result shown is average of one or more laboratory replicate analyses

Concentrations of arsenic, copper, mercury, and zinc were greater than WQC in one or more samples and are described in more detail, as follows:

- ◆ Arsenic concentrations in filtered seep water from Seeps 61 and 76 (72.4 and 253 µg/L, respectively), are greater than both the marine chronic and acute WQC (36 and 69 µg/L, respectively).
- ◆ For copper, all eight of the detected concentrations in filtered samples were greater than the marine acute and chronic WQC, with concentrations ranging from 8.16 to 22.8 µg/L. Five of the nine concentrations reported as undetected in filtered samples were greater than the marine acute WQC; all nine undetected concentrations were greater than the chronic WQC. Copper concentrations in twelve samples (nine filtered and three unfiltered) that were originally reported as detected by the laboratory were qualified as undetected during data validation because copper was detected in rinsate blanks.
- ◆ Mercury concentrations in unfiltered samples from Seep 54 (0.582 µg/L), Seep 71 (0.0322 µg/L) and Seep 76 (0.0616 µg/L) were greater than the marine chronic WQC of 0.025 µg/L.
- ◆ Zinc concentrations in filtered samples from Seep 76 (138 µg/L) and Seep 82 (164 µg/L in the sample and 158 µg/L in the field duplicate sample) were greater than the marine chronic and acute WQC (81 and 90 µg/L, respectively).

3.2.1.2 VOCs and SVOCs

VOCs or SVOCs were only detected in seep water samples collected from two locations: Seep 54 and Seep 80 (Table 3-6). Carbon disulfide and chlorobenzene were the only VOCs detected in unfiltered seep water samples. Carbon disulfide was detected at a concentration of 2.1 µg/L at Seep 54, and at a concentration of 1.1 µg/L at Seep 80. Chlorobenzene was detected in the sample from Seep 54 at 6.5 µg/L. There are no Washington State WQC for the VOCs detected in LDW seep water samples. Results for all VOCs are presented in Appendix F.

Seep 54 was the only location where any SVOCs were detected in seep water. In the unfiltered sample from Seep 54, three chlorinated benzene compounds were detected (Table 3-6). In the filtered sample from Seep 54, only 1,3-dichlorobenzene and 1,4-dichlorobenzene were detected, and at concentrations an order of magnitude lower than in the unfiltered sample. There are no Washington State WQC for the SVOCs detected in LDW seep water samples. Results for all SVOCs are presented in Appendix F.

Table 3-6. Concentrations of VOCs and SVOCs in seep water samples with any VOCs or SVOCs detected

ANALYTE (µg/L)	SEEP 54		SEEP 80
	FILTERED	UNFILTERED	UNFILTERED
VOCs			
Carbon disulfide	na	2.4	1.1
Chlorobenzene	na	6.5	1.0 U
SVOCs			
1,2-Dichlorobenzene	1.0 U	2.9	1.0 U
1,3-Dichlorobenzene	3.6	58.3	1.0 U
1,4-Dichlorobenzene	3.9	40.2	1.0 U

U – not detected at reporting limits shown

3.2.1.3 PCBs and organochlorine pesticides

PCBs were detected in 3 of 14 unfiltered seep water samples (at Seeps 54, 64, and 71) and in 1 of 17 filtered seep water samples (at Seep 54; Table 3-7). At Seep 71, only Aroclor 1254 was detected. Aroclors 1248, 1254, and 1260 were detected at Seeps 54 and 64. Total calculated PCB concentrations in unfiltered seep water were as follows: 8.9 µg/L at Seep 54, 0.46 µg/L at Seep 64, and 0.020 µg/L at Seep 71. The seep water sample from Seep 54 was the only filtered sample in which PCBs were detected; the total PCB concentration in this filtered sample was 0.26 µg/L. PCB concentrations in unfiltered samples from Seeps 54 and 64 were greater than the marine chronic WQC of 0.03 µg/L, but not the marine acute value of 10 µg/L.

Table 3-7. Concentrations of Aroclors and organochlorine pesticides in seep water samples where at least one Aroclor or pesticide was detected

ANALYTE (µg/L)	SEEP 39		SEEP 54		SEEP 64	SEEP 71	CHRONIC WQC	ACUTE WQC
	FILTERED	UNFILTERED	FILTERED	UNFILTERED	UNFILTERED	UNFILTERED		
Aroclor-1248	0.017 U	0.017 U	0.21	4.7	0.092	0.017 U	nc	nc
Aroclor-1254	0.017 U	0.017 U	0.15 U	2.3 J	0.21 J	0.020 J	nc	nc
Aroclor-1260	0.017 U	0.017 U	0.047	1.9	0.16	0.017 U	nc	nc
PCBs (total calc'd) ^a	0.017 U	0.017 U	0.26	8.9 J	0.46 J	0.020 J	0.03	10
Heptachlor epoxide	0.0090	0.0076	0.016 U	0.0083 U	na	0.00080 U	0.0036 ^b	0.053 ^b

U – not detected at reporting limit shown

J – estimated concentration

na – not analyzed

nc – no criteria for individual Aroclors

^a – Total PCBs calculated as the sum of the detected Aroclors. Summing rules are presented in Appendix H.

