

## Quality Assurance Project Plan

### Assessing Sediment and Toxic Chemical Loads from the Green River, WA to the Lower Duwamish Waterway

**Prepared for:**

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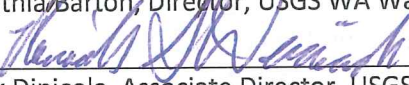
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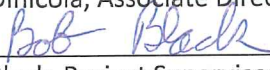
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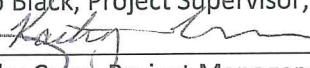
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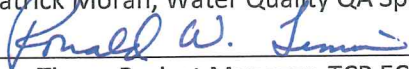
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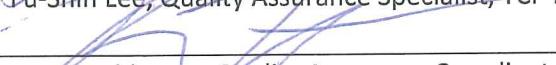
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## Abbreviations and Acronyms

ADCP	Acoustic Doppler current profiler
ADVM	Acoustic Doppler velocity meter
BCM	Bed composition model
CASRN	Chemical Abstract Service Registry Number
cPAHs	Carcinogenic polycyclic aromatic hydrocarbons
CVO	USGS Cascades Volcano Observatory Sediment Laboratory
DL	Detection limit
Ecology	Washington State Department of Ecology
EDI	Equal-discharge increment
EIM	Environmental Information Management
EWI	Equal-width increment
FY	Federal fiscal year
HRMS	High-resolution mass spectrometry
LCS	Laboratory control sample
LDW	Lower Duwamish Waterway
LEP	Laboratory evaluation program
LMCL	Lower method calibration limit
MS	Matrix spike
NWIS	National Water Information System
PCBs	Polychlorinated biphenyls
PSD	Particle size distribution
QL	Quantitation limit
RL	Reporting limit
RM	River Mile
RPD	Relative percent difference
SDL	Sample-specific detection limit
SLEDS	Sediment Laboratory Environmental Data System
SSC	Suspended sediment concentration
STM	Sediment transport model
TOC	Total organic carbon
USEPA	U.S. Environmental Protection Agency

USGS U.S. Geological Survey  
VOCs Volatile organic compounds  
WaWSC USGS Washington Water Science Center

## Background

The Lower Duwamish Waterway (LDW) in Seattle, Washington is the site of intense current and historical anthropogenic influence, including numerous industrial, commercial, and residential uses. The land uses in the drainage basin include: residential (35 percent) such as the towns of South Park and Georgetown; industrial (18 percent) and commercial (11 percent) including marinas, boat manufacturing, concrete manufacturing, food processing, and airplane parts manufacturing; rights-of-way (18 percent) such as roads and highways; and open or undeveloped areas (17 percent) including parks. Decades of intense anthropogenic activities have resulted in contaminated sediments in the LDW. In 2001-2002, the U.S. Environmental Protection Agency (USEPA) and the Washington State Department of Ecology (Ecology) required remedial investigations and feasibility studies on the 5-mile, 441-acre LDW under the federal Superfund law and Washington's Model Toxics Control Act due to concern over human health risks from exposure to contaminated sediments. The main contaminants of concern for human health include polychlorinated biphenyls (PCBs), dioxins/furans, carcinogenic polycyclic aromatic hydrocarbons (cPAHs), and arsenic. The draft preferred USEPA cleanup plan for the LDW was released for public comment in early 2013, and includes a number of cleanup alternatives, including dredging, capping, and/or natural recovery.

To support the implementation of a cleanup plan of contaminated sediments in the LDW, sources of sediment to the site were evaluated. Three sources of sediment to the LDW were identified: upstream sources that are transported by the Green River to the LDW, lateral sources from land adjacent to the LDW, and re-suspended bed sediment within the LDW. The Sediment Transport Model (STM), developed for the LDW, predicts that every year more than 185,000 MT of sediment enters the LDW, and greater than 99 percent of that originates from upstream sources while approximately 0.5 percent originates from lateral sources and 0.2 percent originates from bed sediment within the LDW (LDWG 2008). There is substantial uncertainty in the average annual upstream sediment load because of large inter-annual variations in precipitation and sediment transport dynamics. The STM predicts that approximately 90 percent of the total bed area in the LDW receives 10 cm of new sediment within 10 years or less. Therefore, the sediment and contaminant transport and loading dynamics from the Green River to the LDW will determine, in large part, the sediment recovery potential of remediated areas in the LDW.

## Research Problem and Objectives

Limited field data are available regarding sediment and contaminant transport and loading dynamics from the Green River to the LDW. The STM estimated suspended and bed sediment loading into the LDW from upstream sources using grain size information and a flow-rating curve for the Green River based on discharge data from 1960-1980 and 1996-1998. That physical model was then coupled with contaminant concentration data to create a Bed Composition Model (BCM). The upstream contaminant data was extrapolated from five historic data sets from King County, Ecology, and the U.S. Army Corps of Engineers. Only one of those data sets (Gries and Sloan, 2009) measured contaminants on suspended sediment (the other

studies measured surface sediment or whole water). The sample size of the Gries and Sloan data set was relatively small (n=7) and samples were not collected during the rising limb of high flow events. The upstream data that were used in the BCM primarily originated from surface bed-sediment data, and it was acknowledged that those values were probably estimates of actual contaminant concentrations because the suspended sediment fraction was not fully represented. In addition, suspended sediment-associated chemical loadings are expected to vary over time as affected by a number of variables including precipitation, streamflow, seasonality, sediment organic carbon content and particle size distribution. Therefore, better estimates of annual sediment loading and toxic chemical loading from suspended sediment in the Green River to the LDW are needed.

The objective of this project is to quantify sediment and toxic chemical loads associated with upstream sources in the Green River to the LDW, including high flow/high turbidity events that may contribute more to the annual loading than average flow conditions. These improved measurements will aid in assessing the potential for future re-contamination of remediated sediment in the LDW and will leverage ongoing U.S. Geological Survey (USGS) efforts to quantify sediment and chemical loading from large rivers to Puget Sound.

## Organization and Timeline

The roles and responsibilities of key personnel involved in this project are provided in this section.

*Ron Timm, Washington State Department of Ecology.* Provide technical management of the project to ensure that activities are conducted in accordance with Department of Ecology guidelines and standards.

*Kathy Conn and Bob Black, USGS Washington Water Science Center.* Implement project objectives including coordination of field sampling, processing, transport of samples for physical and chemical analysis, and data retrieval. Analyze data and provide interpretive findings to Ecology. Ensure that the project is conducted according to USGS guidelines and standards.

*Fu-Shin Lee, Washington State Department of Ecology, Quality Assurance Specialist, Toxics Cleanup Program.* Review sampling plan and data for adherence to Ecology quality assurance and control standards, including those required for input into the Environmental Information Management (EIM) database.

*Patrick Moran, USGS Washington Water Science Center's Interim Water Quality Specialist.* Review sampling plan and data for adherence to USGS quality assurance and control standards.

*Karin Feddersen, Washington State Department of Ecology, Quality Assurance Coordinator.* Manage analytical chemistry contract including development of Statement of Work, evaluation of bidding laboratories, and payment. Provide EPA Level 4 validation of analytical data as described in Data Validation section.

Contract Laboratories and Consultants:

Ecology will contract with a Washington State accredited laboratory for analytical chemistry and grain size services. Ecology will coordinate the analytical laboratory contract, and those analytical service costs are not included in the overall agreement between Ecology and the USGS. The USGS will utilize one USGS laboratory for physical sediment analysis of suspended sediment in water samples. The USGS will manage all data from both the USGS sediment lab and the contract analytical laboratory (see USGS Washington Water Science Center responsibilities below).

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The WaWSC will be responsible for overseeing the collection, transport, shipping, and interpretation of all physical and chemistry data related to this project. This includes water, suspended sediment, and bed sediment samples. The WaWSC will also be responsible for payment of physical sediment analysis conducted by the USGS sediment lab. USGS analytical guidelines and quality parameters will be reviewed and compared for compliance and a data quality evaluation (see USGS Office of Water Quality Technical Memorandum 2007.01: <http://water.usgs.gov/admin/memo/QW/qw07.01.html>) will be the responsibility of the WaWSC. The WaWSC will review all field and lab data comparable to an EPA Level 2 review and conduct data analysis and report preparation. In addition, the publication and transmittal of all final reports and the long-term storage of data in Ecology and USGS databases will be the primary responsibility of the WaWSC.

**USGS Cascades Volcano Observatory Sediment Laboratory (CVO)**

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The CVO will be responsible for the analysis of water samples for physical characterization of suspended sediment, including particle size distribution (PSD) and suspended sediment concentration (SSC). SSC is a measure of the amount of sediment in a given volume of water, reported as milligrams per liter (mg/L). Water samples collected using two techniques will be compared: (1) from the bridge using depth- and width-integrated techniques that ensure the



sample is representative of the river's entire cross-section (as the samples for water chemistry will be collected) and (2) from the bank using a pump from a point source (as the samples for suspended sediment chemistry will be collected). See the Field Sampling section and Table 2 for more details.

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Ecology's Manchester Lab will be responsible for managing the analytical laboratory contract for chemical analysis of water, suspended sediment and bed sediment samples and grain size analysis of bed sediment samples. This will include the development of the Statement of Work, evaluation of bidding laboratories, and payment for analytical services. The Manchester Laboratory will also be responsible for conducting laboratory data validation comparable to USEPA Level 4 validation. See Data Validation section for more details.

**Contract Laboratory**

The contract laboratory will be responsible for the chemical analysis of water, suspended sediment, and bed sediment samples for all analytes listed in Appendix A as well as grain size analysis of bed sediment samples. The analysis of the high resolution compounds - the dioxins/furans, and 209 PCB congeners - may be conducted by a second lab specializing in those services. The laboratory(s) will provide a designated project manager for direct communication with Ecology and the USGS. The laboratory will provide bottles, coolers, preservatives, filters, and chain of custody forms for each sampling event. They will provide an USEPA Level 4 data package deliverable to the USGS and Ecology, which includes a summary narrative and raw data. The data will be transmitted in an electronic format that is compatible with Ecology's EIM database.

The timeline for the project is shown in Table 1.

**Table 1. Timeline of project tasks.**

Task	Federal Fiscal Year (FY) 2014				FY 2015		
	Oct-Dec	Jan-Mar	Apr-June	July-Sept	Oct-Dec	Jan-Mar	Apr-June
Study Design							
Equipment Installation							
Field Sampling							
Equipment Operation & Maintenance							
Data Review and Analysis							
Report Preparation							

## Data Quality Objectives

The overall data quality objective is to ensure that data of known and acceptable quality are generated. To achieve this goal, data must be reviewed for 1) precision, 2) accuracy (or bias), 3) representativeness, 4) completeness, 5) comparability, and 6) sensitivity.

1) Precision- is a measure of mutual agreement among individual measurements of the same property, under prescribed similar conditions. For this project, sampling precision from field samples will be addressed by collecting and submitting for analysis sequential replicate or split samples obtained during the same sampling event. Two sequential field replicates of water and two field splits of homogenized bed sediment material will be collected for chemical analysis. A field replicate will not be collected for suspended sediment because of the mass limitations. Results from the field replicate and split samples will be included in the final report.

Precision of field parameters is specific to the instrumentation. Quality objectives for field parameters are:

- A Teledyne Rio Grande or similar acoustic Doppler current profiler (ADCP) will be used to measure:
  - Water depth from 0.5 to 30 m, accurate to  $\pm 1$  cm, and
  - Instantaneous velocity up to 20 m/s, accurate to 2 mm/sec.
- A YSI 6280 V2 sonde or similar multi-parameter sonde will be used to measure:
  - Water temperature between -5 and 50 °C, resolution 0.01 °C  $\pm 0.15$  °C
  - Dissolved oxygen between 0 and 50 mg/L, resolution 0.01 mg/L  $\pm 0.1$  mg/L or 1%, whichever is greater
  - pH between 0 and 14 units, resolution 0.01 unit  $\pm 0.2$  unit

- Specific conductance between 0 and 100 mS/cm, resolution 0.001 mS/cm  $\pm 0.5\%$  of reading
- Turbidity between 0 and 1000 NTU, resolution 0.1 NTU  $\pm 2\%$  or 0.3 NTU, whichever is greater.

Quality objectives for analysis of SSC and PSD at CVO are:

- SSC: For concentrations of 0-50 mg/L  $\pm 15\%$ , detection limit of 0.5 mg/L
- SSC: For concentrations  $>50$  mg/L  $\pm 5\%$ , detection limit of 0.5 mg/L
- PSD: Size fractions reported to the nearest 1%  $\pm 5\%$

The analytical laboratory(s) will conduct laboratory blank, laboratory control samples (LCS), and laboratory control replicates according to their quality assurance and control plan (with every batch of approximately 20 samples). In addition, laboratory replicates and matrix spikes (MS) of environmental samples from this project will be requested at approximately a 10% frequency. Laboratory replicates will be prepared by splitting a sample in the laboratory, and carrying the subsamples through the entire analytical process. Precision is expressed as the relative percent difference (RPD). Method control limits for individual compounds will be used where available. Where no limits are published, the following limits for both water and sediment will be used:

- 60% to 135% recovery or better of LCS and MS for high-resolution organic analyses.
- 30% to 160% recovery or better of LCS and MS for organic analyses.
- 75% to 125% recovery of LCS and MS for general chemistry analyses (i.e. total organic carbon, TOC).
- 80% to 120% recovery of LCS for metals analyses.
- 75% to 125% recovery of MS for metals analyses.
- RPD between lab replicates  $\leq 40\%$  for high-resolution organic analyses.
- RPD between lab replicates  $\leq 40\%$  for organic analyses.
- RPD between lab replicates  $\leq 20\%$  for inorganic analyses (general chemistry and metals).

