

Prepared in cooperation with the Washington State Department of Ecology

Chemical Concentrations in Water and Suspended Sediment, Green River to Lower Duwamish Waterway near Seattle, Washington, 2016–17



Data Series 1073

Cover:

Background: U.S. Geological Survey personnel collecting a water sample for analysis of suspended-sediment concentration, Duwamish River, Washington, September 17, 2016.

Top: Colloidal sample captured on a filter for chemical analysis, Duwamish River, Washington, August 30, 2016.

Middle: Continuous-flow centrifuges used for collection of suspended sediment from large volumes of water for chemical analysis, Duwamish River, Washington, September 27, 2016.

Bottom: Filtration equipment inside mobile water-quality trailer used for collecting colloidal and dissolved samples, Duwamish River, Washington, September 17, 2016.

All photographs by Kathy Conn, U.S. Geological Survey.

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Elena A. Chapman

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**U.S. Department of the Interior
U.S. Geological Survey**

U.S. Department of the Interior

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U.S. Geological Survey

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Conversion Factors

U.S. Customary Units to International System of Units

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Flow rate	
cubic foot per second (ft ³ /s)	0.02831	cubic meter per second (m ³ /s)

International System of Units to U.S. Customary Units

Multiply	By	To obtain
	Length	
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
	Area	
square kilometer (km ²)	247.1	acre
	Volume	
liter (L)	0.2642	gallon (gal)
	Mass concentration unit	
milligram per kilogram (mg/kg)	equals	part per million (ppm)
microgram per kilogram (μg/kg)	equals	part per billion (ppb, 10 ⁹)
nanogram per kilogram (ng/kg)	equals	part per trillion (ppt, 10 ¹²)
	Liquid concentration unit	
milligram per liter (mg/L)	equals	part per million (ppm)
picogram per liter (pg/L)	equals	part per quadrillion (ppqn, 10 ¹⁵)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as:

$$^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32.$$

Datums

Horizontal coordinate information is referenced to North American Datum of 1983 (NAD 83).

Gage height is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 1929).

Supplemental Information

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (μS/cm at 25 °C).

Turbidity is given in Formazin Nephelometric Units (FNU) or Nephelometric Turbidity Units (NTU).

Concentrations of chemical constituents in water are given in milligrams per liter (mg/L), micrograms per liter (μg/L), or picograms per liter (pg/L).

Abbreviations

cPAHs	carcinogenic polycyclic aromatic hydrocarbons
CVO	U.S. Geological Survey Cascades Volcano Observatory Sediment Laboratory
DL	detection limit
DOC	dissolved organic carbon
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
GFF	glass-fiber filters
HPAH	high molecular-weight polycyclic aromatic hydrocarbons
HRMS	high-resolution mass spectrometry
LDW	Lower Duwamish Waterway
LPAH	low molecular-weight polycyclic aromatic hydrocarbons
MS	matrix spike
MSD	matrix spike duplicate
NIST	National Institute of Standards and Technology
PAHs	polycyclic aromatic hydrocarbons
PCBs	polychlorinated biphenyls
PSD	particle-size distribution
RL	reporting limit
SSC	suspended-sediment concentration
TEQ	toxic equivalent
USGS	U.S. Geological Survey

Chemical Concentrations in Water and Suspended Sediment, Green River to Lower Duwamish Waterway near Seattle, Washington, 2016–17

By Kathleen E. Conn, Robert W. Black, Norman T. Peterson, Craig A. Senter, and Elena A. Chapman

Abstract

From August 2016 to March 2017, the U.S. Geological Survey (USGS) collected representative samples of filtered and unfiltered water and suspended sediment (including the colloidal fraction) at USGS streamgage 12113390 (Duwamish River at Golf Course, at Tukwila, Washington) during 13 periods of differing flow conditions. Samples were analyzed by Washington-State-accredited laboratories for a large suite of compounds, including metals, dioxins/furans, semivolatile compounds including polycyclic aromatic hydrocarbons, butyltins, the 209 polychlorinated biphenyl (PCB) congeners, and total and dissolved organic carbon. Concurrent with the chemistry sampling, water-quality field parameters were measured, and representative water samples were collected and analyzed for river suspended-sediment concentration and particle-size distribution. The results provide new data that can be used to estimate sediment and chemical loads transported by the Green River to the Lower Duwamish Waterway.

Introduction

The Lower Duwamish Waterway (LDW) is the final 8-kilometer-long reach of the Green/Duwamish River. The LDW enters Puget Sound's Elliott Bay in Seattle, Washington (fig. 1) and is the site of intense current and historical anthropogenic-influenced contamination of sediments. In 2001–02, the U.S. Environmental Protection Agency (EPA) and the Washington State Department of Ecology (Ecology) required remedial investigations and feasibility studies of the 1.8-square-kilometer LDW under the Federal Superfund Law and the Washington Model Toxics Control Act because of concerns about human health risks from exposure to contaminated sediments. The main contaminants of concern for human health include polychlorinated biphenyls (PCBs), dioxins/furans, arsenic, and carcinogenic polycyclic aromatic hydrocarbons (cPAHs), which are defined in Washington State

Administrative Code 173-340-200 as polycyclic aromatic hydrocarbons (PAHs). Additionally, about 41 compounds (including individual metals, PCBs, PAHs, phthalates, and other semivolatile organic compounds) have been selected as contaminants of concern for benthic invertebrates. Released in November 2014, the EPA's final cleanup plan for LDW included using combinations of dredging, capping, natural sedimentation, and enhanced natural recovery (U.S. Environmental Protection Agency, 2014).