^b WQC for heptachlor

The only organochlorine pesticide detected in seep water samples was heptachlor epoxide, which was detected in both the filtered and unfiltered samples collected at Seep 39 at concentrations of 0.0090 and 0.0076 µg/L, respectively. Heptachlor epoxide is a degradation product of heptachlor. The marine chronic WQC for heptachlor is 0.0036 µg/L, which is less than the concentrations of heptachlor epoxide reported in both filtered and unfiltered samples from Seep 39.

Other than heptachlor epoxide, no organochlorine pesticides were detected in seep water. However, some reporting limits in seep water samples from Seeps 54 and 61 were greater than the marine chronic WQC, as shown in Table 3-8. These reporting limits were elevated as a result of analytical interferences. All sample results for Aroclors and organochlorine pesticides are presented in Appendix F.

Table 3-8. Elevated reporting limits for non-detected pesticides in seep water samples from Seeps 54 and 61 compared to WQC

ANALYTE	SEEP SAMPLE	REPORTING LIMIT (µg/L)	MARINE CHRONIC WQC (µg/L)
4,4'-DDT	LDW-SP-54-C-U	0.017	0.001
	LDW-SP-61-C-U	0.0020	
Aldrin	LDW-SP-54-C-U	0.0083	0.0019 ^a
Dieldrin	LDW-SP-54-C-F	0.0095	0.0019 ^a
	LDW-SP-54-C-U	0.11	
	LDW-SP-61-C-U	0.027	
Endrin	LDW-SP-54-C-U	0.057	0.0023
Heptachlor	LDW-SP-54-C-U	0.0083	0.0036
Toxaphene	LDW-SP-54-C-U	0.83	0.0002
	LDW-SP-61-C-U	0.10	0.0002

^a WQC represents sum of aldrin and dieldrin

The reporting limit for 4,4' DDT in seeps other than Seeps 54 and 61 was 0.0017 µg/L, which is slightly greater than the marine chronic WQC of 0.001 µg/L. The reporting limit for toxaphene in seeps other than Seeps 54 and 61 was 0.083 µg/L, which is greater than the marine chronic WQC of 0.0002 µg/L.

3.2.1.4 Petroleum hydrocarbons

Petroleum hydrocarbons were detected only in filtered and unfiltered seep water samples collected from Seeps 54 and 80 (Table 3-9). TPH-G and TPH-MO¹² were detected only in the unfiltered sample from Seep 54.¹³ TPH-D was detected in both filtered and unfiltered seep water samples from Seeps 54 and 80 at concentrations ranging from 0.41 to 2.2 mg/L. There are no Washington State WQC for petroleum hydrocarbons.

¹² Motor oil-range petroleum hydrocarbon components are reported along with the analysis of TPH-D.

¹³ TPH-G was not analyzed in filtered samples because gasoline components are volatile and would be lost during the filtering process.

Table 3-9. Concentrations of TPH in seep water samples with any TPH detections

ANALYTE (MG/L)	SEEP 54		SEEP 80		SEEP 80 (FIELD DUPLICATE)	
	FILTERED	UNFILTERED	FILTERED	UNFILTERED	FILTERED	UNFILTERED
TPH-G	na	0.29	na	0.25 U	na	0.25 U
TPH-D	1.4	2.2	0.59	0.61	0.41	0.47
TPH-MO	0.50 U	1.9	0.50 U	0.50 U	0.50 U	0.50 U

U – not detected at reporting limit shown

na – not analyzed; volatile compounds were not analyzed in filtered samples

3.2.1.5 Conventional parameters

Maximum and minimum values for field conventional parameters are presented in Table 3-10. Results for all samples are presented in Appendix F.

Table 3-10. Range of conventional parameter results in seep water samples

PARAMETER	MINIMUM	MAXIMUM
Turbidity (NTU)	0.26	14
Temperature (°C)	13.6	20.0
Specific Conductivity (µmhos/cm)	1,020	49,360
Dissolved Oxygen (mg/L)	0.830	10.4
pH	5.83	7.42
Oxidation-reduction potential (mV)	-60	294

DOC was detected in water samples collected from six seeps at concentrations ranging from 1.96 to 14.8 mg/L (Table 3-11). DOC was not detected at a reporting limit of 1.50 mg/L in the remaining seep water samples.