2) Accuracy- is a measure of the bias of a system or measurement. It is the closeness of agreement between an observed measurement value to the expected value or to the most-probable value. Quality-assurance check measurements on the ADCPs will be performed annually, after an instrument is first acquired, after factory repair, or after firmware or hardware upgrades. The multi-parameter sonde will be calibrated at the WaWSC laboratory or in the onsite mobile laboratory on the day of each sampling event.

Quality assurance of SSC and PSD data produced by the USGS CVO is assessed through the Sediment Laboratory Quality Assurance (SLQA) Project. Historic results from annual single-blind studies are available at <http://bqs.usgs.gov/slqa/>.

Accuracy of chemical analysis will be assessed through laboratory matrix spikes and matrix spike duplicates requested at approximately a 10% frequency, as specified in the analytical contract. Accuracy will also be assessed through continuing calibration data generated by each laboratory. When isotope dilution methods are available, they will be used, from which analyte concentrations are adjusted based on the extraction recovery and analytical performance of its isotope.

At one or more times during the project, suspended sediment and bed sediment samples will be batched with the Puget Sound Reference Material (QATS catalog # PS-SRM) for analysis of low-level dioxins/furans, PCB congeners and PCB Aroclors. The Puget Sound Reference Material has been established for dioxins/furans and PCB congener analysis using HRMS methods. This sediment reference material is also suitable for Aroclor analysis using gas chromatography/electron capture detection methods. There are no established values for any other analytes which is why it will not be analyzed for any other parameters. All other analyses of suspended sediment and bed sediment samples will be conducted as they are collected within their respective holding times.

3) Representativeness- expresses the degree to which data accurately and precisely represents a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. For this project, representativeness will be determined by the station selection, timing of the sampling events, sample collection methods, acceptance criteria, and sample handling and storage. To ensure samples for chemical analysis are representative, they will be collected:

- From a location in the Duwamish River that is close to the LDW but far enough upstream to minimize potential tidal influences determined during previous studies (Gries and Sloan 2009, Embrey and Frans 2003, Santos and Stoner 1972), and to minimize the probable resuspension, advection, and deposition of the sediment mass that oscillates landward and seaward in the transitional regime of the estuarine river (Ganju and others, 2004).
- During high flow conditions when the tidal influence is overcome or during low tide conditions, to maximize collection of sediment being transported downstream from upstream sources, again minimizing the probable resuspension, advection, and deposition of the sediment mass that oscillates landward and seaward in the transitional regime of the estuarine river.
- During a range of flow and sediment conditions, including high-flow, high-turbidity events; capturing the rising limb of a storm when logistically possible.
- From one or more locations within the water column at the sampling station that represents average conditions, as determined by water quality parameters (specific conductance, turbidity, pH, dissolved oxygen), flow, and visual observations.
- Using USGS field sampling protocols for representative samples when available and appropriate (Mueller and Wagner, 2009; U.S. Geological Survey, variously dated; Wilde and others, 2004; Davis and the Federal Interagency Sedimentation Project, 2005; Shelton 1997; Edwards and Glysson, 1999; Radke and others, 2005), as well as protocols used throughout the region (for example, Ecology, 2008).

Specifically, samples of water and suspended sediment (for physical parameters) will be flow-weighted (in other words, collected from multiple stations in the river's horizontal cross-section) and depth-integrated, and will be collected using samplers (nozzles, bottles, and bags) that have been tested for non-biased sampling (the velocity through the nozzle into the sampler is the same as the velocity of the river, so as not to bias the sediment representation). Water samples will be composited in a Teflon churn prior to bottle filling to minimize sample variability between bottles. Bed sediment samples, collected from multiple locations near the station, will be targeted from areas with a high deposition of fine sediment material in order to aptly represent the presence of recently deposited fine material.

The USGS has developed a draft protocol for the collection and concentration of suspended sediment using a continuous-flow centrifuge (Appendix B). For this project, suspended sediment samples collected for chemistry will be pumped from a point source in the river at 0.6 times the depth at the thalweg. See the Field Sampling section and Table 2 for more details.

4) Completeness- is a measure of the amount of acceptable analytical data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. Target completeness values are 10 storm events (of 20 total events) as defined as peak discharge and/or turbidity values at least two times greater than recent baseline values. Of those 10 events, a target of five events will capture the rising limb of the storm stage. The remaining events will capture smaller storms and low-flow conditions. Target completeness values are 90% for chemical analyses of water and bed sediment. Due to suspended sediment mass limitations during low flow events, only prioritized analytical methods may be performed (see Analytical Methods). Target completeness values are 90% for priority methods in suspended sediment (dioxins/furans, PCB congeners, metals, and low-level PAHs).

5) Comparability- expresses the confidence with which one data set can be compared to another. For this project, comparability will be achieved through the use of standard EPA-approved laboratory methods. In addition, standard techniques to collect and analyze representative samples will be used. This will allow comparison to previous (for example, Embrey and Frans 2003) and ongoing (for example, ongoing USGS study on large Puget Sound rivers) data sets. While there are differences in suspended sediment field collection and processing protocols between this project and the Gries and Sloan (2009) project, both projects utilize continuous-flow centrifugation for concentration of suspended sediment. Both projects include measures of centrifuge sediment capture efficiency, TOC, SSC and PSD, which will aid in comparing the suspended sediment chemistry results between projects.

6) Sensitivity- is a measure of the analytical capability of the methods to meet the project objectives. The analytical detection limit (DL) and reporting limit (RL) goals for each compound in water and sediment are presented in Appendix A. The contract analytical laboratory will be selected specifically because of its ability to meet these low-level limits. Due to the high risk of contamination by volatile organic compounds (VOCs), a trip blank (a sample of deionized water filled at the analytical laboratory and transported in the cooler to and from the site during field sampling) will be included in each of the 20 sampling events. Five sets of paired water trip blanks and field equipment blanks will be collected (10 samples total). The trip blank will be organic-free water transported from the WaWSC in its original container and poured directly into sample bottles in the mobile laboratory at the field station.

The field equipment blank will be organic-free water transported from the WaWSC in its original container and processed through the field sampling equipment (Teflon nozzle, collection bag or bottle, and churn) before bottle filling. At least three of the paired trip blanks and field equipment blanks will be collected within the first five sampling events to identify early in the project any contamination, particularly of the dioxins/furans and 209 PCB congeners, associated with field sampling and processing protocols.

Two suspended sediment quality control samples will be collected including a “source sediment” (a river sediment burned at 450 °C) and an equipment blank (the “source sediment” mixed into a slurry with organic-free water and processed through the field and centrifuge equipment). Results from the field and equipment blanks will indicate if the equipment cleaning, sampling collection, handling, and processing procedures introduce contamination that could increase the low reporting limits.

## Sampling Design

Approach: The USGS will install and operate two new real-time stream gaging stations in tidally-influenced reaches of the Duwamish River – one just upstream of the Upper Turning Basin in the LDW at River Mile (RM) 5.0 and one approximately five miles upstream of the LDW boundary at RM 10.4 (Figure 1). Each station will utilize an Acoustic Doppler Velocity Meter (ADVM) and turbidity sensor to provide continuous real-time publicly-available discharge and turbidity data. The downstream station is located at a bridge just upstream of the Upper Turning Basin in the LDW and samples collected there will incorporate contributions from all upstream sources of discharge and sediment to the LDW. However, this station is in estuarine conditions affected by reverse saltwater flows that would complicate chemical and sediment loading calculations due to the mass of sediment that likely oscillates seaward and landward with the tide (Ganju and others, 2004). Therefore, samples for chemical analysis will not be collected from this downstream station. It is unknown to what extent sediment from the LDW is re-suspended and transported upstream during incoming tides, vessel turning, and dredging activities. It is also unknown how long it will take and/or what conditions are necessary to flush that sediment back down into the LDW. To address these unknowns, sediment, flow, and salt dynamics at the downstream station will be investigated by analyzing continuous acoustic ADVM data, as well as continuous turbidity, temperature, and specific conductance data over the duration of the project (through June 2015). Vertical and longitudinal profiles of conductivity and temperature may be conducted at different times of the year to determine the frequency and extent of saltwater intrusion. In addition, discrete samples for SSC and PSD will be collected in tandem with samples at the upstream station (see below).

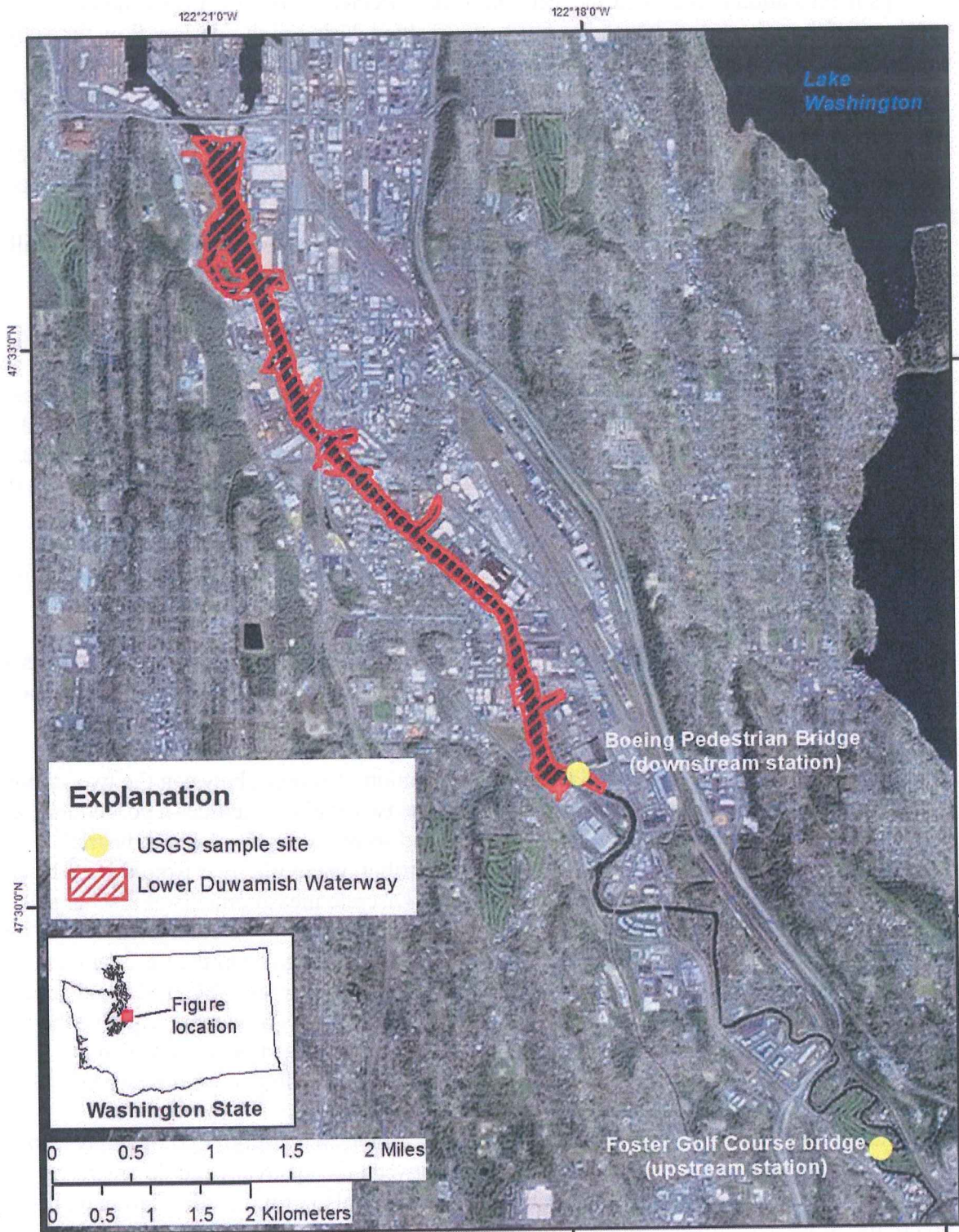


Figure 1. Map of upstream and downstream sampling locations relative to the Lower Duwamish Waterway Superfund Site in Seattle, WA.