To support implementation of an LDW cleanup plan, Ecology is leading source control activities and a watershed-scale pollutant loading assessment to identify sources of sediment recontamination adjacent to and upstream of the LDW. From 2013 to 2017, the U.S. Geological Survey (USGS), in cooperation with Ecology, collected new data to provide estimates of sediment loading and toxic chemical loading from suspended sediment transported by the Green/Duwamish River to the LDW. The data included concurrent, representative measurements of water, suspended-sediment concentration (SSC) and particle-size distribution (PSD), and suspended-sediment chemistry collected over a range of conditions at a location near the LDW upper boundary. Results from the first, pilot phase (2013) and the second phase (2013–15) are available in Conn and Black (2014) and Conn and others (2015). This report presents data from the third phase (2016–17) of discrete sampling of water and suspended sediment at USGS streamgage 12113390 (Duwamish River at Golf Course, at Tukwila, Washington) on the Duwamish River upstream of the LDW from August 2016 to March 2017. The streamgage is upstream of the estuarine environment but still within the tidally-influenced section of the basin. Field measurements were made of temperature, pH, specific conductance, dissolved oxygen, turbidity, and barometric pressure. Unfiltered-water and suspended-sediment samples were analyzed for PCB congeners, dioxins/furans, metals, PAHs and other semivolatile organic compounds, butyltins, and total organic carbon. Filtered-water samples were analyzed for dissolved organic carbon (DOC) and metals.

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National Agricultural Imagery Program (NAIP), 2013, 1 meter imagery,
U.S. Department of Agriculture, Farm Service Agency,
Washington State Plane South, NAD83

Figure 1. Study area and location of U.S. Geological Survey (USGS) streamgage station 12113390 (Duwamish River at Golf Course, at Tukwila, Washington), Green River to Lower Duwamish Waterway near Seattle, Washington. Modified from Conn and Black (2014).

A new Phase 3 component was the collection and analysis of PCB congeners on colloidal material and dissolved in water to support the development of a site-specific PCB partition coefficient.

The results from the three phases, coupled with the continuous record of river streamflow and turbidity at the same USGS streamgage, can be used to estimate sediment loads and chemical loads transported from upstream sources by the Green River to the LDW. These results will improve the understanding of the potential for recontamination of recently remediated sediment within the LDW.

Methods

Field Sampling and Processing

From August 2016 to March 2017, the USGS collected representative samples of water and suspended sediment from the Duwamish River at river kilometer 16.7 (USGS streamgage 12113390, Duwamish River at Golf Course, at Tukwila, Washington) during 13 periods of differing hydrological conditions representing seasonal, storm-, and dam-related variations in flow and turbidity. Real-time turbidity and streamflow conditions from the same USGS streamgage were used to initiate sampling periods. The methods and study designs have been described previously (Conn and Black, 2014; Conn and others, 2015; Conn and Black, 2016; Conn and others, 2016) and are briefly summarized here, including Phase 3 modifications ([table 1](#)). They included six field tasks:

1. Monitoring of general water-quality field parameters,
2. Collection of a depth- and width-integrated water sample for chemical analysis (water chemistry),
3. Collection of a depth- and width-integrated water sample for determination of suspended-sediment concentration (SSC) and particle-size distribution (PSD),
4. Collection of a point sample of suspended sediment by centrifugation for chemical analysis (suspended-sediment chemistry),
5. Collection of a colloid sample on a filter from the water exiting the centrifuges for PCB analysis (colloidal PCBs), and
6. Collection of a dissolved sample on XAD-2 resin from the water exiting the filter for PCB analysis (dissolved PCBs).

A summary of these tasks is contained in [table 1](#). During the final three sampling periods, the suspended-sediment chemistry sample (task 4) was collected from a point location approximately 100 m downstream of, and 3 m higher in the water column than, the sampling location used for all previous sampling events.

Tasks 5 and 6 were added in Phase 3 to support PCB partition and load estimates. A subsample of the water exiting the centrifuges (task 4) was passed through 0.45-micrometer (μm)-pore baked glass-fiber filters (GFF) (Advantec GC-50, Sterlitech Corp., Kent, Washington) followed by concentration on XAD-2 resin ([fig. 2](#)). The XAD-2 resin was acquired, cleaned, quality-control tested, spiked with surrogate compounds, and packed in stainless steel columns by SGS AXYS Analytical Services, Ltd., using laboratory Standard Operating Procedure SLA-076 “Filtration and XAD-2 Extraction of Large Volume Water Samples.” The columns were sealed and stored at 4 °C until field sampling, and sealed and stored again after field sampling until analysis. The filters were frozen until analysis. The particulates captured on the filter were called the “colloid” sample (particles $>0.45 \mu\text{m}$ not captured by the centrifuges). The sample concentrated on the XAD-2 resin was called the “dissolved” sample (freely dissolved or sorbed to particulates less than $0.45 \mu\text{m}$).

Analytical Methods

Using EPA-approved methods ([table 2](#)), Washington-State-accredited laboratories analyzed unfiltered-water and suspended-sediment samples for a large suite of chemical compounds, including the 209 PCB congeners, dioxins and furans, cPAHs and other semivolatile compounds, butyltins, metals (including arsenic and mercury), and total organic carbon. Filtered-water samples were analyzed for metals and dissolved organic carbon. Because of limited sample mass and low frequency of detection, the following compound groups included for analysis in Phases 1 and 2 were not analyzed during Phase 3—volatile organic compounds, PCB Aroclors by low-resolution mass spectrometry, hexavalent chromium, and pesticides. In Phase 3, PAHs in unfiltered-water samples were analyzed by an additional method using large-volume injection to lower the detection levels. Mercury in unfiltered- and filtered-water samples also was analyzed using a low-level method ([table 2](#)). The glass-fiber filters and XAD-2 resin samples were analyzed for PCB congeners only. Depth- and width-integrated water samples (task 3) were analyzed for SSC and percentage of fine sediment less than $62.5 \mu\text{m}$ by the USGS Cascades Volcano Observatory Sediment Laboratory (CVO) by weighing oven-dried solids (Guy, 1969). When there was sufficient suspended sediment in the water sample, a full PSD analysis also was done by CVO by washed sieving of particles greater than or equal to $62.5 \mu\text{m}$ or by settling velocity for particles less than $62.5 \mu\text{m}$ (Guy, 1969). Analytical parameter groups, sample types, methods, and analyzing laboratories are summarized in [table 2](#). During low-turbidity sampling periods, even with consecutive days of water collection, there was insufficient suspended-sediment composited from the centrifuges to analyze all parameters. In these cases, analyses for semivolatile compounds and butyltins were omitted.