Table 3-11. Concentrations of DOC, TOC, and TSS in seep water samples, along with field turbidity measurements

SEEP NUMBER	DOC (MG/L)	TOC (MG/L)	TSS (MG/L)	TURBIDITY (NTU) ^a	
				1	2
Seep 10	1.96 J ^b	1.50 U	na	5.7 ^c	nm ^c
Seep 12	1.50 UJ	1.50 U	15.6 J	4.4	0.86
Seep 20	1.50 UJ	1.50 U	4.3 J	1.8	2.4
Seep 39	1.50 UJ	1.50 U	5.8 J	0.63	0.28
Seep 41	1.50 UJ	1.50 U ^b	7.1 J ^b	0.26	0.71
Seep 48	1.50 UJ	1.50 U	12.8 ^b	0.80	1.0
Seep 54	5.00 J	6.42	14.3	2.8	2.6
Seep 61	1.50 UJ	2.57	15.8 ^b	1.8	0.86
Seep 62	1.50 UJ	1.50 U	na	14 ^c	nm ^c
Seep 64	1.75 J	1.50 U	na	3.7	3.9
Seep 69	5.81 J	8.55	25.0 ^b	1.9	1.9
Seep 71	1.50 UJ	2.08 ^b	11.3	2.8	2.0
Seep 75	1.50 UJ	3.15 ^b	24.3 ^b	0.59	3.6
Seep 76	6.57 J	7.78	5.2	2.2	1.4
Seep 80	14.8 J	13.4	33.3	3.2	4.8
Seep 82	1.50 UJ	1.60	5.8	2.1	3.9
Seep 82 (field duplicate sample)	1.50 UJ	2.50	11.2	2.1	3.9

U – not detected at reporting limit shown

J – estimated concentration

na – not analyzed

^a Turbidity measures 1 and 2 were taken from the first and second mini-piezometers, respectively, except where noted.

^b Result shown is average of one or more laboratory replicate analyses.

^c Sample was collected using funnel and attached tubing, so turbidity was only measured once.

TOC was detected in 9 of the 14 seep water samples analyzed for TOC, at concentrations ranging from 1.60 to 13.4 mg/L (Table 3-11). TOC was not detected at a reporting limit of 1.50 mg/L in the remaining seep water samples. TSS was detected in all of the 14 samples analyzed for TSS at concentrations ranging from 4.3 to 33.3 mg/L (Table 3-11).

3.2.1.6 Field quality control sample results

A summary of the results for the field QC samples is presented below. Two types of field QC samples were analyzed, field blanks and field replicates. The detection of analytes in field blanks, including rinsate, atmospheric, and trip blanks, may result in qualification of the sample results for the detected analyte. Field replicates were analyzed and whenever possible the relative percent difference (RPD) was calculated. This information does not result in data validation qualifiers. A complete discussion of

these results and any resulting validation qualifiers is presented in the data validation report (Appendix E).

Metals

Chromium and copper were detected in two rinsate blank samples: LDW-SP-64-RB-MP-U (4.05 and 1.59 $\mu\text{g}/\text{L}$, respectively) and LDW-SP-64-RB-S-U (5.25 and 1.61 $\mu\text{g}/\text{L}$, respectively). Other metals were not detected in rinsate blanks. The RPDs for the filtered field replicate ranged from 0.606% for copper to 29.4% for silver. The RPDs for the unfiltered field replicate ranged from 2.79% for chromium to 113% for lead.

Mercury

Mercury was not detected in the field blanks. The RPD for the filtered field replicate was 25.1% and the RPD for the unfiltered field replicate was 35.8%.

Arsenic

Arsenic was not detected in the field blanks. The RPD for the filtered field replicate was 5.12% and the RPD for the unfiltered field replicate was 34.7%.

VOCs

Rinsate blanks were not analyzed for VOCs. VOCs were not detected in the trip blank samples. Field replicate precision could not be evaluated because VOCs were not detected in the sample and field replicate.

SVOCs

Bis (2-ethylhexyl)phthalate was detected in both rinsate blanks: LDW-SP-64-RB-S-U (1.2 $\mu\text{g}/\text{L}$) and LDW-SP-64-RB-MP-U (2.4 $\mu\text{g}/\text{L}$). Field replicate precision could not be evaluated because concentrations in the samples were in the range associated with laboratory blanks.

PCBs and organochlorine pesticides

One pesticide, delta-BHC, was detected in one rinsate blank (LDW-SP-64-RB-MP-U) at a concentration of 0.0035 $\mu\text{g}/\text{L}$. Delta-BHC was not detected in any LDW seep samples. Field replicate precision could not be evaluated because pesticides were not detected in the field replicates. PCBs were not detected in either the rinsate blanks or the field replicates.

Petroleum hydrocarbons

Gasoline-range TPH was not detected in the rinsate blanks and was not detected in the field replicates. Therefore, field replicate precision could not be evaluated. Diesel-range TPH was not detected in the rinsate blanks. The RPD for diesel-range TPH was 36% for the filtered field replicate and 25.9% for the unfiltered field replicate.

Conventional parameters

Rinsate blanks were not analyzed for TSS, TOC, or DOC. The RPD was 63.5% for the TSS replicate and 43.9% for the TOC replicate. DOC was not detected in the sample or the replicate so field replicate precision could not be evaluated.