The upstream station is tidally influenced, but is not affected by reverse flows and is upstream of the salt wedge, which has been documented during high tide-low flow times by Gries and Sloan (2009) at RM 6.7 and by Santos and Stoner (1972) as far upstream as the Foster Bridge (RM 8.7). The upstream station also has an existing bridge that is safe, secure, and well suited for sample collection, as described in the "Site description" section of this QAPP. Those features will maximize the potential to collect complete high-quality suites of data during the severe weather conditions that generate the high-flow, high-turbidity events during the rising limb of a storm hydrograph that are a primary target for the sampling. Between November 2013 and June 2015, the USGS Washington Water Science Center will collect representative samples of water, suspended sediment, and bed sediment from the upstream stream gaging station during a range of hydrological conditions representing seasonal, storm-, and dam-related variations in flow and/or turbidity. This is a continuation of the field sampling activities conducted between February and June 2013 during the initial phase of the project. Samples will be analyzed by Washington State-accredited laboratories for a large suite of compounds, including cPAHs and other semi-volatile compounds, PCB Aroclors and the full suite of 209 congeners, volatile compounds, metals including arsenic, dioxins/furans, pesticides, butyltins, and TOC. Concurrent with the chemistry sampling at the upstream station, the USGS will measure instantaneous discharge, general water quality parameters, SSC and PSD. The USGS will develop regression relations between the continuous and discrete data to estimate annual sediment and chemical loads transported by the Green River to the LDW.

Chemical results from the upstream station will not be complicated by the potential effects of reverse flows, saltwater, and re-suspended sediment that may impact the downstream station, which is why all chemical analysis in this phase of the project will occur at the upstream station. However, the upstream station is approximately five miles upstream of the LDW boundary, and the number, type, and relative contribution of sources between the two stations is unknown. Development along the river between the two stations includes a golf course, a small commercial complex, residential properties, and some commercial and industrial properties along the waterway. The contaminant contributions to the river from this reach are expected to primarily consist of stormwater outfalls. Discrete measurements of discharge, sediment (SSC and PSD), and general water quality parameters will be conducted concurrently at both stations throughout the study. The paired data from the upstream and downstream stations (continuous discharge and turbidity, and discrete SSC, PSD, and general water quality parameters) will be compared to qualitatively assess how representative the loading estimates from the upstream station are in capturing all upstream sources to the LDW. For example, a small change in the discharge ratio and sediment ratio between stations measured during storm events as compared to baseline events may suggest that the contributions from storm drains between stations are minor. In addition, Ecology may also compile data on land use and storm drain outfalls between the upstream and downstream stations. The continuous Doppler data at both stations will also provide information on bi-directional flows and cross-sectional sediment dynamics. These assessments will inform sample design in future phases of the project, such as the potential benefits of chemistry sampling at the downstream station relative to the substantial increase in costs.

Site Description: Field activities will be conducted at the two new stream gaging stations on the Duwamish River. The downstream stream gaging station will be located at the pedestrian



footbridge at the Boeing Development Center at RM 5.0 (Figure 1 and 2). This station, which is just upstream of the LDW Upper Turning Basin, is in the estuarine portion of the Duwamish River and may be influenced by salinity and navigational/dredging effects. No historic USGS water quality data is available for this station. The station (Figure 2) is an ideal location for an ADVM station for a number of reasons. The river cross-section between the two bridge pilings is uniform in depth and flow. The bridge piling in the water will allow easy mounting of the ADVM for high-quality side-looking data collection. Other instrumentation can easily be mounted to and later removed from the bridge, including a wire weight gage, radar system for measuring gage height, and an antenna for transmitting real-time data. There is limited vehicle traffic on the bridge and parking is available.



**Figure 2. Photo of the downstream station - the pedestrian bridge at the Boeing Development Center- located at River Mile 5.0.**

Field activities at the upstream station (Figure 1 and 3), which has a USGS Station ID of “USGS 12113390 - Duwamish River at Golf Course, Tukwila, WA”, will build on the preliminary USGS data set collected at this station between February and June 2013 as well as historic USGS water quality data collected at this station through the USGS National Water Quality Assessment (NAWQA) program. Between 1995 and 2004, samples were collected approximately monthly at this site as part of the NAWQA program. Discharge, specific conductance, nutrients, metals, pesticides and organics in water and a limited number of bed sediment samples were measured. Instantaneous discharge values ranged from 230 to 13,200 cubic feet per second (cfs), with a median value of 1390 cfs (n=116). The highest measured instantaneous discharges were recorded during large storm events in the late winter season (January through April) in 1996 and 1997 (note that this is an instantaneous, not continuous, discharge record). Elevated SSC values were often measured concurrently with elevated discharge. SSC ranged from 3 to 787 mg/L (n=114), with a median value of 19 mg/L.



**Figure 3. Photo of the upstream station, USGS 12113390 – Duwamish River at Golf Course at Tukwila, WA, located at River Mile 10.4.**

The cross-section at the upstream station promotes good mixing of the water column as the bridge supports are on the bank and there are no large bridge abutments or other disruptions to flow and mixing in the water (Figure 3). In addition, the site location provides safe sampling access because it is a wide bridge with limited golf cart and foot traffic only. After hours, the bridge can only be accessed through a locked gate (for which the USGS has a key), providing heightened security compared to other sites.

## Continuous Real-Time Monitoring

The USGS has recently published approved methods for reporting discharge in tidally-influenced river reaches using ADVN instrumentation (Levesque and Oberg 2012). By measuring particle backscatter through acoustic Doppler principles, an ADVN can provide powerful information regarding forward and reverse flow throughout the entire vertical and horizontal river cross-section at a station. At both stations in this project, a new USGS stream gaging station will be installed including instrumentation to measure velocity, stage, and water temperature for continuous, real-time discharge data. A turbidity sensor will be co-located and continuous, real-time turbidity data also will be available. The turbidity sensor (DTS-12, Forest Technology Systems, Inc.) uses Nephelometric geometry to measure backscattered light, reported as turbidity. The instrumentation will be operated and maintained by the USGS for the duration of the agreement. The provisional real-time data will be publicly available and the data records will be compiled, reviewed, and approved by the USGS in a timely manner consistent with USGS protocols (Levesque and Oberg 2012, Wagner and others 2006). An example of real-time discharge and turbidity data is available for USGS 12101500 – Puyallup River at Puyallup, WA at [http://waterdata.usgs.gov/nwis/uv?site\\_no=12101500](http://waterdata.usgs.gov/nwis/uv?site_no=12101500). (Note that this station is not in a tidally-influenced reach and therefore uses a traditional ADCP.) This real-time data will be valuable in informing USGS sampling events and will improve the ability to capture a representative range of flow and sediment conditions. In addition, the real-time data may be useful to other agencies, tribes and the public to guide river-related activities such as flood management.

## Field Sampling Methods

Over the duration of the project (approximately 19 months), 20 discrete bridge-based sampling events will be conducted at the upstream station. The 19-month duration will allow more opportunity to capture high-flow events including the first fall rains, and will better represent the seasonal and inter-annual variability of the river system. Sampling will occur approximately monthly, targeting high flow and/or high turbidity events due to storms and dam releases. A target of at least 10 of the 20 events will capture storms of varying sizes with discharge and/or turbidity values at least double recent baseline values. The remaining events will capture non-storm conditions including summer and winter conditions. These targets will guide the sampling scheme, though actual sampling will be determined by real-time data, personnel availability, and safety.

Similar to the study design in the first phase of this project (FY13), five tasks will be conducted during each of the 20 bridge-based sampling events at the upstream station to measure the following parameters: 1) instantaneous discharge, 2) general water quality, 3)

water chemistry, 4) suspended sediment physical parameters, and 5) suspended sediment chemistry. On five separate occasions during low flow/low tide conditions, a sixth task will be conducted to measure the following parameter: 6) bed sediment chemistry. A summary of these tasks is contained in Table 2 and a more detailed description is provided below.

**Task 1) Instantaneous discharge.** Discharge will be measured using an ADCP following standard USGS protocols (Mueller and Wagner, 2009) to calibrate the ADVm.

**Task 2) General water quality.** Water quality parameters including water temperature, pH, dissolved oxygen, specific conductance, and turbidity will be measured using a multiparameter sonde (YSI Inc., Yellow Springs, OH). The sonde will be co-located with the point sampling intake (see Task 5). Measurements will be made periodically over the duration of pumping for suspended sediment chemistry (see Task 5).

**Task 3) Water chemistry.** Based on the discharge measurements and stream width, the river cross-section will be divided into equal discharge increments (EDI) for water chemistry analysis and suspended sediment physical parameter analysis (see Task 4) using standard USGS protocols (U.S. Geological Survey, variously dated) including those specific for sampling of trace organic chemicals (Wilde and others, 2004). This sampling technique collects a depth- and width-integrated sample that is representative of the entire river cross-section at that sampling station. Briefly, a sampler (Figure 4) is lowered at a consistent transit rate from the surface to the bottom and back to the surface of the water column at each station. The process is repeated as necessary to obtain sufficient sample. Water samples will be collected from each cross-section station in Teflon bottles or bags using an approved sampler, such as the D-96 (Davis and the Federal Interagency Sedimentation Project, 2005). The water samples will be composited in a 14-L Teflon churn and immediately processed in an on-site mobile laboratory (see Sample Processing). VOCs will be collected separately using a USGS tested and designed hand-held sampler to avoid losses due to sample pouring, transferring, and churning (Shelton 1997). The sampler, containing four 40 mL glass vials will be lowered to a mid-point in the vertical water column at a single station in the centroid of flow. Water fills the bottles slowly from the bottom to avoid turbulence and head space that could result in analyte losses. A complete list of analytes being characterized in all water samples is contained in Appendix A.

**Table 2 (continued on next page). Summary of field collection tasks, parameters collected, collection methods, references, and laboratories completing each task. Task numbers correspond to the task numbers discussed in the text.**

Task No.	Task Description	Parameter Collected	Collection Method	Published Collection Methods	Laboratory	Notes
1	Instantaneous discharge	River discharge (ft <sup>3</sup> /sec)	Acoustic Doppler Current Profiler (ADCP)	Muller and Wagner, 2009.	USGS-Tacoma	-
2	General water quality (field parameters)	Water temperature (°C), pH, dissolved oxygen (mg/L), specific conductance (µS/cm), turbidity (NTU)	Teledyne YSI multiparameter sonde	USGS National Field Manual for the Collection of Water-Quality Data (NFM), variously dated.	USGS-Tacoma	-
3	Water chemistry	Dioxins/Furans, PCB Aroclors and 209 congeners, Semivolatile Compounds, PAHs, Pesticides, Butyltins, Trace Elements (metals) including mercury and hexavalent chromium, total organic carbon. See Appendix A for complete list of analytes.	Depth- and width-integrated sample representative of entire river cross-section using Teflon samplers. Sample transferred to Teflon churn for complete homogenization prior to sample processing in on-site mobile lab.	Wilde and others, 2004; Davis and the Federal Interagency Sedimentation Project, 2005; USGS NFM, variously dated.	Contract laboratory	-
3	Water chemistry (VOCs)	Volatile Organic Compounds (VOCs) (µg/l). See Appendix A for complete list of analytes.	USGS hand-held VOC sampler designed to minimize chemical loss. Sample collected at 60% of depth at the centroid of flow.	Shelton, 1997.	Contract laboratory	-
4	Suspended sediment physical parameters	Characterization of abundance of suspended sediment in a volume of water, expressed as suspended sediment concentration (SSC, mg/L). Characterization of size distribution of suspended sediment particles, expressed as a particle size distribution (PSD).	Depth- and width-integrated sample representative of entire river cross-section. This cross-section sample will be collected immediately after the water chemistry cross-section sample using USGS suspended sediment sampling protocol.	Edwards and Glysson, 1999; Radke and others, 2005.	USGS Cascades Volcano Observatory Sediment Laboratory (CVO), Vancouver, WA	No chemical analyses will be conducted on these samples. Results will be interpreted with the suspended sediment chemistry sampling results (Task 5) to assess potential load of suspended sediment-bound chemicals.

**Table 2 (continued from previous page). Summary of field collection tasks, parameters collected, collection methods, references, and laboratories completing each task. Task numbers correspond to the task numbers discussed in the text.**

Task No.	Task Description	Parameter Collected	Collection Method	Published Collection Methods	Laboratory	Notes
5	Suspended sediment chemistry	Dioxins/Furans, PCB Aroclors and 209 congeners, Semivolatile Compounds, PAHs, Pesticides, Butyltins, Trace Elements (metals) including mercury and hexavalent chromium, VOCs, total organic carbon. See Appendix A for complete list of analytes.	Concurrent with water chemistry sampling, 1000-2000 liters of sediment-laden river water will be pumped at 60% of depth at centroid of flow through a Teflon tube into Teflon-lined containers. Suspended sediment will be separated from water by continuous-flow centrifugation for chemical analysis.	Sample collection methods: see draft SOP in Appendix B. Sediment handling methods: Shelton and Capel, 1994.	Contract laboratory	An additional 5-10 liters of water will be pumped to compare SSC and PSD in the pumped sample to SSC and PSD in the depth- and width-integrated sample (Task 4). Also, the centrifuge effluent water will be analyzed for SSC and PSD to determine efficiency rates and the size distribution of un-captured sediment. Chemical analyses will be performed as the samples are collected, within the method holding time limits. In exception, all suspended sediment samples submitted within the first year for analysis of dioxins/furans, 209 PCB congeners, and PCB Aroclors will be appropriately stored at the contract laboratory, and analyzed as one batch with a Puget Sound Sediment Reference Material.