Table 1. Field tasks, data collected, collection methods, references for collection methods, and analytical laboratories, U.S. Geological Survey streamgauge 12113390 (Duwamish River at Golf Course, at Tukwila, Washington), 2016–17.

[Task No.: Corresponds to the task numbers discussed in the text. **Abbreviations:** NTU, Nephelometric Turbidity Unit; PAH, polycyclic aromatic hydrocarbon; PCB, polychlorinated biphenyl; °C, degrees Celsius; mg/L, milligram per liter; mm Hg, millimeter of mercury; µg/L, microgram per liter; µm, micrometer; µS/cm, microsiemen per centimeter at 25 °C; mm, millimeter; -, none]

Task No.	Field tasks	Parameter collected	Collection method	Published collection methods	Laboratory	Notes
1	General water quality (field parameters)	Water temperature (°C), pH, dissolved oxygen (mg/L), specific conductance (µS/cm), turbidity (NTU), barometric pressure (mm Hg)	YSI, Inc., multiparameter sonde deployed mid-depth in the river thalweg	Wilde (variously dated)	U.S. Geological Survey Washington Water Science Center	-
2	Water chemistry	209 PCB congeners, dioxins/furans, PAHs and other semivolatile compounds, metals, butyltins, total and dissolved organic carbon	Depth- and width-integrated sample using Teflon™ samplers. Sample transferred to Teflon™ churn in on-site mobile laboratory for complete homogenization prior to sample processing	Wilde and others (2004); Davis (2005); U.S. Geological Survey (variously dated)	Analytical Resources, Inc., Tukwila, Washington; King County Environmental Laboratory, Seattle, Washington; Manchester Environmental Laboratory, Port Orchard, Washington; SGS AXYS Analytical Services, Ltd., Sidney, British Columbia	-
3	Sediment concentration and particle-size distribution	Characterization of abundance and size distribution of suspended sediment	Depth- and width-integrated sample. A stand-alone sample collected using USGS suspended-sediment sampling protocols immediately after water chemistry sample	Edwards and Glysson (1999)	U.S. Geological Survey Cascades Volcano Observatory Sediment Laboratory	These samples did not receive chemical analyses. Results were used with the suspended-sediment chemistry sampling results (see below) to estimate suspended-sediment-bound chemicals.

Table 1. Field tasks, data collected, collection methods, references for collection methods, and analytical laboratories, U.S. Geological Survey streamgage 12113390 (Duwamish River at Golf Course, at Tukwila, Washington), 2016–17.—Continued

Task No.	Field tasks	Parameter collected	Collection method	Published collection methods	Laboratory	Notes
4	Suspended-sediment chemistry	209 PCB congeners, dioxins/furans, PAHs and other semivolatle compounds, metals, butyltins, total and dissolved organic carbon	Concurrent with water chemistry sampling, 500–5,000 liters of sediment-laden water pumped from the thalweg at 80 percent depth through Teflon™ tube into Teflon™ lined basins. Suspended sediment collected by flow-through centrifuge for chemical analysis.	Conn and others (2016)	Analytical Resources, Inc., Tukwila, Washington; King County Environmental Laboratory, Seattle, Washington; Manchester Environmental Laboratory, Port Orchard, Washington; SGS AXYS Analytical Services, Ltd., Sidney, British Columbia, Canada	During the final three sampling periods, the suspended-sediment chemistry sample was collected from a point location approximately 100 m downstream and 3 m higher in the water column than the sampling location used for all previous sampling events.
5	Colloidal PCBs	209 PCB congeners	A sub-sample of the water exiting the centrifuges (task 4) was passed through 0.45 µm glass-fiber filters. The particles captured on the filters was called the “colloid” sample, operationally defined as particles larger than 0.45 µm that were not captured by the centrifuges.	Wilde and others (2004)	SGS AXYS Analytical Services, Ltd., Sidney, British Columbia, Canada	New to Phase 3.
6	Dissolved PCBs	209 PCB congeners	The water passing through the 0.45-µm filters (task 5) was concentrated on XAD-2 resin, and called the “dissolved” sample, operational defined as freely dissolved or sorbed to particulates less than 0.45 µm.	SGS AXYS Analytical Services, Ltd., Standard Operating Procedure SLA-076 “Filtration and XAD-2 Extraction of Large Volume Water Samples”	SGS AXYS Analytical Services, Ltd., Sidney, British Columbia, Canada	New to Phase 3.