3.2.2 Data validation results

Data validation resulted in the following qualifiers added to the dataset:

- ◆ all results for 2-chloroethylvinylether were rejected
- ◆ one result for bis(2-ethylhexyl)phthalate (BEHP) was rejected
- ◆ some of the detected results for chromium, copper, nickel, mercury, zinc, Aroclor 1254, and DOC were qualified as estimated
- ◆ some of the results for chromium, copper, and BEHP reported by the laboratory as detected were qualified as undetected
- ◆ some of the reporting limits for undetected results for VOCs, BEHP, and endrin aldehyde were qualified as estimated

These rejected and qualified data are described in more detail in this section for each chemical group. The complete data validation report is presented in Appendix E.

3.2.2.1 Metals

The following qualifiers were added to metals results:

- ◆ Chromium and copper were detected in both rinsate blanks at concentrations of 4.04 to 5.24 µg/L and 1.59 to 1.61 µg/L, respectively.¹⁴ All sample results between 5 and 10 times the blank concentration were qualified as estimated (none of the chromium results and 52 percent of the copper results). All sample results below 5 times the blank concentration were qualified as undetected (97 percent of chromium results and 39 percent of the copper results).
- ◆ Chromium, nickel, copper, and zinc concentrations in sample LDW-SP-76-C-F and the lead concentration in sample LDW-SP-48-C-F were qualified as estimated because internal standard relative intensities were outside the recommended limit.

3.2.2.2 VOCs

Low recoveries for the laboratory control standard (LCS), laboratory control standard duplicate (LCSD), matrix spike (MS), or matrix spike duplicate (MSD) samples resulted in the qualification or rejection of results, as follows:

- ◆ Bromomethane reporting limits were qualified as estimated in 47 percent of the sample results because of low LCS recovery.
- ◆ Reporting limits for approximately 10 VOCs in either LDW-SP-54-C-U or LDW-SP-41-C-U were qualified as estimated because of low MS or MSD recoveries.
- ◆ The reporting limit for 2-chloroethylvinylether was rejected in all samples because the MS and MSD recovery values were less than 10%.

¹⁴ Neither chromium nor copper was detected in the reverse-osmosis water analyzed by the laboratory during the week the seep water samples were collected.

In addition, elevated sample temperatures (14°C) when samples were received by the laboratory resulted in the qualification of VOC results as estimated for LDW-SP-10-C-U and LDW-SP-62-C-U.

3.2.2.3 SVOCs

There were two data quality issues for phthalates analyzed in the seep samples. The first issue, which relates to all phthalate results, arose because the laboratory did not wrap the rubber stopper used in the laboratory filtering apparatus with Teflon tape during filtering. Because of this, all of the filtered samples had the potential to be contaminated with phthalates from the rubber stopper. Therefore, all phthalates in the filtered samples were qualified as undetected. In addition, an elevated BEHP result in LDW-SP-61-C-F was rejected because a much higher BEHP concentration of 2,600 µg/L was detected in the filtered sample from Seep 61 (LDW-SP-61-C-F) than the BEHP concentration in the unfiltered sample from that seep (3.1 µg/L).

The second phthalate data quality issue involved method blanks. A method blank associated with one sample batch contained BEHP at a concentration of 1.2 µg/L. Criteria for method blanks require that analyte concentrations are below the reporting limit or below 10% of the lowest associated sample concentration. As a result, detected concentrations of BEHP in filtered and unfiltered samples were qualified as undetected. Although BEHP was only detected in one method blank, all results were qualified during data validation because BEHP is a common laboratory contaminant that is sporadically detected in method blanks.

3.2.2.4 Organochlorine pesticides and PCB Aroclors

Several qualifiers were applied to organochlorine pesticide and PCB Aroclor results, as follows:

- ◆ All endrin aldehyde reporting limits were qualified as estimated because of low LCS recoveries in both batches.
- ◆ The Aroclor 1254 concentration in sample LDW-SP-71-C-U was qualified as estimated because of low surrogate recoveries.
- ◆ The Aroclor 1254 concentrations in samples LDW-SP-64-C-U and LDW-SP-54-C-U were qualified as estimated because of pattern overlap with Aroclors 1248 and 1260.
- ◆ In sample LDW-SP-54-C-F, the pattern match for Aroclor 1254 was determined to be insufficient for identification. Thus, the laboratory resubmitted the results for this sample as a non-detect with an elevated reporting limit.

3.2.2.5 Total petroleum hydrocarbons

TPH-D, TPH-MO, and TPH-G data were considered acceptable for use as reported by the laboratory, and no data qualifiers were added.

3.2.2.6 Conventional parameters

DOC samples were not acidified upon receipt at the laboratory, but were instead acidified prior to analysis, which was 6 to 10 days after sample collection. Thus, all DOC results were qualified as estimated. In addition, the RPD for one sample batch laboratory duplicate exceeded the data quality indicator. As a result, TSS results for that sample batch were qualified as estimated (36 percent of the TSS results).

3.2.3 Summary of results

Table 3-12 presents a summary of chemicals detected in LDW seeps in comparison to WQC. This comparison is made as a point of reference; WQC are not directly applicable to seep data. The applicability of chronic WQC to seep water, in particular, as an indicator of risk to aquatic organisms is questionable because the extended exposure period conditions specified for chronic criteria (i.e., either 24-hour or 4-day average concentrations) are implausible for exposure of aquatic organisms to seeps in the LDW because of the tidal cycle.