**Table 2 (continued from previous page). Summary of field collection tasks, parameters collected, collection methods, references, and laboratories completing each task. Task numbers correspond to the task numbers discussed in the text.**

Task No.	Task Description	Parameter Collected	Collection Method	Published Collection Methods	Laboratory	Notes
6	Bed sediment chemistry	Dioxins/Furans, PCB Aroclors and 209 congeners, Semivolatile Compounds, PAHs, Pesticides, Butyltins, Trace Elements (metals) including mercury and hexavalent chromium, VOCs, total organic carbon and grain size. See Appendix A for complete list of analytes.	The top 10 cm of sediment from approximately 10 depositional areas containing fine-grained particles located within one mile up- or down-stream of the upstream station will be collected and composited with Teflon and glass sampling equipment. Half of the sample will be sieved to <2 mm and the other half sieved to <63 µm resulting in 2 samples submitted per event. Trace element and mercury samples will be sieved with a nylon sieve. Organic samples will be sieved with a stainless steel sieve.	Radke and others, 2005; Shelton and Capel, 1994; Ecology, 2008.	Contract laboratory	The entire sieved sample (for each size fraction) will be collected and homogenized prior to jar filling. Analyses will be performed as the samples are collected, within the method holding time limits. In exception, all bed sediment samples submitted for analysis of dioxins/furans, 209 PCB congeners, and PCB Aroclors will be collected within the first year, appropriately stored at the contract laboratory, and analyzed as one batch (along with frozen suspended sediment samples) with a Puget Sound Sediment Reference Material.

**Task 4) Suspended sediment physical parameters.** After completing one cross-section of depth- and width-integrated sampling for water chemistry, a second cross-section of depth- and width-integrated sampling will be completed to characterize the abundance and size distribution of suspended sediment using standard USGS protocols (Edwards and Glysson 1999, Radke and others, 2005). Again, approved samplers, nozzles, bags, and bottles will be used. The volume of water collected will depend on current sediment conditions, and is expected to range between 5 and 50 L. The samples will be stored until transport to CVO for analysis of SSC and PSD using published USGS methods (Guy 1977). These samples will not receive any chemical analyses, but will be used to characterize the abundance and size distribution of suspended sediment at the time of concurrent suspended sediment chemistry sampling (see below). An accurate representation of the abundance and size distribution of suspended sediment will be combined with the suspended sediment chemistry sampling results (see Task 5) to estimate the potential load of suspended sediment-bound chemicals being transported downstream.



**Figure 4. Photo of example USGS sampling equipment, including a crane, reel, and sampler for representative collection of depth- and width-integrated samples.**



**Task 5) Suspended sediment chemistry.** Concurrent with tasks 3 and 4, a separate team will pump river water from a point source through Teflon tubing into Teflon-lined containers for suspended sediment chemistry analysis. An ISCO pump (Teledyne ISCO, Lincoln, Nebraska) or similar unscreened, high-flow pumping device will be used. The point-sampling location will be located at a depth approximately 0.6 times the main channel depth in a section favoring fine particulates as determined based on ADCP data during each sampling trip. The volume of water collected will depend on the current river turbidity and sediment conditions, and will likely be between 1000 and 2000 liters. Samples will be collected during high flow/high turbidity events when tidal backwater effects will be overcome by the high flows or at low tide during baseline events. Pumping for suspended sediment will continue until sufficient suspended sediment has been collected for chemistry analysis, until the flow returns to pre-storm (tidally-influenced) conditions, or until pumping is no longer feasible due to resource limitations or safety concerns. Suspended sediment from the collected water will be concentrated using a continuous-flow centrifuge (see Sample Processing) either on-site or at the WaWSC. Sediment collected from the centrifuge will be analyzed for those compounds listed in Appendix A. A sample of pumped water will also be collected into a large container for analysis of SSC and PSD at CVO to compare to the results from the representative samples collected in Task 4.

**Task 6) Bed sediment chemistry.** A bed sediment sample will be collected during five non-storm events during low-flow/low-tide conditions shortly succeeding the other sampling activities. Samples will be collected according to Ecology and USGS protocols (Ecology, 2008; Radke and others, 2005; Shelton and Capel, 1994) for the same suite of chemical parameters as the suspended sediment samples (Appendix A) and grain size analysis. Depending on the conditions, the samples will be collected from the bridge, bank, or boat. Samples (0-10 cm depth) from approximately 10 locations near the upstream station will be composited into a single sample. Locations will be selected to focus on areas with a high deposition of fine material. The composited sample immediately will be processed in an on-site mobile laboratory (see Sample Processing). Additional bed sediment samples may be collected in accordance with the site selection and sampling approaches and protocols outlined in Ecology's Sediment Sampling and Analysis Plan (Ecology 2008).

## Sample Processing

### **Dissolved Water Chemistry Sample Processing (see Task 3 above)**

In the mobile laboratory, the composited water sample will be churned in a closed chamber according to USGS protocols (U.S. Geological Survey, variously dated) to minimize contamination and ensure sample homogenization prior to bottle filling. A sub-sample of churned water will be filtered through a 0.45  $\mu\text{m}$  filter for analysis of dissolved trace elements. Pre-acidified bottles will be used for samples requiring preservation (See Table 3). Labels will be completed and samples will be stored on ice until transportation within 6 hours to the contract laboratory.

Table 3. Method, sample container, minimum sediment required, preservative, and holding time of each parameter group.

Analytical Parameter	EPA Method	Sample Container		Min. Sed. Required (dry weight)	Preservative	Holding Time	
		Water	Sediment			Water	Sediment
Dioxins/Furans, and 209 PCB congeners	1613B/1668C	2 x 500 mL AG	8 oz. WMG (amber)	10 g	Cool ≤ 6 °C	1 yr, chilled	1 yr, frozen
Semivolatile Compounds	8270D	2 x 500 mL AG	8 oz. WMG	15 g	Cool ≤ 6 °C	7 d	14 d
Low-Level Polycyclic Aromatic Hydrocarbons	8270D-SIM	2 x 500 mL AG	8 oz. WMG	15 g	Cool ≤ 6 °C	7 d	14 d
PCB Aroclors	8082A	2 x 500 mL AG	8 oz. WMG	15 g	Cool ≤ 6 °C	7 d	14 d
Pesticides	8081B	2 x 500 mL AG	8 oz. WMG	15 g	Cool ≤ 6 °C	7 d	14 d
Butyltins	8270D	2 x 500 mL AG	8 oz. WMG	5 g	Cool ≤ 6 °C	7 d	14 d
Trace Elements, Total and Dissolved <sup>1</sup>	200.8	500 mL HDPE	4 oz. WMG	2 g	2.5 mL 1:1 HNO <sub>3</sub> <sup>2</sup>	6 mo	6 mo
Low-Level Mercury	7470A, 7471B	500 mL HDPE	4 oz. WMG	2 g	5 mL 1:1 HNO <sub>3</sub> <sup>2</sup>	28 d	28 d
Hexavalent Chromium	7196A or Standard Methods 3500 CrD	500 mL HDPE	4 oz. WMG	5 g	Cool ≤ 6 °C	24 hr	28 d
Volatile Organic Compounds	8260C	3 x 40 mL vial, no headspace	2 oz. WMGS (no headspace)	5 g	Cool ≤ 6 °C	7 d	14 d
Total organic carbon	Standard Methods 5310B or PSEP 1986	250 mL AG	4 oz. WMG	1 g	Cool ≤ 6 °C + pH <2 w/ 2mL H <sub>2</sub> SO <sub>4</sub> <sup>2</sup>	28 d	14 d
Particle size distribution (bed sed.)	PSEP 1986	-	16 oz. WMP	50 g	Cool ≤ 6 °C	-	14 d
Particle size distribution (susp. sed.)	Guy 1977	3 L HDPE	-	-	None	None	None
Suspended sediment concentration	Guy 1977	3 L HDPE	-	-	None	None	None

<sup>1</sup> Antimony, Arsenic, Barium, Beryllium, Cadmium, Copper, Lead, Nickel, Selenium, Silver, Thallium, Vanadium, and Zinc

<sup>2</sup> Acid preservation for water samples only

AG = amber glass Boston round bottle

HDPE = high-density polypropylene

WMG = wide-mouth glass jar

WMGS = wide-mouth glass jar with septa

### **Suspended Sediment Chemistry Sample Processing (see Task 5 above)**

Water in the Teflon-lined containers will be pumped into a continuous-flow centrifuge (CFC Express, Scientific Methods, Inc., Granger, IN) to concentrate the suspended sediment (Figure 5). The centrifuge runs at a fixed speed of 10,000 revolutions per minute, and preliminary testing suggests that the inflow rate be less than 500 mL/min to ensure sediment capture efficiencies greater than 90 % (by weight). Water samples will be pumped from chilled containers using Teflon tubing and a peristaltic pump with C-FLEX tubing into the centrifuge. At a flow rate of 350 mL/min using a single centrifuge, approximately 50 to 100 hours of total centrifuge time will be required for each sampling event. Additional centrifuges may be used to reduce processing time. Pre-centrifuged water will be kept at 4 °C until it is pumped into the centrifuge. Every eight hours or less, concentrated sediment from the centrifuge bowl will be composited in a pre-tared glass jar and stored quiescently at 4 °C. The centrifugation will occur either in the field in an enclosed area on the river bank or at the WaWSC Field Services Unit located in Tacoma, WA. See Appendix B for a draft SOP of the sampling and processing procedure for suspended sediment.

Excess overlying water in the glass jar will be decanted by pipette and centrifuged on a traditional centrifuge. Any additional spun sediment will be added to the sample. The total wet weight of the sediment will be recorded. In addition, SSC of centrifuge influent and effluent will be compared to determine sediment capture efficiency. Finally, the PSD of un-captured sediment in the centrifuge effluent will be determined during each sampling event.



**Figure 5. Flow-through centrifuge set-up (a) and centrifuge bowl (b).**

### **Bed Sediment Chemistry Sample Processing (see Task 6 above)**

The bed sediment sample will be composited and homogenized in glass or Teflon containers using a Teflon spatula in the mobile laboratory immediately after sample collection. Approximately half of the sample will be wet sieved through a 2 mm diameter sieve and collected in a Teflon or glass container using USGS protocol (Shelton and Capel 1994). The sieved sample will then be homogenized using a Teflon spatula prior to jar filling. The other half

of the sample will be wet sieved through a 63  $\mu\text{m}$  diameter sieve and collected in a separate Teflon or glass container using USGS protocol (Shelton and Capel 1994). The sieved sample will then be homogenized using a Teflon spatula prior to jar filling. Samples for metals analysis will be processed through an acid-cleaned plastic sieve, and samples for all other analyses will be processed through a methanol-cleaned stainless steel sieve. The processing will result in two samples per event submitted for chemical analysis.

## Analytical Methods

Samples of water (Task 3), suspended sediment (Task 5), and bed sediment (Task 6) will be analyzed for chemical analytes using the methods presented in Table 3 by a Washington State-accredited laboratory. The individual analytes are listed in Appendix A. The full criteria to be met by the lab(s) are described in the Statement of Work for the analytical contract. Ecology's Manchester lab will manage the analytical contract, including the development of the Statement of Work, the posting, evaluation, and awarding of the contract, and payment. In addition, Ecology's Manchester lab will conduct data validation of a representative subset of samples comparable to an EPA Level 4 validation report. The analytical laboratory costs and Level 4 validation costs are not included in the USGS-Ecology budget agreement.

Found in Appendix A, for both water and sediment, are the analytes listed individually with the following information:

- Chemical Abstract Service Registry Number (CASRN),
- Expected Reporting Limit (RL) – The lowest concentration that can be reliably achieved within specific limits of precision and accuracy during routine operating conditions. This is often synonymous with a Quantitation Limit (QL). For high-resolution mass spectrometry (HRMS) compounds including dioxins/furans and 209 PCB congeners, this can be reported as the Lower Method Calibration Limit (LMCL), which is determined by prorating the concentration of the lowest calibration limit for sample size and extract volume. The following equation is used:  $((\text{lowest level calibration standard}) \times (\text{extract volume})) / \text{sample size}$ ,
- Expected Detection Limit (DL) – The lowest result that can be reliably distinguished from a blank with a false positive rate  $\leq 1\%$ . For HRMS compounds, this is often reported as a Typical Sample-specific Detection Limit (SDL), which is defined as the concentration equivalent to 3 times the estimated chromatographic noise height, determined individually for every sample analysis run.