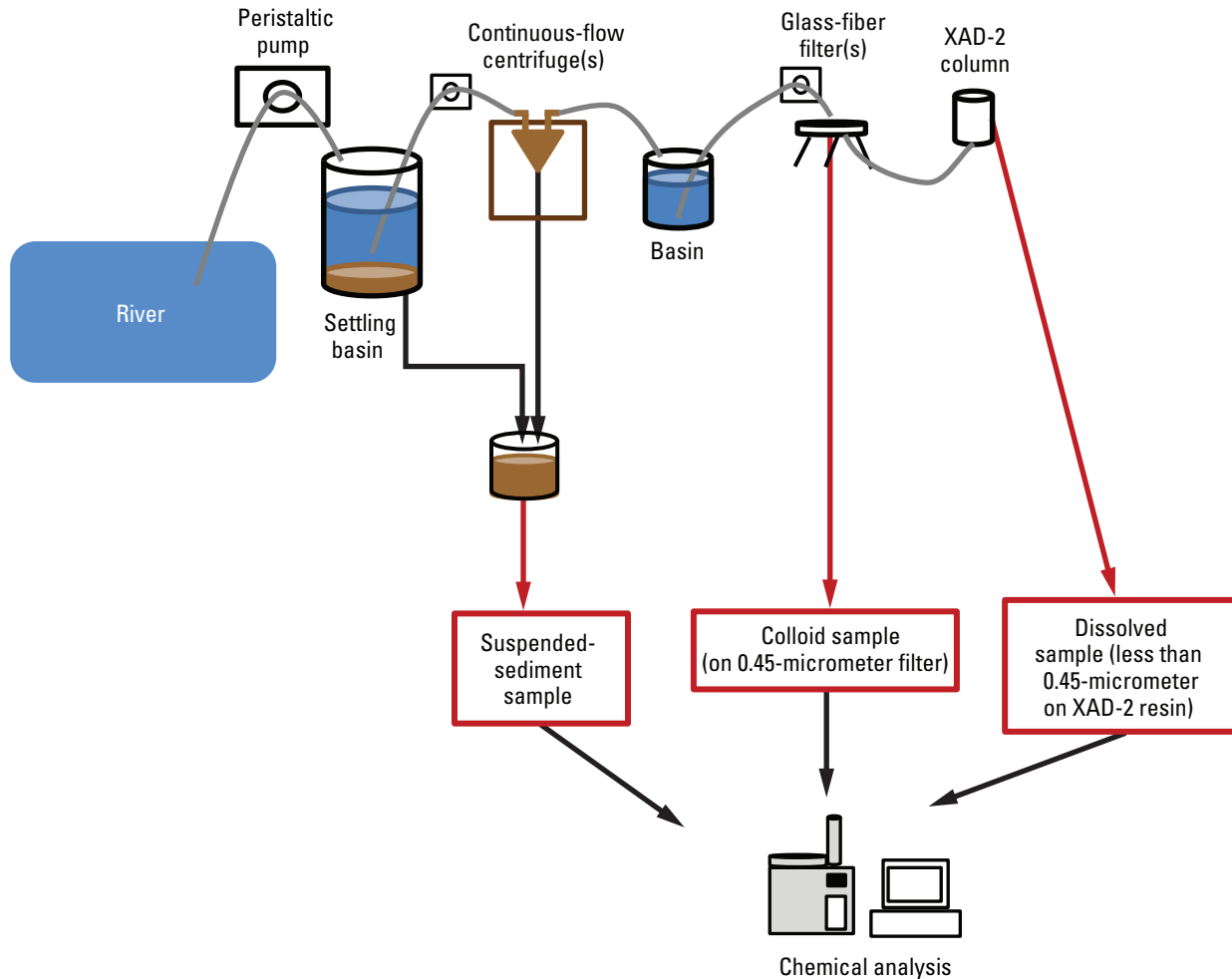


Figure 2. Centrifugation field configuration.

Quality Assurance and Quality Control

Standard USGS quality-assurance procedures for surface-water measurements and water-quality sampling and analysis were followed (Wilde, 2004; Wilde and others, 2004; Wilde, 2005; U.S. Geological Survey, 2006; Wilde and others, 2014; Conn and others, 2017). These procedures included guidelines for equipment selection, equipment cleaning, personnel training, and low-level organic compounds and metals sampling. Sampling equipment for chemical analyses was made of Teflon™ that had been pre-cleaned with phosphate-free soap, rinsed three times with tap water, soaked in 5-percent hydrochloric acid, rinsed with deionized water, rinsed with high-purity methanol, and air-dried. Field sampling techniques included various measures to avoid sample contamination, including the two-person “clean hands, dirty hands” technique and processing of water samples in a clean mobile laboratory (Wilde and others, 2004). Hydrologists and hydrologic technicians on this project were trained at the USGS National Training Center in the collection

of water-quality samples, including samples for trace organic and low-level mercury analyses. Field quality-control samples included:

- One equipment blank sample each for water, glass-fiber filter, and XAD-2 resin, in which laboratory water was processed through pre-cleaned field sampling equipment, including the nozzle, bag, and churn for the water sample, and the glass-fiber filter, XAD-2 resin and associated tubing for the filter and XAD-2 samples;
- One concurrent field replicate sample each for water, glass-fiber filter, and XAD-2 resin;
- Two mercury field blank samples per method protocols; and
- One water sample bottle blank (a solvent-rinsed bottle to assess PCBs and dioxins/furans contributions from the bottle).

Table 2. Analytical parameter groups, sample type, methods, and analyzing laboratory for samples collected at U.S. Geological Survey streamgage 12113390 (Duwamish River at Golf Course, at Tukwila, Washington), 2016–17.