Copper was the chemical most frequently detected at concentrations greater than the WQC. Copper was detected in seep water from seven seeps at concentrations greater than acute WQC. Arsenic and zinc were detected in seep water at concentrations greater than acute WQC at two seeps each. Chemicals detected in at least one seep at concentrations greater than their marine chronic WQC were copper, arsenic, zinc, mercury, total PCBs, and heptachlor epoxide.¹⁵ Total petroleum hydrocarbons, chlorinated benzene compounds, and carbon disulfide were detected at two seeps, but WQC are not available for these chemicals. Interpretation of the relevance and applicability of acute and chronic WQC to seep water data will be discussed in the Phase 2 risk assessments and RI.

¹⁵ Heptachlor epoxide was detected in one seep at a concentration greater than the marine chronic WQC of heptachlor. WQC are not available for heptachlor epoxide.

Table 3-12. Summary of chemicals with concentrations greater than marine WQC in LDW seep water samples

SEEP NUMBER	METALS WITH CONCENTRATIONS IN FILTERED SAMPLES GREATER THAN MARINE ACUTE OR CHRONIC WQC (µg/L) ^a			PCB, PESTICIDE, OR MERCURY WITH CONCENTRATIONS IN UNFILTERED SAMPLES GREATER THAN MARINE CHRONIC WQC (µg/L) ^a			CHEMICALS DETECTED BUT WITH NO WQC AVAILABLE ^c
	ARSENIC	COPPER	ZINC	HEPTACHLOR EPOXIDE	MERCURY	TOTAL PCBs	
Marine chronic WQC	36	3.1	81	0.0036 ^e	0.025	0.03	
Marine acute WQC	69	4.8	90	0.053 ^e	1.8	10	
Seep 10		8.69 J ^a					
Seep 12		12.5 J ^a					
Seep 20		8.16 J ^a					
Seep 39		10.1 J ^a		0.0076			
Seep 41		5.24 U ^a					
Seep 48		11.1 J ^a					
Seep 54		4.53 U			0.582	8.9 J	TPH-D (2.2 mg/L) TPH-G (0.29 mg/L) TPH-MO (1.9 mg/L) 1,2-dichlorobenzene (2.9 µg/L) 1,3-dichlorobenzene (58.3 µg/L) 1,4-dichlorobenzene (40.2 µg/L) carbon disulfide (2.4 µg/L)
Seep 61	72.4 ^a	4.72 U					
Seep 62		7.77 U ^a					
Seep 64		6.99 U ^a				0.46 J	
Seep 69		4.63 U					
Seep 71		6.07 U ^a			0.0322		
Seep 75		6.79 U ^a					
Seep 76	253 ^a	3.28 UJ ^a	138 J ^a		0.0616		
Seep 80		22.8 ^a					TPH-D (0.61 mg/L) ^d carbon disulfide (1.1 µg/L)
Seep 82		8.22 J ^{a,b}	164 ^{a,b}				