The expected RLs and DLs listed in Appendix A are target levels identified by Ecology. The analytical laboratory(s) will be selected because of its ability to meet these low-level limits. Results will be reported down to the SDL for the HRMS compounds. For non-detect HRMS values, the DL will be reported with a "UJ" qualifier. For all other non-detected analytes, the RL will be reported with a "U" qualifier. The related qualifiers used are defined as:

- “J” – The analyte was positively identified. The associated numerical result is an estimate.
- “U” – The analyte was not detected at or above the reporting limit. (This qualifier likely will not be used for HRMS which are reported down to the SDL.)
- “UJ”- The analyte was not detected at or above the estimated reporting limit.

A minimum of 100 to 150 g of dry sediment is required to complete the chemical analyses. During low-turbidity sampling events, even with consecutive days of water collection, there may be insufficient sediment concentrated from the centrifuge to complete all 11 methods. In these cases, a priority list of analytical methods will be followed (with #1 being the top priority):

1. Percent solids (always completed; needed to report a dry weight concentration)
2. TOC (always completed; needed to report a TOC-normalized concentration)
3. Dioxins/Furans and PCB Congeners (a single co-extraction by a contract laboratory)
4. Metals (including mercury)
5. PAHs
6. PCB Aroclors
7. Semi-volatile compounds
8. Pesticides
9. Butyltins
10. Hexavalent Chromium
11. VOCs

The VOCs are the lowest priority because, based on their volatility and the turbulent sampling techniques (pumping and centrifuging), analyte losses during suspended sediment collection are likely. All efforts will be made to collect sufficient sediment to complete all 11 methods, and it is expected that there will be sufficient sediment to analyze the priority methods (#1-6) during all events.

## Quality Assurance and Control Procedures

USGS quality assurance and control procedures for surface-water measurements and water-quality sampling and analysis will be followed (Wagner and others, 2007; U.S. Geological Survey, variously dated). This includes the proper equipment selection, cleaning procedures, and sampling protocols for low level organic compounds, VOCs, and metals. Sampling equipment for chemical analyses will be Teflon and will be pre-cleaned with phosphate-free soap, rinsed three times with tap water, soaked in 5% hydrochloric acid, rinsed with deionized water, rinsed with high purity methanol, and air dried before being stored in clean bags for field transport. Field sampling techniques include various measures to avoid sample contamination including the “clean hands, dirty hands” technique and processing of water samples in a clean mobile laboratory. Hydrologists and hydrological technicians on this project have been trained at the USGS National Training Center in the collection of water quality samples, including samples for trace organic and low level mercury analyses.

The field folder will include copies of the QAPP and the protocols referenced within. Deviations from the QAPP will be noted on the field sheet. Results from field assurance samples (trip blanks and equipment blanks) will be reviewed by the project investigators. Field protocols will be modified to correct any identified contamination issues. Laboratory quality assurance samples (a blank, replicate, and matrix spike per batch of 20 samples) will be reviewed by laboratory personnel. If values exceed the control limits (see Analytical Methods) then laboratory personnel will take appropriate corrective actions such as re-runs and re-extractions and/or discuss modifications to the protocol with the principal investigator.

While the selected lab(s) will be State-accredited, they will not be associated with the USGS's National Water Quality Laboratory and may not perform the same quality assurance and control procedures necessary to permit immediate inclusion in the USGS's national and publically accessible database. Therefore, a Laboratory Evaluation Program (LEP) will be conducted by USGS project personnel according to the guidance provided by the USGS Branch of Quality Systems (<http://devbqs.cr.usgs.gov/LEP/index.php>) and in accordance with USGS Office of Water Quality Technical Memorandum 2007.01 to allow the USGS to include the results in its database.

## **Data Management, Verification, and Validation**

A field form, modified from the standard USGS Surface Water Quality Notes, will be completed during each sampling event (Appendix C). Field parameters recorded will include date, time, sampling team, field conditions, sampler types, sampling methods, meter and probe serial numbers and calibration information, number and type of quality assurance samples collected, and any deviations from the sampling protocol.

General water quality field parameters, including water temperature, specific conductance, dissolved oxygen, pH, and turbidity will be compiled on the field form and reviewed by one of the USGS principal investigators prior to entry into the USGS National Water Information System (NWIS). The instantaneous discharge record during each sampling event will be reviewed and approved according to standard USGS protocols (Mueller and Wagner, 2009). The continuous records will be reviewed and approved according to standard USGS protocols for the ADVDM (Levesque and Oberg 2012) and turbidity sensor (Wagner and others 2006), which includes verification and validation by secondary and tertiary reviewers prior to entry into NWIS. Quality assurance procedures used by the WaWSC for activities related to the collection, processing, storage, analysis, and publication of surface-water data are described in detail by Kresch and Tomlinson (2004).

Quality assurance procedures utilized by USGS sediment laboratories for analysis of suspended-sediment concentration are provided by Knott and others (1992; 1993) and Matthes and others (1992). Prior to sending samples to the laboratory, analytical services requests for determination of suspended-sediment concentration and particle-size analysis and sample site and other information are entered into the Sediment Laboratory Environmental Data System (SLEDS). The laboratory results are also entered into the system. Documentation of SLEDS is available online at <http://eris.wr.usgs.gov/SedLab/framework.html>.

All analytical results from the contract lab(s) will be compiled and transmitted electronically as Level 4 data packages to the USGS Washington Water Science Center and Ecology's Manchester Environmental Laboratory. The Level 4 deliverable includes a written narrative, including any deviations from the methods, and all raw data needed to perform an independent review of the results (i.e. calibration reports, chromatograms and spectra for all calibration standards and samples, and bench sheets). In addition, the data will also be delivered electronically in a format that is compatible for entry into Ecology's EIM database

All data, including the field parameters, physical sediment results, and analytical chemistry results, will be reviewed and verified by WaWSC project personnel, equivalent to an USEPA Level 2 review. Subsequently, the Quality Assurance Coordinator at Ecology's Manchester lab will validate a representative subset of the data as a 3<sup>rd</sup>-party independent reviewer, comparable to an USEPA Level 4 validation. Data qualifiers or flags may be applied to data by either laboratory or project personnel pending review of quality assurance data and the Level 4 validator. Potential data qualifiers provided by commercial labs include, but are not limited to:

- B Analyte detected in the sample and the associated method blank,
- C Congener co-elution,
- D Dilution data,
- J Indicates an estimated value where the concentration of the analyte is less than the RL but greater than the DL,
- K A peak was detected that did not meet all the criteria for identification as the target analyte; the reported value is the estimated maximum possible concentration. This is equivalent to the "N" qualifier used in Ecology's Environmental Information Management system.
- U Not detected.

When applicable, data will be amended by the Level 2 reviewer and/or Level 4 validator using a simplified qualifier approach consistent with Ecology's Toxics Cleanup Program data reporting protocols (Ecology 2008) as outlined in the EPA Functional Guidelines (EPA 2008, 2009, 2010, 2011). Briefly, data that has been flagged or qualified by the laboratory or during the Level 2 or Level 4 review process with qualifiers other than "U"- and "J"-containing qualifiers will be censored and the qualifier removed. For example, environmental samples with a "B" qualifier which have a concentration greater than 5 times the concentration in the associated method blank (or 10 times greater for common laboratory contaminants such as acetone, 2-butanone, methylene chloride, toluene, and phthalate esters) will be reported unqualified. Environmental samples with a "B" qualifier which have a concentration less than 5 times the concentration in the associated method blank (10 times for common lab contaminants) will be reported at the DL or RL as appropriate with the "U" or "UJ" qualifier. In addition, an "R" or "REJ" qualifier will be allowed indicating that "the sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control objectives. The presence or absence of the analyte cannot be verified" (EPA 2008, 2009, 2010, 2011). The USGS review process follows the USGS' Fundamental Science Practices (<http://www.usgs.gov/fsp/default.asp>) to provide

unbiased, objective, and impartial scientific information. Reviewed, validated, and approved data will be entered into the Ecology database systems for long-term storage and access.

## Reporting

Regression relations will be developed between continuous data (ADVM velocity, stage, and turbidity) and discrete data (instantaneous discharge, SSC, and chemical concentrations in water and sediment) to provide estimates of loading of water, sediment, and sediment-bound contaminants from the Green River to the LDW over the project duration. A draft of the findings, in the form of a USGS Scientific Investigations Report, will be prepared with the available data in early summer 2015 and submitted to Ecology by the end of the project. The draft will contain loading calculations based on discharge and water chemistry concentrations (for whole-water loading) and discharge, SSC, and particulate-bound contaminants (for particulate-bound loading). For analytes that are not detected during the study, a loading calculation will be calculated based on the reporting limit and reported as “less than” the calculated value. For analytes that are detected during some, but not all, sampling events, a value of zero will be used for the non-detects to calculate the loading, and the data will be qualified. Loading estimates will be calculated using software such as LOADEST (<http://water.usgs.gov/software/loadest/>). The results from this 2-year study will provide current estimates of sediment loading and chemical loading from the Green River to the LDW, and will inform future investigations for improving these loading estimates.

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**Appendix A. List of analytes, Chemical Abstract Service Registry Numbers (CASRN) and expected reporting limits (RL) and detection limits (DL) in water, suspended sediment, and bed sediment samples from the Duwamish River, WA.**

Parameter Name	CASRN	Water			Sediment		
		Unit	RL	DL	Unit	RL	DL
Total Organic Carbon		mg/L	1.5	0.093	%	0.02	0.003
Chromium, Hexavalent	18540-29-9	mg/L	0.01	0.003	mg/kg	1	0.03
<i>Metals</i>							
Antimony	7440-36-0	ug/l	0.2	0.01	mg/kg	0.5	0.04
Arsenic	7440-38-2	ug/l	0.2	0.048	mg/kg	0.5	0.3
Barium	7440-39-3	ug/l	0.5	0.02	mg/kg	1	0.2
Beryllium	7440-41-7	ug/l	0.2	0.021	mg/kg	0.5	0.06
Cadmium	7440-43-9	ug/l	0.1	0.01	mg/kg	0.3	0.04
Chromium	7440-47-3	ug/l	0.5	0.045	mg/kg	1	0.4
Copper	7440-50-8	ug/l	0.5	0.158	mg/kg	1	0.1
Lead	7439-92-1	ug/l	0.1	0.046	mg/kg	0.3	0.15
Mercury	7439-97-6	ng/l	20	2.6	mg/kg	0.05	0.004
Nickel	7440-02-0	ug/l	0.5	0.079	mg/kg	1	0.15
Selenium	7782-49-2	ug/l	0.5	0.127	mg/kg	1	0.4
Silver	7440-22-4	ug/l	0.2	0.008	mg/kg	0.5	0.025
Thallium	7440-28-0	ug/l	0.2	0.004	mg/kg	0.5	0.01
Vanadium	7440-62-2	ug/l	0.2	0.043	mg/kg	0.5	0.15
Zinc	7440-66-6	ug/l	4	0.5	mg/kg	10	1.1
<i>Semivolatiles</i>							
Phenol	108-95-2	ug/l	1	0.52	ug/kg	20	10
Bis-(2-Chloroethyl) Ether	111-44-4	ug/l	1	0.58	ug/kg	20	5
2-Chlorophenol	95-57-8	ug/l	1	0.53	ug/kg	20	3
1,3-Dichlorobenzene	541-73-1	ug/l	1	0.36	ug/kg	20	3
1,4-Dichlorobenzene	106-46-7	ug/l	1	0.4	ug/kg	20	3
Benzyl Alcohol	100-51-6	ug/l	2	2	ug/kg	20	8
1,2-Dichlorobenzene	95-50-1	ug/l	1	0.36	ug/kg	20	3
2-Methylphenol	95-48-7	ug/l	1	0.53	ug/kg	20	6
2,2'-Oxybis(1-Chloropropane)	108-60-1	ug/l	1	0.62	ug/kg	20	4
4-Methylphenol	106-44-5	ug/l	2	0.52	ug/kg	20	7
N-Nitroso-Di-N-Propylamine	621-64-7	ug/l	1	0.56	ug/kg	20	4
Hexachloroethane	67-72-1	ug/l	2	0.35	ug/kg	20	3
Nitrobenzene	98-95-3	ug/l	1	0.58	ug/kg	20	4