[**Analysis method:** Unless an alternate reference is given, method numbers refer to the U.S. Environmental Protection Agency's SW-846 publication titled Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (U.S. Environmental Protection Agency, 2017). **Abbreviations:** ARI, Analytical Resources, Inc., Tukwila, Wash.; ASTM, American Society for Testing and Materials; AXYS, SGS AXYS Analytical Services, Ltd., Sidney, British Columbia, Canada; CVO, U.S. Geological Survey Cascade Volcano Observatory Sediment Laboratory; KCEL, King County Environmental Laboratory, Seattle, Wash; MEL, Manchester Environmental Laboratory, Port Orchard, Wash.; mm, millimeter; PSEP, Puget Sound Estuary Program; SIM, selected ion monitoring; \geq greater than or equal to; $<$, less than; μm , micrometer]

Analytical parameter	Sample type					Analysis method	Analysis method description	Analyzing laboratory
	Unfiltered water	Filtered water	Suspended sediment	Glass-fiber filters	XAD-2 resin			
Dioxins/furans	X		X			1613B	High-resolution gas chromatography/mass spectrometry	AXYS
209 Polychlorinated biphenyl congeners (PCBs)	X		X	X	X	1668C	High-resolution gas chromatography/mass spectrometry	AXYS
Organic carbon	X	X	X			5310B (water), Puget Sound Estuary Program (1986) (sediment)	High-temperature combustion	MEL
Trace elements	X	X	X			6020	Inductively coupled plasma-mass spectrometry	MEL
Low-level mercury	X	X	X			1631E (water), 7471B (sediment)	Cold-vapor atomic absorption spectrometry	MEL
Butyltins	X		X			8270D	Gas chromatography/mass spectrometry	ARI
Semivolatile compounds	X		X			8270D	Gas chromatography/mass spectrometry	ARI
Low-level polycyclic aromatic hydrocarbons	X		X			8270D SIM	Gas chromatography/mass spectrometry	ARI
Ultra low-level polycyclic aromatic hydrocarbons	X					8270D SIM with large-volume injection	Gas chromatography/mass spectrometry	KCEL
Suspended-sediment concentration	X					ASTM D3977-97(2013)e1	Weight of oven-dried solids	CVO
Particle-size distribution (of suspended sediment)	X					Guy (1969)	Wet sieve ($\geq 62.5 \mu\text{m}$) and fall diameter ($< 62.5 \mu\text{m}$)	CVO

In accord with their quality-assurance plans, analytical laboratories (table 2) processed laboratory blank, spike, and replicate analyses of every batch of approximately 20 samples (Analytical Resources, Inc., 2014; Washington State Department of Ecology, 2016; King County, 2017; SGS AXYS Analytical Services, Ltd., 2017). If values exceeded control limits for analytes detected in associated environmental samples, corrective actions such as re-runs and re-extractions were taken when sufficient sample was available and holding times had not been exceeded. The metals laboratory participated in the USGS Standard Reference Sample inter-laboratory comparison study in spring 2017 (U.S. Geological Survey, 2017) for analysis of trace elements and mercury in filtered water. A National Institute of Standards and Technology (NIST) Sediment Reference Material 1944 (National Institute of Standards and Technology, 2017) was purchased and submitted to each laboratory for analysis. Additional details regarding the quality-assurance project plan are available in Conn and Black (2016).

Data Reporting

Data reporting protocols have been described previously (Conn and others, 2015). Briefly, field forms, field parameter results, SSC and PSD data from CVO, and non high-resolution mass spectrometry (HRMS) chemistry data were reviewed and approved by USGS project managers and stored in the USGS National Water Information System. The HRMS chemistry data received an EPA Level 4 validation by the Quality Assurance Coordinator at the Ecology Manchester Environmental Laboratory in Port Orchard, Washington. This included recalculation of results from instrument responses to confirm the correct identification and quantitation of analytes, tentatively identified compounds, and non-detected compounds. A report summarizing the Level 4 validation results for each method was issued to the USGS and Ecology project managers.

The detection limit (DL) for compounds analyzed by HRMS (the dioxins/furans and PCB congeners) is defined as “concentration equivalent to 2.5 times the estimated chromatographic noise height, determined individually for each compound for every sample analysis run.” The reporting limit (RL) for HRMS compounds is determined by prorating the concentration of the lowest calibration limit for sample size and extract volume by using the following equation:

$$RL = [(lowest\ level\ calibration\ standard) \times (extract\ volume)]/sample\ size. \quad (1)$$

The DL for non-HRMS analyses is defined as the lowest result that can be reliably distinguished from a blank based on historical method blank detections with a false positive rate of less than or equal to 1 percent. The RL for non-HRMS analyses is defined as the lowest concentration that can be reliably achieved within specific limits of precision and accuracy during routine operating conditions.

Results are reported unqualified at and greater than the RL for all compounds. Results are reported as estimated (J qualified) between the RL and the DL, with the exception of organic carbon and metals, which were not reported when less than the reporting limit. Non-detects are reported at the DL with a UJ qualifier for HRMS compounds and at the RL for non-HRMS compounds.

Differences between various laboratory and agency protocols for qualifying analytical data to address measurement considerations and abnormalities are common. Adjustments to the laboratory-provided qualifiers from laboratories used in this study were made by Ecology’s Quality Assurance Coordinator to be consistent with the Ecology Toxics Cleanup Program data reporting protocols (Washington State Department of Ecology, 2008) as outlined in the EPA Functional Guidelines (U.S. Environmental Protection Agency, 2008, 2009, 2010, 2011) and previously described in Conn and others (2015, appendix A). The complete analytical results for all individual compounds with Ecology-amended results and qualifiers are presented in appendix A and are stored in the publicly available Ecology Environmental Information Management database (Washington State Department of Ecology, 2015).

Over the course of the project, DL and RL varied between compounds and for an individual compound between samples, owing to annual laboratory RL and DL updates, sample dilutions, and sample-specific calculations. The DL and RL values are stored with the sample results in the publicly available Ecology Environmental Information Management database (Washington State Department of Ecology, 2015).

Estimated data (J qualifier) are included in the summed or calculated values, while N- (did not meet quantification criteria) and U- (not detected) qualified data are not. Toxic Equivalent (TEQ) concentrations are reported for dioxins/furans and cPAHs. If a compound was not detected greater than the DL, a value of one-half of the DL was used in the TEQ calculations. The TEQ values are presented to facilitate comparison to other Duwamish datasets; however, the use of a substituted value for censored data can result in large differences in the resulting estimates of summary statistics (Helsel and Hirsch, 2002). The summed and calculated values are presented in the data results.