^a Concentration also greater than marine acute WQC

^b 8.27J µg/L for copper and 158 µg/L for zinc in the field replicate sample

^c Concentrations in unfiltered samples

^d 0.47 mg/L in the field replicate sample

^e WQC for heptachlor

4.0 References

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5.0 Oversized Figures

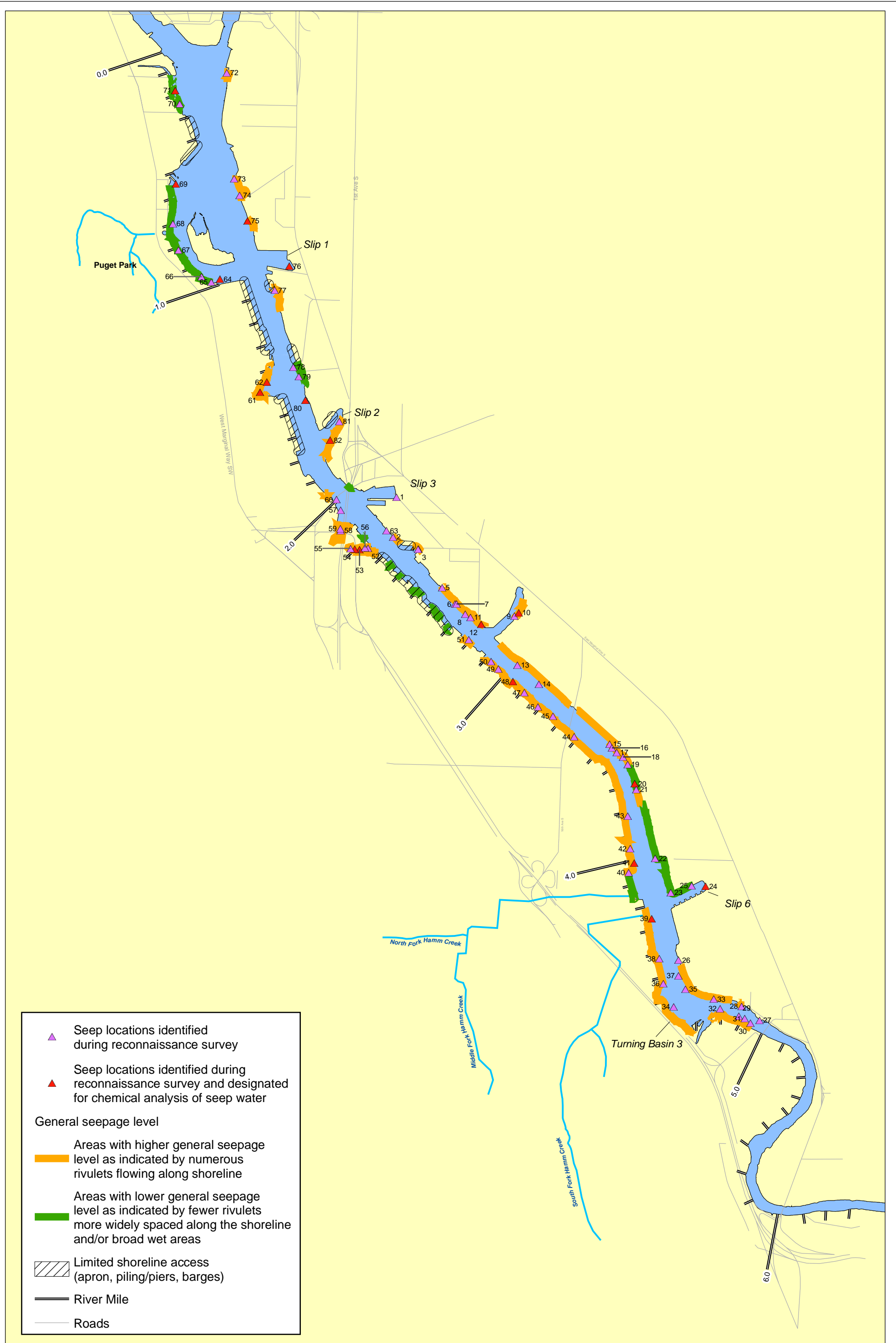
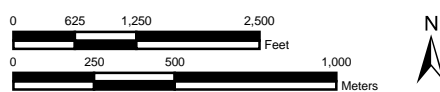