Isophorone	78-59-1	ug/l	1	0.48	ug/kg	20	3
2-Nitrophenol	88-75-5	ug/l	3	2	ug/kg	100	40
2,4-Dimethylphenol	105-67-9	ug/l	3	0.36	ug/kg	40	4
Benzoic Acid	65-85-0	ug/l	20	5.1	ug/kg	400	100
bis(2-Chloroethoxy) Methane	111-91-1	ug/l	1	0.56	ug/kg	20	2
2,4-Dichlorophenol	120-83-2	ug/l	3	2.6	ug/kg	200	25
1,2,4-Trichlorobenzene	120-82-1	ug/l	1	0.38	ug/kg	20	4
4-Chloroaniline	106-47-8	ug/l	5	2.6	ug/kg	270	25
Hexachlorobutadiene	87-68-3	ug/l	3	0.31	ug/kg	20	5
4-Chloro-3-methylphenol	59-50-7	ug/l	3	2.4	ug/kg	99	15
Hexachlorocyclopentadiene	77-47-4	ug/l	5	1.2	ug/kg	400	70
2,4,6-Trichlorophenol	88-06-2	ug/l	3	2.4	ug/kg	99	25
2,4,5-Trichlorophenol	95-95-4	ug/l	5	2.2	ug/kg	99	25
2-Chloronaphthalene	91-58-7	ug/l	1	0.48	ug/kg	20	3
2-Nitroaniline	88-74-4	ug/l	3	2.6	ug/kg	99	20
Dimethylphthalate	131-11-3	ug/l	1	0.53	ug/kg	20	3
3-Nitroaniline	99-09-2	ug/l	3	2.3	ug/kg	99	25
2,4-Dinitrophenol	51-28-5	ug/l	20	3.5	ug/kg	840	120
4-Nitrophenol	100-02-7	ug/l	10	2.6	ug/kg	99	35
2,6-Dinitrotoluene	606-20-2	ug/l	3	2.4	ug/kg	99	30
2,4-Dinitrotoluene	121-14-2	ug/l	3	2.5	ug/kg	99	20
Diethylphthalate	84-66-2	ug/l	1	0.58	ug/kg	50	40
4-Chlorophenyl-phenylether	7005-72-3	ug/l	1	0.45	ug/kg	20	6
4-Nitroaniline	100-01-6	ug/l	3	2.2	ug/kg	99	40
4,6-Dinitro-2-Methylphenol	534-52-1	ug/l	10	3.1	ug/kg	200	25
N-Nitrosodiphenylamine	86-30-6	ug/l	1	0.46	ug/kg	20	6
4-Bromophenyl-phenylether	101-55-3	ug/l	1	0.42	ug/kg	20	5
Hexachlorobenzene	118-74-1	ug/l	1	0.47	ug/kg	20	5
Pentachlorophenol	87-86-5	ug/l	10	2.4	ug/kg	200	50
Carbazole	86-74-8	ug/l	1	0.31	ug/kg	20	3
Di-n-Butylphthalate	84-74-2	ug/l	1	0.54	ug/kg	20	10
Butylbenzylphthalate	85-68-7	ug/l	1	0.56	ug/kg	20	7
3,3'-Dichlorobenzidine	91-94-1	ug/l	5	1.5	ug/kg	150	20
bis(2-Ethylhexyl)phthalate	117-81-7	ug/l	1	1.9	ug/kg	25	15
Di-n-Octyl phthalate	117-84-0	ug/l	1	0.51	ug/kg	20	6
<b>PAHs (Low Level)</b>							
Naphthalene	91-20-3	ug/l	0.01	0.00085	ug/kg	0.5	0.3
2-Methylnaphthalene	91-57-6	ug/l	0.01	0.00072	ug/kg	0.5	0.3
1-Methylnaphthalene	90-12-0	ug/l	0.01	0.00088	ug/kg	0.5	0.3
Acenaphthylene	208-96-8	ug/l	0.01	0.00081	ug/kg	0.5	0.3
Acenaphthene	83-32-9	ug/l	0.01	0.00083	ug/kg	0.5	0.3

Fluorene	86-73-7	ug/l	0.01	0.0014	ug/kg	0.5	0.3
Phenanthrene	85-01-8	ug/l	0.01	0.001	ug/kg	0.5	0.3
Anthracene	120-12-7	ug/l	0.01	0.00058	ug/kg	0.5	0.3
Fluoranthene	206-44-0	ug/l	0.01	0.00092	ug/kg	0.5	0.3
Pyrene	129-00-0	ug/l	0.01	0.0007	ug/kg	0.5	0.3
Benzo(a)anthracene	56-55-3	ug/l	0.01	0.0013	ug/kg	0.5	0.3
Chrysene	218-01-9	ug/l	0.01	0.0016	ug/kg	0.5	0.3
Benzo(a)pyrene	50-32-8	ug/l	0.01	0.0011	ug/kg	0.5	0.3
Indeno(1,2,3-cd)pyrene	193-39-5	ug/l	0.01	0.0018	ug/kg	0.5	0.3
Dibenz(a,h)anthracene	53-70-3	ug/l	0.01	0.00097	ug/kg	0.5	0.3
Benzo(g,h,i)perylene	191-24-2	ug/l	0.01	0.0019	ug/kg	0.5	0.3
Dibenzofuran	132-64-9	ug/l	0.01	0.00094	ug/kg	0.5	0.3
Total Benzofluoranthenes	TOTBFA	ug/l	0.02	0.0025	ug/kg	0.5	0.3
<b><i>Tin Species</i></b>							
Tributyltin Ion	36643-28-4	ug/L	0.19	0.043	ug/kg	3.7	1
Dibutyltin Ion	14488-53-0	ug/L	0.29	0.096	ug/kg	5.6	3.5
Butyltin	78763-54-9	ug/L	0.2	0.11	ug/kg	3.9	2
<b><i>PCB Aroclors</i></b>							
Aroclor 1016	12674-11-2	ug/l	0.01	0.0025	ug/kg	3.9	1
Aroclor 1221	11104-28-2	ug/l	0.01	0.0028	ug/kg	3.9	1.5
Aroclor 1232	11141-16-5	ug/l	0.01	0.0028	ug/kg	3.9	1.5
Aroclor 1242	53469-21-9	ug/l	0.01	0.0028	ug/kg	3.9	1.5
Aroclor 1248	12672-29-6	ug/l	0.01	0.0028	ug/kg	3.9	1.5
Aroclor 1254	11097-69-1	ug/l	0.01	0.0028	ug/kg	3.9	1.5
Aroclor 1260	11096-82-5	ug/l	0.01	0.0028	ug/kg	3.9	1.5
Aroclor 1262	37324-23-5	ug/l	0.01	0.0028	ug/kg	3.9	1.5
Aroclor 1268	11100-14-4	ug/l	0.01	0.0028	ug/kg	3.9	1.5
<b><i>Pesticides</i></b>							
alpha-BHC	319-84-6	ug/l	0.05	0.0085	ug/kg	1.6	0.2
beta-BHC	319-85-7	ug/l	0.05	0.0098	ug/kg	1.6	0.4
delta-BHC	319-86-8	ug/l	0.05	0.0087	ug/kg	1.6	0.3
gamma-BHC (Lindane)	58-89-9	ug/l	0.05	0.016	ug/kg	1.6	0.2
Heptachlor	76-44-8	ug/l	0.05	0.011	ug/kg	1.6	0.3
Aldrin	309-00-2	ug/l	0.05	0.01	ug/kg	1.6	0.3
Heptachlor Epoxide	1024-57-3	ug/l	0.05	0.0079	ug/kg	4	0.3
Endosulfan I	959-98-8	ug/l	0.05	0.0089	ug/kg	1.6	0.3
Dieldrin	60-57-1	ug/l	0.1	0.017	ug/kg	3.2	0.3
4,4'-DDE	72-55-9	ug/l	0.1	0.018	ug/kg	3.2	0.3
Endrin	72-20-8	ug/l	0.1	0.017	ug/kg	3.2	0.3
Endosulfan II	33213-65-9	ug/l	0.1	0.014	ug/kg	3.2	0.3
4,4'-DDD	72-54-8	ug/l	0.1	0.019	ug/kg	3.2	0.3

Endosulfan Sulfate	1031-07-8	ug/l	0.1	0.024	ug/kg	3.2	0.3
4,4'-DDT	50-29-3	ug/l	0.1	0.017	ug/kg	3.2	0.3
Methoxychlor	72-43-5	ug/l	0.5	0.074	ug/kg	16	5
Endrin Ketone	53494-70-5	ug/l	0.1	0.015	ug/kg	3.2	0.3
Endrin Aldehyde	7421-93-4	ug/l	0.1	0.016	ug/kg	3.2	0.3
trans-Chlordane	5103-74-2	ug/l	0.05	0.0082	ug/kg	1.6	0.3
cis-Chlordane	5103-71-9	ug/l	0.05	0.0082	ug/kg	1.6	0.3
Toxaphene	8001-35-2	ug/l	5	0.22	ug/kg	200	100
<i>Volatile Organic Compounds</i>							
Chloromethane	74-87-3	ug/l	0.5	0.1	ug/kg	1.7	0.5
Bromomethane	74-83-9	ug/l	1	0.25	ug/kg	1.7	0.5
Vinyl Chloride	75-01-4	ug/l	0.2	0.06	ug/kg	1.7	0.5
Chloroethane	75-00-3	ug/l	0.2	0.09	ug/kg	1.7	0.5
Methylene Chloride	75-09-2	ug/l	1	0.48	ug/kg	3.3	0.5
Acetone	67-64-1	ug/l	5	2.1	ug/kg	8.4	0.5
Carbon Disulfide	75-15-0	ug/l	0.2	0.04	ug/kg	1.7	0.5
1,1-Dichloroethene	75-35-4	ug/l	0.2	0.05	ug/kg	1.7	0.5
1,1-Dichloroethane	75-34-3	ug/l	0.2	0.05	ug/kg	1.7	0.5
trans-1,2-Dichloroethene	156-60-5	ug/l	0.2	0.05	ug/kg	1.7	0.5
cis-1,2-Dichloroethene	156-59-2	ug/l	0.2	0.04	ug/kg	1.7	0.5
Chloroform	67-66-3	ug/l	0.2	0.03	ug/kg	1.7	0.5
1,2-Dichloroethane	107-06-2	ug/l	0.2	0.07	ug/kg	1.7	0.5
2-Butanone	78-93-3	ug/l	5	0.81	ug/kg	8.4	0.5
1,1,1-Trichloroethane	71-55-6	ug/l	0.2	0.04	ug/kg	1.7	0.5
Carbon Tetrachloride	56-23-5	ug/l	0.2	0.04	ug/kg	1.7	0.5
Vinyl Acetate	108-05-4	ug/l	0.2	0.07	ug/kg	8.4	0.5
Bromodichloromethane	75-27-4	ug/l	0.2	0.05	ug/kg	1.7	0.5
1,2-Dichloropropane	78-87-5	ug/l	0.2	0.04	ug/kg	1.7	0.5
cis-1,3-Dichloropropene	10061-01-5	ug/l	0.2	0.06	ug/kg	1.7	0.5
Trichloroethene	79-01-6	ug/l	0.2	0.05	ug/kg	1.7	0.5
Dibromochloromethane	124-48-1	ug/l	0.2	0.05	ug/kg	1.7	0.5
1,1,2-Trichloroethane	79-00-5	ug/l	0.2	0.13	ug/kg	1.7	0.5
Benzene	71-43-2	ug/l	0.2	0.03	ug/kg	1.7	0.5
trans-1,3-Dichloropropene	10061-02-6	ug/l	0.2	0.08	ug/kg	1.7	0.5
2-Chloroethylvinylether	110-75-8	ug/l	1	0.25	ug/kg	8.4	0.5
Bromoform	75-25-2	ug/l	0.2	0.06	ug/kg	1.7	0.5
4-Methyl-2-Pentanone (MIBK)	108-10-1	ug/l	5	0.97	ug/kg	8.4	0.5
2-Hexanone	591-78-6	ug/l	5	0.9	ug/kg	8.4	0.5
Tetrachloroethene	127-18-4	ug/l	0.2	0.05	ug/kg	1.7	0.5
1,1,2,2-Tetrachloroethane	79-34-5	ug/l	0.2	0.06	ug/kg	1.7	0.5
Toluene	108-88-3	ug/l	0.2	0.04	ug/kg	1.7	0.5