Dioxins/Furans

- Total dioxins/furans, as a sum of 17 congener concentrations.
- Total dioxins/furans, as a TEQ according to the World Health Organization 2005 guidelines (Van den Berg and others, 2006). If a compound was not detected at greater than the detection level, a value of one-half the DL was used in the calculations.

Polycyclic Aromatic Hydrocarbons

- Total cPAHs as a summed concentration of benz[*a*]anthracene, chrysene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, dibenz[*a,h*]anthracene, and total benzofluoranthenes (sum of *b*-, *j*-, and *k*- isomers).
- Total cPAHs as a TEQ according to the potency equivalency factors adopted by the California Environmental Protection Agency (2005). If a compound was not detected at greater than the DL, a value of one-half the DL was used in the calculations.
- Total high molecular-weight PAHs (HPAH) as a summed concentration of fluoranthene, pyrene, benz[*a*]anthracene, chrysene, total benzofluoranthenes (sum of *b*-, *j*-, and *k*- isomers), benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, dibenz[*a,h*]anthracene, and benzo[*ghi*]perylene.
- Total low molecular-weight PAHs (LPAH) as a summed concentration of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene.

Select PAHs were analyzed by multiple methods in water and sediment samples and the results are presented for all methods in the appendix tables. The more selective and sensitive method, for example, the selective ion mode (SIM) method, is preferred for interpretation as compared to the general semivolatiles method.

Polychlorinated Biphenyls

- Total PCBs, as a sum of the 209 congeners.
- Summed homologues (for example, total monochloro biphenyls, total dichloro biphenyls).

Other than the TEQ calculations (in which a value of one-half the DL was used for not detected compounds), only detected concentrations (including J-qualified detections) were included in summed values. If all compounds in a summed calculation were not detected, the total value is represented by the single highest DL (with a UJ qualifier) or RL (with a U qualifier). All sediment chemistry concentrations were reported by the laboratories as a dry weight concentration. PCB concentrations in filter and XAD-2 samples were converted from pg/sample reported by the laboratory to pg/L by dividing by the volume of water processed during each sampling event (between 60 and 175 L).

Hydrology and Field Parameter Data

The 13 sampling periods occurred over a range of hydrologic conditions ([table 3](#)) including 8 storms, 1 mixed storm-plus-dam release, and 4 baseline periods. The four hydrologic conditions were defined as:

- Storm: 48-hour antecedent rainfall was greater than or equal to 0.4 in.;
- Dam release: The previous day's mean river discharge at USGS streamgage 12105900 (Green River below Howard A Hanson Dam, Washington) was greater than or equal to 2,000 ft³/s;
- Storm plus Dam: Storm and dam release conditions were true; and
- Baseline: Neither storm nor dam release conditions were true.

Precipitation totals were from the NOAA precipitation station at Seattle-Tacoma Airport (GHCND:USW00024233). The previous day's mean daily river discharge at USGS 12105900 (RKM 103; not shown) was used to account for the travel time between stations (approximately 15 hours). The hydrologic conditions and field parameter results are presented in [table 3](#).

Table 3. General hydrology, water quality, and field conditions during sampling at U.S. Geological Survey streamgage 12113390 (Duwamish River at Golf Course, at Tukwila, Washington), 2016–17.

[Precipitation values are the daily total on the sampling date (“Day of sampling precipitation”) summed with daily totals from previous days (for the 48-hour and 30-day values) from the NOAA precipitation station at Seattle-Tacoma Airport (GHCND:USW00024233). **Unit:** °C, degrees Celsius; ft³/s, cubic foot per second; ft, foot; FNU, Formazin Nephelometric Unit; mg/L, milligram per liter; na, not applicable; NTU, Nephelometric Turbidity Unit; in., inch; L, liter; mm, millimeter; mm Hg, millimeter of mercury; μS/cm, microsiemens per centimeter at 25 °C; –, not analyzed. **Sampling date:** Storm+Dam, storm and dam release. –, not analyzed; <, less than]

Parameter name	Unit	Sampling date									
		08-30-16	09-17-16	09-27-16	10-07-16	10-13-16	12-20-16	01-11-17			
Hydrologic condition	na										
Day of sampling precipitation	in.	0.00	0.22	0.02	0.11	1.75	0.01	0.00			
48-hour antecedent precipitation	in.	0.00	0.22	0.02	0.42	1.76	0.82	0.07			
30-day antecedent precipitation	in.	0.06	0.95	1.06	1.00	3.4	4.56	3.24			
Previous day's mean daily discharge at USGS streamgage 12105900	ft ³ /s	420	391	471	534	911	675	620			
Discharge, during sonde deployment	ft ³ /s	460	853	566	6.76	1,240	2,080	1,120			
Gage height, during sonde deployment	ft	5.27	5.02	4.09	8.96	6.04	10.72	6.99			
Water temperature	°C	17.54	15.54	16.30	14.09	12.12	5.37	3.17			
pH	na	6.95	6.68	6.52	6.84	6.67	6.84	7.02			
Specific conductance	μS/cm	126	137	121	109	85	111	109			
Dissolved oxygen	mg/L	8.41	8.48	8.85	9.12	9.69	11.84	12.32			
Barometric pressure	mm Hg	–	759.7	767.3	761.6	753.8	766.7	754.1			
Turbidity, from in-situ DTS-12 sensor	FNU	5.0	–	3.2	3.1	9.4	8.8	5.1			
Turbidity, from hand-held YSI sonde	NTU	2.5	5.0	2.6	2.3	5.4	6.1	3.7			
Suspended-sediment concentration	mg/L	7	52	9	7	78	11	8			
Suspended-sediment percent fines (<62.5 μm)	percent	84	40	86	67	61	93	91			
Estimated pump duration (for sediment chemistry)	hour	9.5	7.33	40	24.5	26	49	45			
Estimated pumped volume (for sediment chemistry)	L	530	740	2,800	1,870	3,100	3,470	3,535			