Figure 2-1. Seep locations identified during the reconnaissance survey



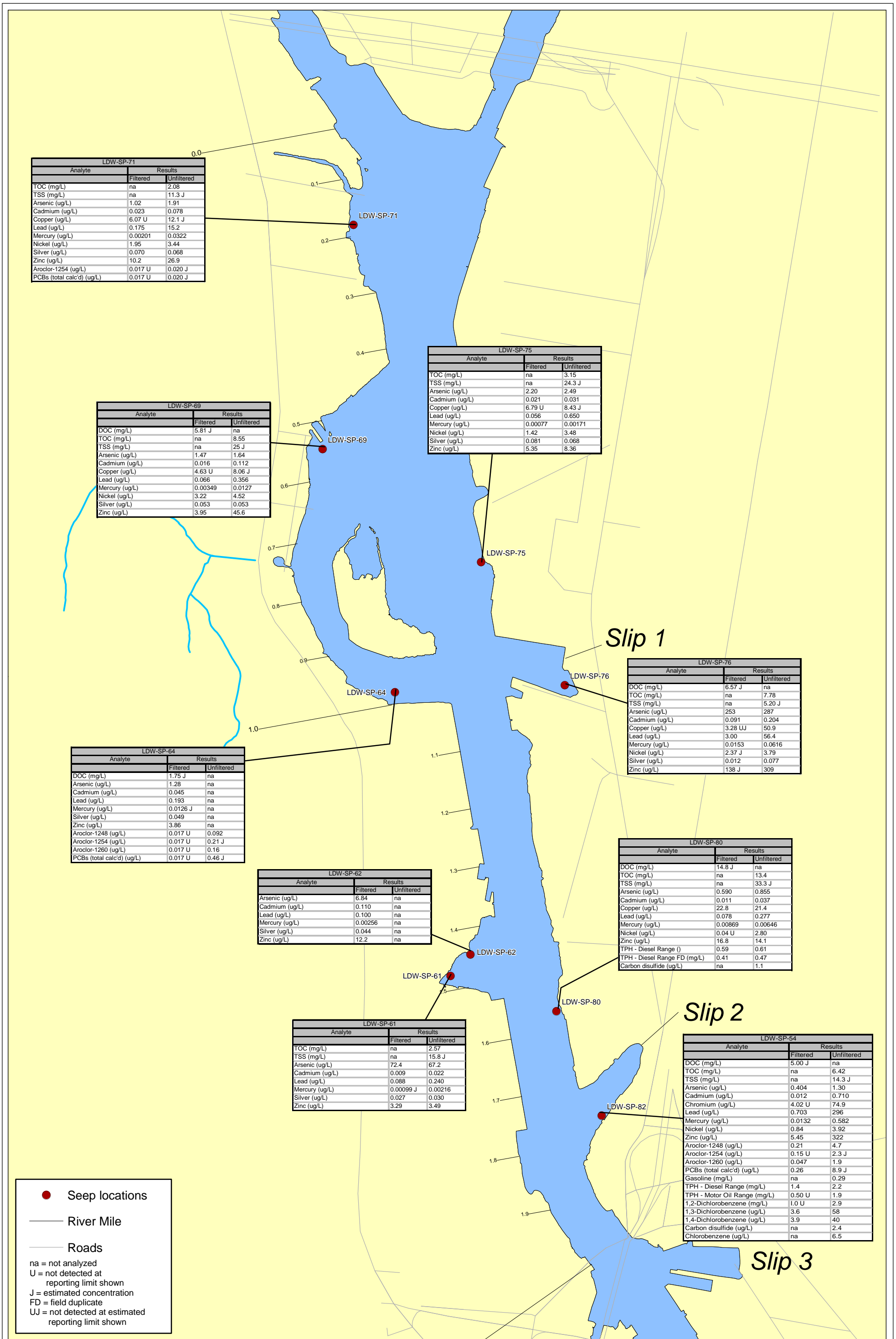
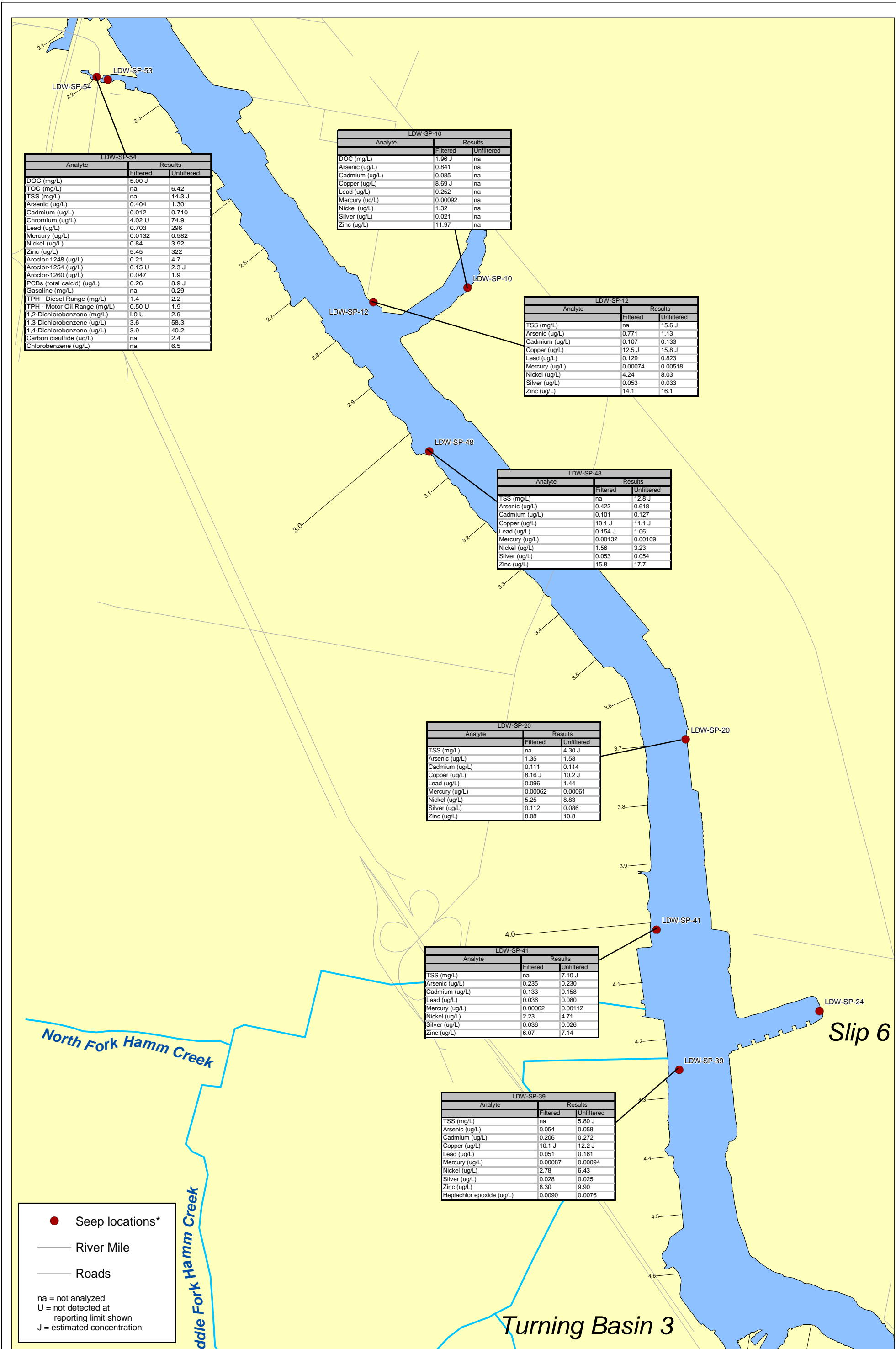