Chlorobenzene	108-90-7	ug/l	0.2	0.02	ug/kg	1.7	0.5
Ethylbenzene	100-41-4	ug/l	0.2	0.04	ug/kg	1.7	0.5
Styrene	100-42-5	ug/l	0.2	0.04	ug/kg	1.7	0.5
Trichlorofluoromethane	75-69-4	ug/l	0.2	0.04	ug/kg	1.7	0.5
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	ug/l	0.2	0.04	ug/kg	3.3	0.5
m, p-Xylene	179601-23-1	ug/l	0.4	0.05	ug/kg	1.7	0.5
o-Xylene	95-47-6	ug/l	0.2	0.04	ug/kg	1.7	0.5
1,2-Dichlorobenzene	95-50-1	ug/l	0.2	0.04	ug/kg	1.7	0.5
1,3-Dichlorobenzene	541-73-1	ug/l	0.2	0.04	ug/kg	1.7	0.5
1,4-Dichlorobenzene	106-46-7	ug/l	0.2	0.04	ug/kg	1.7	0.5
Acrolein	107-02-8	ug/l	5	2.5	ug/kg	84	20
Iodomethane	74-88-4	ug/l	1	0.23	ug/kg	1.7	
Bromoethane	74-96-4	ug/l	0.2	0.04	ug/kg	3.3	1
Acrylonitrile	107-13-1	ug/l	1	0.6	ug/kg	8.4	2
1,1-Dichloropropene	563-58-6	ug/l	0.2	0.03	ug/kg	1.7	0.5
Dibromomethane	74-95-3	ug/l	0.2	0.14	ug/kg	1.7	0.3
1,1,1,2-Tetrachloroethane	630-20-6	ug/l	0.2	0.04	ug/kg	1.7	0.5
1,2-Dibromo-3-chloropropane	96-12-8	ug/l	0.5	0.04	ug/kg	8.4	1
1,2,3-Trichloropropane	96-18-4	ug/l	0.5	0.13	ug/kg	3.3	1
trans-1,4-Dichloro-2-butene	110-57-6	ug/l	1	0.32	ug/kg	8.4	1
1,3,5-Trimethylbenzene	108-67-8	ug/l	0.2	0.02	ug/kg	1.7	0.5
1,2,4-Trimethylbenzene	95-63-6	ug/l	0.2	0.02	ug/kg	1.7	0.5
Hexachlorobutadiene	87-68-3	ug/l	0.5	0.07	ug/kg	8.4	0.7
1,2-Dibromoethane	106-93-4	ug/l	0.2	0.08	ug/kg	1.7	0.3
Bromochloromethane	74-97-5	ug/l	0.2	0.06	ug/kg	1.7	0.5
2,2-Dichloropropane	594-20-7	ug/l	0.2	0.05	ug/kg	1.7	0.5
1,3-Dichloropropane	142-28-9	ug/l	0.2	0.06	ug/kg	1.7	0.5
Isopropylbenzene	98-82-8	ug/l	0.2	0.02	ug/kg	1.7	0.5
n-Propylbenzene	103-65-1	ug/l	0.2	0.02	ug/kg	1.7	0.5
Bromobenzene	108-86-1	ug/l	0.2	0.06	ug/kg	1.7	0.5
2-Chlorotoluene	95-49-8	ug/l	0.2	0.02	ug/kg	1.7	0.5
4-Chlorotoluene	106-43-4	ug/l	0.2	0.02	ug/kg	1.7	0.5
tert-Butylbenzene	98-06-6	ug/l	0.2	0.03	ug/kg	1.7	0.5
sec-Butylbenzene	135-98-8	ug/l	0.2	0.02	ug/kg	1.7	0.5
4-Isopropyltoluene	99-87-6	ug/l	0.2	0.03	ug/kg	1.7	0.5
n-Butylbenzene	104-51-8	ug/l	0.2	0.02	ug/kg	1.7	0.5
1,2,4-Trichlorobenzene	120-82-1	ug/l	0.5	0.11	ug/kg	8.4	0.5
Naphthalene	91-20-3	ug/l	0.5	0.12	ug/kg	8.4	0.5
1,2,3-Trichlorobenzene	87-61-6	ug/l	0.5	0.11	ug/kg	8.4	0.5
<b>Dioxins/Furans</b>							
2,3,7,8-TCDD	1746-01-6	pg/L	2	0.5	pg/g	0.2	0.05



1,2,3,7,8-PECDD	40321-76-4	pg/L	10	0.5	pg/g	1	0.05
1,2,3,4,7,8-HXCDD	39227-28-6	pg/L	10	0.5	pg/g	1	0.05
1,2,3,6,7,8-HXCDD	57653-85-7	pg/L	10	0.5	pg/g	1	0.05
1,2,3,7,8,9-HXCDD	19408-74-3	pg/L	10	0.5	pg/g	1	0.05
1,2,3,4,6,7,8-HPCDD	35822-46-9	pg/L	10	0.5	pg/g	1	0.05
OCDD	3268-87-9	pg/L	20	0.5	pg/g	2	0.05
2,3,7,8-TCDF	51207-31-9	pg/L	2	0.5	pg/g	0.2	0.05
1,2,3,7,8-PECDF	57117-41-6	pg/L	10	0.5	pg/g	1	0.05
2,3,4,7,8-PECDF	57117-31-4	pg/L	10	0.5	pg/g	1	0.05
1,2,3,4,7,8-HXCDF	70648-26-9	pg/L	10	0.5	pg/g	1	0.05
1,2,3,6,7,8-HXCDF	57117-44-9	pg/L	10	0.5	pg/g	1	0.05
1,2,3,7,8,9-HXCDF	72918-21-9	pg/L	10	0.5	pg/g	1	0.05
2,3,4,6,7,8-HXCDF	60851-34-5	pg/L	10	0.5	pg/g	1	0.05
1,2,3,4,6,7,8-HPCDF	67562-39-4	pg/L	10	0.5	pg/g	1	0.05
1,2,3,4,7,8,9-HPCDF	55673-89-7	pg/L	10	0.5	pg/g	1	0.05
OCDF	39001-02-0	pg/L	20	0.5	pg/g	2	0.05

**PCB Congeners**

PCB-001	2051-60-7	pg/L	20	2	pg/g	4	2
PCB-002	2051-61-8	pg/L	20	2	pg/g	4	2
PCB-003	2051-62-9	pg/L	20	2	pg/g	4	2
PCB-004	13029-08-8	pg/L	4	2	pg/g	0.4	0.2
PCB-005	16605-91-7	pg/L	4	2	pg/g	0.4	0.2
PCB-006	25569-80-6	pg/L	4	2	pg/g	0.4	0.2
PCB-007	33284-50-3	pg/L	4	2	pg/g	0.4	0.2
PCB-008	34883-43-7	pg/L	4	2	pg/g	0.4	0.2
PCB-009	34883-39-1	pg/L	4	2	pg/g	0.4	0.2
PCB-010	33146-45-1	pg/L	4	2	pg/g	0.4	0.2
PCB-011	2050-67-1	pg/L	4	2	pg/g	0.4	0.2
PCB-012/013		pg/L	4	2	pg/g	0.4	0.2
PCB-014	34883-41-5	pg/L	4	2	pg/g	0.4	0.2
PCB-015	2050-68-2	pg/L	4	2	pg/g	0.4	0.2
PCB-016	38444-78-9	pg/L	4	2	pg/g	0.4	0.2
PCB-017	37680-66-3	pg/L	4	2	pg/g	0.4	0.2
PCB-018/030		pg/L	4	2	pg/g	0.4	0.2
PCB-019	38444-73-4	pg/L	4	2	pg/g	0.4	0.2
PCB-020/028		pg/L	4	2	pg/g	0.4	0.2
PCB-021/033		pg/L	4	2	pg/g	0.4	0.2
PCB-022	38444-85-8	pg/L	4	2	pg/g	0.4	0.2
PCB-023	55720-44-0	pg/L	4	2	pg/g	0.4	0.2
PCB-024	55702-45-9	pg/L	4	2	pg/g	0.4	0.2
PCB-025	55712-37-3	pg/L	4	2	pg/g	0.4	0.2

PCB-026/029		pg/L	4	2	pg/g	0.4	0.2
PCB-027	38444-76-7	pg/L	4	2	pg/g	0.4	0.2
PCB-031	16606-02-3	pg/L	4	2	pg/g	0.4	0.2
PCB-032	38444-77-8	pg/L	4	2	pg/g	0.4	0.2
PCB-034	37680-68-5	pg/L	4	2	pg/g	0.4	0.2
PCB-035	37680-69-6	pg/L	4	2	pg/g	0.4	0.2
PCB-036	38444-87-0	pg/L	4	2	pg/g	0.4	0.2
PCB-037	38444-90-5	pg/L	4	2	pg/g	0.4	0.2
PCB-038	53555-66-1	pg/L	4	2	pg/g	0.4	0.2
PCB-039	38444-88-1	pg/L	4	2	pg/g	0.4	0.2
PCB-040/041/071		pg/L	4	2	pg/g	0.4	0.2
PCB-042	36559-22-5	pg/L	4	2	pg/g	0.4	0.2
PCB-043	70362-46-8	pg/L	4	2	pg/g	0.4	0.2
PCB-044/047/065		pg/L	4	2	pg/g	0.4	0.2
PCB-045/051		pg/L	4	2	pg/g	0.4	0.2
PCB-046	41464-47-5	pg/L	4	2	pg/g	0.4	0.2
PCB-048	70362-47-9	pg/L	4	2	pg/g	0.4	0.2
PCB-049/069		pg/L	4	2	pg/g	0.4	0.2
PCB-050/053		pg/L	4	2	pg/g	0.4	0.2
PCB-052	35693-99-3	pg/L	4	2	pg/g	0.4	0.2
PCB-054	15968-05-5	pg/L	4	2	pg/g	0.4	0.2
PCB-055	74338-24-2	pg/L	4	2	pg/g	0.4	0.2
PCB-056	41464-43-1	pg/L	4	2	pg/g	0.4	0.2
PCB-057	70424-67-8	pg/L	4	2	pg/g	0.4	0.2
PCB-058	41464-49-7	pg/L	4	2	pg/g	0.4	0.2
PCB-059/062/075		pg/L	4	2	pg/g	0.4	0.2
PCB-060	33025-41-1	pg/L	4	2	pg/g	0.4	0.2
PCB-061/070/074/076		pg/L	4	2	pg/g	0.4	0.2
PCB-063	74472-34-7	pg/L	4	2	pg/g	0.4	0.2
PCB-064	52663-58-8	pg/L	4	2	pg/g	0.4	0.2
PCB-066	32598-10-0	pg/L	4	2	pg/g	0.4	0.2
PCB-067	73575-53-8	pg/L	4	2	pg/g	0.4	0.2
PCB-068	73575-52-7	pg/L	4	2	pg/g	0.4	0.2
PCB-072	41464-42-0	pg/L	4	2	pg/g	0.4	0.2
PCB-073	74338-23-1	pg/L	4	2	pg/g	0.4	0.2
PCB-077	32598-13-3	pg/L	4	2	pg/g	0.4	0.2
PCB-078	70362-49-1	pg/L	4	2	pg/g	0.4	0.2
PCB-079	41464-48-6	pg/L	4	2	pg/g	0.4	0.2
PCB-080	33284-52-5	pg/L	4	2	pg/g	0.4	0.2
PCB-081	70362-50-4	pg/L	4	2	pg/g	0.4	0.2
PCB-082	52663-62-4	pg/L	4	2	pg/g	0.4	0.2

PCB-083/099		pg/L	4	2	pg/g	0.4	0.2
PCB-084	52663-60-2	pg/L	4	2	pg/g	0.4	0.2
PCB-085/116/117		pg/L	4	2	pg/g	0.4	0.2
PCB-086/087/097/108/119/125		pg/L	4	2	pg/g	0.4	0.2
PCB-088/091		pg/L	4	2	pg/g	0.4	0.2
PCB-089	73575-57-2	pg/L	4	2	pg/g	0.4	0.2
PCB-090/101/113		pg/L	4	2	pg/g	0.4	0.2
PCB-092	52663-61-3	pg/L	4	2	pg/g	0.4	0.2
PCB-093/095/098/100/102		pg/L	4	2	pg/g	0.4	0.2
PCB-094	73575-55-0	pg/L	4	2	pg/g	0.4	0.2
PCB-096	73575-54-9	pg/L	4	2	pg/g	0.4	0.2
PCB-103	60145-21-3	pg/L	4	2	pg/g	0.4	0.2
PCB-104	56558-16-8	pg/L	4	2	pg/g	0.4	0.2
PCB-105	32598-14-4	pg/L	4	2	pg/g	0.4	0.2
PCB-106	70424-69-0	pg/L	4	2	pg/g	0.4	0.2
PCB-107/124		pg/L	4	2	pg/g	0.4	0.2
PCB-109	74472-35-8	pg/L	4	2	pg/g	0.4	0.2
PCB-110/115		pg/L	4	2	pg/g	0.4	0.2
PCB-111	39635-32-0	pg/L	4	2	pg/g	0.4	0.2
PCB-112	74472-36-9	pg/L	4	2	pg/g	0.4	0.2
PCB-114	74472-37-0	pg/L	4	2	pg/g	0.4	0.2
PCB-118	31508-00-6	pg/L	4	2	pg/g	0.4	0.2
PCB-120	68194-12-7	pg/L	4	2	pg/g	0.4	0.2
PCB-121	56558-18-0	pg/L	4	2	pg/g	0.4	0.2
PCB-122	76842-07-4	pg/L	4	2	pg/g	0.4	0.2
PCB-123	65510-44-3	pg/L	4	2	pg/g	0.4	0.2
PCB-126	57465-28-8	pg/L	4	2	pg/g	0.4	0.2
PCB-127	39635-33-1	pg/L	4	2	pg/g	0.4	0.2
PCB-128/166		pg/L	4	2	pg/g	0.4	0.2
PCB-129/138/160/163		pg/L	4	2	pg/g	0.4	0.2
PCB-130	52663-66-8	pg/L	4	2	pg/g	0.4	0.2
PCB-131	61798-70-7	pg/L	4	2	pg/g	0.4	0.2
PCB-132	38380-05-1	pg/L	4	2	pg/g	0.4	0.2
PCB-133	35694-04-3	pg/L	4	2	pg/g	0.4	0.2
PCB-134/143		pg/L	4	2	pg/g	0.4	0.2
PCB-135/151/154		pg/L	4	2	pg/g	0.4	0.2
PCB-136	38411-22-2	pg/L	4	2	pg/g	0.4	0.2
PCB-137	35694-06-5	pg/L	4	2	pg/g	0.4	0.2
PCB-139/140		pg/L	4	2	pg/g	0.4	0.2
PCB-141	52712-04-6	pg/L	4	2	pg/g	0.4	0.2
PCB-142	41411-61-4	pg/L	4	2	pg/g	0.4	0.2