Table 3. General hydrology, water quality, and field conditions during sampling at U.S. Geological Survey streamgage 12113390 (Duwamish River at Golf Course, at Tukwila, Washington), 2016–17.—Continued

Parameter name	Unit	Sampling date							
		01-18-17	02-09-17	02-10-17	03-03-17	03-07-17	03-14-17		
Hydrologic condition	na								
Day of sampling precipitation	in.	1.21	1.63	1.65	0.36	0.75	Storm+Dam	0.39	
48-hour antecedent precipitation	in.	2.95	2.33	2.35	0.45	0.75		1.04	
30-day antecedent precipitation	in.	5.38	8.68	8.7	9.32	7.64		6.92	
Previous day's mean daily discharge at USGS streamgage 12105900	ft ³ /s	462	565	598	687	718		2,680	
Discharge, during sonde deployment	ft ³ /s	2,500	2,780	4,260	1,940	1,680		5,340	
Gage height, during sonde deployment	ft	9.20	10.46	11.44	8.16	8.89		12.99	
Water temperature	°C	4.87	4.77	4.90	6.82	5.80		7.05	
pH	na	6.74	6.46	6.81	8.07	7.31		7.73	
Specific conductance	µS/cm	96	95	73	122	115		61	
Dissolved oxygen	mg/L	11.96	12.03	12.07	11.09	11.56		11.66	
Barometric pressure	mm Hg	743.1	744.4	757.4	755.5	757.5		757.2	
Turbidity, from in-situ DTS-12 sensor	FNU	79	27 P	66 P	5.5 P	4.8 P		37 P	
Turbidity, from hand-held YSI sonde	NTU	58	19.2	50.2	1.4	2.7		23.8	
Suspended-sediment concentration	mg/L	58	61	142	10	10		157	
Suspended-sediment percent fines (<62.5 µm)	percent	95	82	75	78	85		42	
Estimated pump duration (for sediment chemistry)	hour	23	4.25	—	67.5	51.5		4.5	
Estimated pumped volume (for sediment chemistry)	L	1,860	920	—	4,910	3,975		900	

Quality-Control Chemical Concentrations

Standard Reference Sample Results

Results for the 17 trace elements and mercury (collectively referred to as “metals” in this report) were within 15 percent of the most probable value determined for the USGS Standard Reference Sample Spring 2017 study. Results are publicly-available at <https://bqs.usgs.gov/srs/> by searching for “Lab 356” in the Spring 2017 study.

Results from analysis of the NIST Sediment Reference Material 1944 ranged from 47-percent-higher to 72-percent-lower than the certified or reference value reported by NIST for metals and PAHs. The median percentage difference was 12 percent lower for metals and 33 percent lower for PAHs. The HRMS analyzing laboratory accidentally omitted the sample from the PCB and dioxin/furan batch, although the reference material was regularly analyzed by the laboratory for other projects and previously for this project with good performance. Results from additional quality-control samples for the project are available in Conn and Black (2014) and Conn and others (2015, 2016).

Laboratory Quality-Control Results

Laboratory quality-control samples, including blank samples, laboratory control samples (spikes in blank water), replicate analyses, and matrix spike/matrix spike duplicates (MS/MSDs), were generally within acceptance limits, with the following notable exceptions:

- Blank detections: Results less than 5 times the laboratory blank sample result were qualified as non-detection (U or UJ). Results greater than 5 times the laboratory blank sample result were unqualified detections. Trace amounts of some PCB congeners were detected in method blank samples. PCB-011 was detected in laboratory blanks for water, sediment, filter, and XAD-2 resin at concentrations that were more than 10 times the Limit of Quantitation. Owing to low environmental concentrations less than 5 times the laboratory blank sample concentration, all water and filter PCB-011 results were censored as non-detection. The octa-, nona-, and deca- congeners (PCB194-209) also were censored as non-detection in most of the XAD-2 resin samples owing to laboratory blank contamination.
- Matrix spikes: Laboratory sediment matrix spikes of manganese were variable and far outside of laboratory acceptance limits (batch 1 had 0 and 47 percent recovery in the MS/MSD samples, respectively; batch 2 had 349 and 658 percent recovery in the MS/MSD samples, respectively). This may have been,

in part, owing to the high source sample concentration, which was greater than 3 times the spike concentration. All sediment manganese results were estimated, and indicated with the J qualifier.

- Method performance: In some samples, chromatographic interference affected the labeled and native mono- and di-substituted PCBs 001, 002, 003, 004 and 015 due to the high boiling point of toluene during extraction. Affected congeners are unquantifiable and qualified unusable (R).

The suspended-sediment sample collected on September 27, 2016, was rejected (REJ) for PCB congeners by the Quality Assurance Coordinator at the Ecology Manchester Environmental Laboratory who validated the data because the results did not meet laboratory method criteria. The entire sample was consumed, so re-extraction and re-analysis could not be done.

The Quality Assurance Coordinator summarized the PCB data usability by saying,

“A total of 11,288 data points were reviewed in this validation report. Approximately 0.1% of the data were qualified unusable due to disturbances in lock mass-ion that prevented quantification of the results. About 8% of the data were qualified estimated due to detections that were less than the limits of quantitation, and chromatographic interferences. About 7% of the data were qualified tentatively identified at estimated concentrations due to out of control mass-ion abundance ratios and 12% of the data were qualified as non-detects due to contamination in the associated blank(s). Except for the ‘R’ qualified mono- and di-substituted PCBs, the rest of the data, as qualified, are acceptable for all uses.” (Ginna Grepo-Grove, Manchester Environmental Laboratory Environmental Assessment Program, written commun., September 13, 2017.)