Figure 3-1a. Locations of seeps for analysis of seep water chemistry and concentrations of detected chemicals (RM 0-2.0)





LDW-SP-54		
Analyte	Results	
	Filtered	Unfiltered
DOC (mg/L)	5.00 J	
TOC (mg/L)	na	6.42
TSS (mg/L)	na	14.3 J
Arsenic (ug/L)	0.404	1.30
Cadmium (ug/L)	0.012	0.710
Chromium (ug/L)	4.02 U	74.9
Lead (ug/L)	0.703	296
Mercury (ug/L)	0.0132	0.582
Nickel (ug/L)	0.84	3.92
Zinc (ug/L)	5.45	322
Aroclor-1248 (ug/L)	0.21	4.7
Aroclor-1254 (ug/L)	0.15 U	2.3 J
Aroclor-1260 (ug/L)	0.047	1.9
PCBs (total calc'd) (ug/L)	0.26	8.9 J
Gasoline (mg/L)	na	0.29
TPH - Diesel Range (mg/L)	1.4	2.2
TPH - Motor Oil Range (mg/L)	0.50 U	1.9
1,2-Dichlorobenzene (mg/L)	1.0 U	2.9
1,3-Dichlorobenzene (ug/L)	3.6	58.3
1,4-Dichlorobenzene (ug/L)	3.9	40.2
Carbon disulfide (ug/L)	na	2.4
Chlorobenzene (ug/L)	na	6.5

LDW-SP-10		
Analyte	Results	
	Filtered	Unfiltered
DOC (mg/L)	1.96 J	na
Arsenic (ug/L)	0.841	na
Cadmium (ug/L)	0.085	na
Copper (ug/L)	8.69 J	na
Lead (ug/L)	0.252	na
Mercury (ug/L)	0.00092	na
Nickel (ug/L)	1.32	na
Silver (ug/L)	0.021	na
Zinc (ug/L)	11.97	na

LDW-SP-12		
Analyte	Results	
	Filtered	Unfiltered
TSS (mg/L)	na	15.6 J
Arsenic (ug/L)	0.771	1.13
Cadmium (ug/L)	0.107	0.133
Copper (ug/L)	12.5 J	15.8 J
Lead (ug/L)	0.129	0.823
Mercury (ug/L)	0.00074	0.00518
Nickel (ug/L)	4.24	8.03
Silver (ug/L)	0.053	0.033
Zinc (ug/L)	14.1	16.1

LDW-SP-48		
Analyte	Results	
	Filtered	Unfiltered
TSS (mg/L)	na	12.8 J
Arsenic (ug/L)	0.422	0.618
Cadmium (ug/L)	0.101	0.127
Copper (ug/L)	10.1 J	11.1 J
Lead (ug/L)	0.154 J	1.06
Mercury (ug/L)	0.00132	0.00109
Nickel (ug/L)	1.56	3.23
Silver (ug/L)	0.053	0.054
Zinc (ug/L)	15.8	17.7

LDW-SP-20		
Analyte	Results	
	Filtered	Unfiltered
TSS (mg/L)	na	4.30 J
Arsenic (ug/L)	1.35	1.58
Cadmium (ug/L)	0.111	0.114
Copper (ug/L)	8.16 J	10.2 J
Lead (ug/L)	0.096	1.44
Mercury (ug/L)	0.00062	0.00061
Nickel (ug/L)	5.25	8.83
Silver (ug/L)	0.112	0.086
Zinc (ug/L)	8.08	10.8

LDW-SP-41		
Analyte	Results	
	Filtered	Unfiltered
TSS (mg/L)	na	7.10 J
Arsenic (ug/L)	0.235	0.230
Cadmium (ug/L)	0.133	0.158
Lead (ug/L)	0.036	0.080
Mercury (ug/L)	0.00062	0.00112
Nickel (ug/L)	2.23	4.71
Silver (ug/L)	0.036	0.026
Zinc (ug/L)	6.07	7.14

LDW-SP-39		
Analyte	Results	
	Filtered	Unfiltered
TSS (mg/L)	na	5.80 J
Arsenic (ug/L)	0.054	0.058
Cadmium (ug/L)	0.206	0.272
Copper (ug/L)	10.1 J	12.2 J
Lead (ug/L)	0.051	0.161
Mercury (ug/L)	0.00087	0.00094
Nickel (ug/L)	2.78	6.43
Silver (ug/L)	0.028	0.025
Zinc (ug/L)	8.30	9.90
Heptachlor epoxide (ug/L)	0.0090	0.0076

● Seep locations*
 — River Mile
 — Roads
 na = not analyzed
 U = not detected at reporting limit shown
 J = estimated concentration

Figure 3-1b. Locations of seeps for analysis of seep water chemistry and concentrations of detected chemicals (RM 2.1-4.6)