Field Blank Results

Mercury was not detected in either of the two field blank samples. PCBs and dioxins/furans were not detected in the bottle blank (a solvent-rinsed bottle to assess bottle contamination). Equipment blank sample results were acceptable (compounds were not detected), with the following exceptions:

- PAHs: Detections of naphthalene in environmental samples analyzed by the large-volume injection method were censored and reported as non-detects because all environmental sample concentrations were within 5 times the equipment blank concentration (0.0015 µg/L). Fluoranthene and 2-methylnaphthalene also were detected in the equipment blank sample,

though at much lower concentrations (both at 0.00056 µg/L). Environmental detections of fluoranthene and 2-methylnaphthalene less than 5 times the equipment blank concentration were estimated, indicated with the J qualifier. No cPAHs were detected in the equipment blank sample.

- Metals: Barium (0.16 µg/L), copper (0.26 µg/L), and zinc (1.5 µg/L) were detected in the filtered water equipment blank sample, but were not detected in the corresponding unfiltered water equipment blank sample. Environmental sample results with detected concentrations less than 5 times the equipment blank concentration were estimated (J-qualified): 0 of 14 barium results, 12 of 14 copper results, and 9 of 10 zinc results.
- PCBs:
 - Total PCBs were detected in the water equipment blank sample at a concentration of 58.4 pg/L, primarily owing to detections of congeners 007, 012/013, 016, and 017. Eight of the 13 environmental samples had total PCB concentrations similar to the equipment blank sample, whereas the remaining 5 samples had concentrations between 2.5 and 46 times higher than the equipment blank sample. The PCB results in water samples are not censored, but the total PCB results for the eight samples with similar concentrations as the equipment blank have been qualified herein with USGS qualifier EB for Equipment Blank.
 - There was 52.9 pg of total PCBs in the GFF equipment blank sample. Total PCB concentrations in environmental samples were more than 30 times higher on a pg/sample basis. Concentrations of individual PCB congeners on a pg/sample basis were at least 2 times higher in environmental samples than the equipment blank sample, with the exception of PCB congeners 001 and 002, which had similar concentrations in the equipment blank as many environmental samples. PCB results were not censored; PCB congeners 001 and 002 contributed between 0.2–2 percent of the total PCB concentration.
 - There was 2,000 pg of total PCBs in the XAD-2 equipment blank sample. Total PCB concentrations in environmental samples were 4–15 times higher on a pg/sample basis. Concentration of individual PCB congeners on a pg/sample basis were 1.4 to more than 10 times higher in environmental samples than the equipment blank sample. PCB results were not censored.

Field Replicate Results

Results for water and filter field replicate samples were acceptable (relative percent difference <40 percent with a few exceptions). The relative percent difference between individual PCB congeners in the XAD-2 field replicate samples was variable (-78 to 103 percent, median = 26 percent). The relative percent difference was acceptable (<40 percent) for the summed parameters (for example, total PCBs and each homologue group), except the total octachloro biphenyls (78 percent).

Other than the censoring described in this section, the results from various field quality-assurance samples were satisfactory, and no additional qualifications were applied to the environmental data.

Environmental Chemical Concentrations in Water and Suspended Sediment

Analytical chemistry results for individual compounds and summed parameters during the 13 sampling periods are presented for unfiltered-water samples ([table A1](#)), filtered-water samples ([table A2](#)), suspended-sediment samples ([table A3](#)), colloidal samples captured on a GFF from the centrifuge effluent ([table A4](#)), and in dissolved samples passing through the filter and captured on XAD-2 resin ([table A5](#)).

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Appendix A. Analytical Chemistry Results

The data presented in tables A1–A5 are the analytical results for individual compounds and calculated values from Analytical Resources, Inc., SGS AXYS Analytical Services Ltd., Washington State Department of Ecology’s Manchester Environmental Laboratory, and King County Environmental Laboratory, with amended results and qualifiers by the Washington State Department of Ecology Quality Assurance Officer and the USGS. The data for individual compounds (not calculated values) are stored in the publicly available Ecology Environmental Information Management database (Washington State Department of Ecology, 2015).

The appendixes are Microsoft® Excel files and are available for download at <https://doi.org/10.3133/ds1073>.

Table A1. Concentrations of organic carbon, metals, polycyclic aromatic hydrocarbons and other semivolatile compounds, butyltins, dioxins/furans, and polychlorinated biphenyls in unfiltered-water samples, U.S. Geological Survey streamgage 12113390 (Duwamish River at Golf Course, at Tukwila, Washington), 2016–17.

Table A2. Concentrations of organic carbon and metals in filtered-water samples, U.S. Geological Survey streamgage 12113390 (Duwamish River at Golf Course, at Tukwila, Washington), 2016–17.

Table A3. Concentrations of organic carbon, metals, polycyclic aromatic hydrocarbons and other semivolatile compounds, butyltins, dioxins/furans, and polychlorinated biphenyls in suspended-sediment samples, U.S. Geological Survey streamgage 12113390 (Duwamish River at Golf Course, at Tukwila, Washington), 2016–17.

Table A4. Concentrations of polychlorinated biphenyls in centrifuge effluent captured on 0.45-micrometer glass-fiber filters (“colloid” samples), U.S. Geological Survey streamgage 12113390 (Duwamish River at Golf Course, at Tukwila, Washington), 2016–17.

Table A5. Concentrations of polychlorinated biphenyls in centrifuge effluent samples passing through a 0.45-micrometer glass-fiber filter and captured on XAD-2 resin (“dissolved” samples), U.S. Geological Survey streamgage 12113390 (Duwamish River at Golf Course, at Tukwila, Washington), 2016–17.

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