PCB-144	68194-14-9	pg/L	4	2	pg/g	0.4	0.2
PCB-145	74472-40-5	pg/L	4	2	pg/g	0.4	0.2
PCB-146	51908-16-8	pg/L	4	2	pg/g	0.4	0.2
PCB-147/149		pg/L	4	2	pg/g	0.4	0.2
PCB-148	74472-41-6	pg/L	4	2	pg/g	0.4	0.2
PCB-150	68194-08-1	pg/L	4	2	pg/g	0.4	0.2
PCB-152	68194-09-2	pg/L	4	2	pg/g	0.4	0.2
PCB-153/168		pg/L	4	2	pg/g	0.4	0.2
PCB-155	33979-03-2	pg/L	4	2	pg/g	0.4	0.2
PCB-156/157		pg/L	8	2	pg/g	0.8	0.2
PCB-158	74472-42-7	pg/L	4	2	pg/g	0.4	0.2
PCB-159	39635-35-3	pg/L	4	2	pg/g	0.4	0.2
PCB-161	74472-43-8	pg/L	4	2	pg/g	0.4	0.2
PCB-162	39635-34-2	pg/L	4	2	pg/g	0.4	0.2
PCB-164	74472-45-0	pg/L	4	2	pg/g	0.4	0.2
PCB-165	74472-46-1	pg/L	4	2	pg/g	0.4	0.2
PCB-167	52663-72-6	pg/L	4	2	pg/g	0.4	0.2
PCB-169	32774-16-6	pg/L	4	2	pg/g	0.4	0.2
PCB-170	35065-30-6	pg/L	4	2	pg/g	0.4	0.2
PCB-171/173		pg/L	4	2	pg/g	0.4	0.2
PCB-172	52663-74-8	pg/L	4	2	pg/g	0.4	0.2
PCB-174	38411-25-5	pg/L	4	2	pg/g	0.4	0.2
PCB-175	40186-70-7	pg/L	4	2	pg/g	0.4	0.2
PCB-176	52663-65-7	pg/L	4	2	pg/g	0.4	0.2
PCB-177	52663-70-4	pg/L	4	2	pg/g	0.4	0.2
PCB-178	52663-67-9	pg/L	4	2	pg/g	0.4	0.2
PCB-179	52663-64-6	pg/L	4	2	pg/g	0.4	0.2
PCB-180/193		pg/L	4	2	pg/g	0.4	0.2
PCB-181	74472-47-2	pg/L	4	2	pg/g	0.4	0.2
PCB-182	60145-23-5	pg/L	4	2	pg/g	0.4	0.2
PCB-183/185		pg/L	4	2	pg/g	0.4	0.2
PCB-184	74472-48-3	pg/L	4	2	pg/g	0.4	0.2
PCB-186	74472-49-4	pg/L	4	2	pg/g	0.4	0.2
PCB-187	52663-68-0	pg/L	4	2	pg/g	0.4	0.2
PCB-188	74487-85-7	pg/L	4	2	pg/g	0.4	0.2
PCB-189	39635-31-9	pg/L	4	2	pg/g	0.4	0.2
PCB-190	41411-64-7	pg/L	4	2	pg/g	0.4	0.2
PCB-191	74472-50-7	pg/L	4	2	pg/g	0.4	0.2
PCB-192	74472-51-8	pg/L	4	2	pg/g	0.4	0.2
PCB-194	35694-08-7	pg/L	4	2	pg/g	0.4	0.2
PCB-195	52663-78-2	pg/L	4	2	pg/g	0.4	0.2

PCB-196	42740-50-1	pg/L	4	2	pg/g	0.4	0.2
PCB-197/200		pg/L	4	2	pg/g	0.4	0.2
PCB-198/199		pg/L	4	2	pg/g	0.4	0.2
PCB-201	40186-71-8	pg/L	4	2	pg/g	0.4	0.2
PCB-202	2136-99-4	pg/L	4	2	pg/g	0.4	0.2
PCB-203	52663-76-0	pg/L	4	2	pg/g	0.4	0.2
PCB-204	74472-52-9	pg/L	4	2	pg/g	0.4	0.2
PCB-205	74472-53-0	pg/L	4	2	pg/g	0.4	0.2
PCB-206	40186-72-9	pg/L	4	2	pg/g	0.4	0.2
PCB-207	52663-79-3	pg/L	4	2	pg/g	0.4	0.2
PCB-208	52663-77-1	pg/L	4	2	pg/g	0.4	0.2
PCB-209	2051-24-3	pg/L	4	2	pg/g	0.4	0.2

## **Appendix B. Draft USGS Standard Operating Procedure (SOP) for the collection and concentration of suspended-sediment samples by continuous-flow centrifugation (under development).**

### **1. Equipment**

#### **1.1 Field Equipment**

- Bridgeboard
- Reel
- 50 pound weight
- 100' rope, taped off in 1' increments from ~0 – 20'
- Cable ties and clippers
- Tubing, Teflon, smooth wall (0.625 OD x 0.062 wall, 0.500 ID) – 50' – Methanol-cleaned
- ISCO Sampler
- ISCO stainless steel strainer
- 2 to 6 12-V batteries, charged
- YSI 6290 or similar multi-parameter sonde with 100' cable
- 50-100 5-gallon buckets
- 50-100 5-gallon PFA bags, methanol-cleaned
- 50-100 twisty ties
- 1-L amber glass bottle
- 3-L polypropylene jars, pre-tared
- 1-L polypropylene bottle
- Ice chests
- Safety equipment
  - Traffic control plan, as applicable
  - Cones and/or Men Working signs
  - High-visibility clothing
  - PFDs with whistle
  - Throw ropes
- Field folder
  - Field forms
  - Bottle labels
  - Rite-in-rain notebook
  - Rite-in-rain pens, pencils, sharpies
- Gloves of various sizes
- Tech wipes

- Deionized water jug
- Deionized water squirt bottle
- Bags of various sizes
- Flagging tape
- Electrical tape
- Scissors/knife
- Tagline/measuring tape
- Tool bag

## 1.2 Processing Equipment

- Continuous-flow centrifuge (CFC Express, Scientific Methods, Inc.)
- AC Power or 2-6 charged 12-V batteries
- 2-6 centrifuge bowls
- Peristaltic pump with C-FLEX tubing, methanol-cleaned
- Teflon tubing (small diameter to fit in C-FLEX tubing, ~5-10'), methanol-cleaned
- 30-gallon drum with lid
- 30-gallon PFA bag, methanol-cleaned
- 45-gallon trash can
- Ice
- Proximity to drain
- Squirt bottle, PFA
- Organic-free water
- 1-L polypropylene bottle
- Amber glass jars (2), 500 mL
- Glass pipette, 50-mL or 100-mL, methanol-cleaned
- Clay Adams Brand Dynac Centrifuge Model 420102
- 4 Teflon or glass centrifuge tubes to fit 101 x 41.4 mm rotor, methanol-cleaned
- TPCN equipment:
  - Savillex (FEP) or glass pressure filtration assembly, including clamp, stopper collection flask
  - Vacuum system
  - Balance
  - 0.7  $\mu\text{m}$  pore size, 25 mm diameter pre-combusted glass fiber filters
  - Teflon forceps
  - Aluminum foil – 6" x 6" squares

## 2. Field Sample Collection

- 2.1 Implement safety plan, which includes:
  - 2.1.1 All field personnel wear PFDs with whistle, current on surface water safety training
  - 2.1.2 Implement Traffic Control Plan using cones and/or signs, with designated traffic signalers as necessary. For the Green River study, there is limited vehicle traffic at both stations.
  - 2.1.3 During all times when equipment is in the water, and especially during high-flow storm events, one person will monitor upstream for large floating debris
  
- 2.2 When handling methanol-cleaned parts that will come in contact with the river water, don clean nitrile gloves. This includes both ends of the Teflon ISCO tubing, the Teflon bags (5-gallon and 30-gallon), and the 1-L amber glass bottle (for TPCN analysis).
  
- 2.3 On bridge directly over thalweg, set up bridgeboard and reel
- 2.4 Attach 50 pound weight to reel cable
- 2.5 Attach rope (with 1' taped increments) to weight
- 2.6 If thalweg water depth is unknown, determine depth on rope by lowering weight to river bed
- 2.7 Attached screened end of ISCO tubing and sonde on rope with cable ties at ~0.6X thalweg depth
- 2.8 Cable tie tubing and sonde cable up rope at least 15' so the highest cable tie will be at least 5' out of water
- 2.9 Quickly lower weight to bottom of channel so it settles directly under the bridge railing
- 2.10 Tie off rope to bridge railing and let reel cable go slack
- 2.11 On bank, attach other end of ISCO tubing to ISCO (Note: vertical pumping limit of ISCO is approximately 28 ft)
- 2.12 Turn on ISCO pump and flush tubing for approximately 3-5 minutes
- 2.13 Begin collecting river water in Teflon-lined 5-gallon bags inside 5-gallon buckets (record sample collection start time)
- 2.14 Close full bags (~4 gallons) with twisty ties and lids; transport to vehicle
- 2.15 Continue until all buckets are full (~4-5 min to fill one bucket, or 12-15 buckets per hour)
- 2.17 Record sample collection end time
- 2.16 Record water quality parameters from sonde hourly, including conditions at the beginning and end of pumping
- 2.17 About halfway through pumping, divert ISCO water into:
  - 1-L polyethylene bottle (for TSS)
  - 1-L glass amber bottle (for TPCN)
  - 3-L polyethylene bottle(s), pre-tared (for SSC and PSD)
 Label bottles with collection time; store amber bottle on ice



- 2.18 When sample collection is done, set-up bridgeboard and raise weight out of water to bridge
- 2.19 Disassemble equipment and load into vehicles for transport to processing laboratory

### 3. Sample Processing

3.1 Upon returning from the field, transfer river water from 5-gallon Teflon bags to 30-gal Teflon bag in drum until drum is full (~7 buckets). Be careful to transfer all sediment out of the 5-gallon bags by periodically re-suspending the sediment as it is being poured. Also, rinse sediment from bags with organic-free water into drum as needed.

#### 3.2 Set-up centrifuge

- Connect effluent tubing (C-FLEX L/S 15 with teflon tubing) securely to effluent port of centrifuge bowl (effluent port is the lower port); put end of effluent tubing in sink drain
- Connect influent tubing (C-FLEX L/S 25 with teflon tubing) securely to influent port of centrifuge bowl (influent port is the higher port)
- Put the influent C-FLEX L/S 25 tubing in the peristaltic pump and clamp down in place
- Adjust the peristaltic pump dial to about “3” (300 mL/min)
- Put the end of the Teflon tubing in the 30-gal Teflon bag (in poly drum) filled with sample water
- Add ice to the garbage can (outside of poly drum) as needed
- Open the centrifuge by turning the knob on the top of the unit to the “unlocked” position, then pushing it down
- The glass doors should pop open, then lift the doors to the upright position
- Push the centrifuge bowl into the rotor
- The influent port should be on the left; the effluent port should be on the right
- Lower the glass doors and secure around the top of the centrifuge bowl. The doors will only close if the bowl is positioned correctly. If the door won’t close, reposition the bowl (both left to right and by pushing it down)
- IMPORTANT – the bowl must be seated on the rotor well, so double check it’s seating by pressing the bowl down a few extra times
- Once the glass doors are shut, turn the knob to the “locked” position

#### 3.3 Run centrifuge

- Flip switch on bottom left side of unit (by plug) to turn unit on (fan will start running)
- Press the round black button on the front of the unit to start the rotor

- IMPORTANT – if you hear a screeching, grinding noise, press the round button again immediately to turn off the unit. The bowl was not seated correctly (probably not down far enough). Open the unit. Inspect the bowl. If there was significant damage (i.e. lots of plastic flakes), clean the unit and start over with a new bowl. If the unit does not power up after a grinding event, you may have blown the fuse. See “Replacing the fuse”.
- The unit will get up to 10,000 RPM within 10 seconds. Once it is up to speed, the noise will reduce a bit. It is ok to run the centrifuge dry.
- Once the centrifuge is running at 10,000 RPM, turn on the peristaltic pump (double check it is still set to “3” – it is easy to hit the knob when adjusting the tubing). Make sure it is pumping correctly, or reposition the C-FLEX in the peristaltic pump.
- Double check that the tubing is sitting at the bottom of the 30-gal drum.
- After the bowl fills (~300 mL = 1 minute), water will start flowing from the effluent line into the sink. You can check the flow rate of the peristaltic pump by measuring the effluent with a graduated cylinder (50 mL in 10 seconds is ideal).
- At some point, collect centrifuge effluent water in a 1-L polyethylene bottle (for TSS), label, and store in fridge
- If the 30-gal drum is full of water, and the pump is running at 300 mL / min, then the system should run unattended for at least 6 hours.

#### 3.4 Periodically remove sediment from bowl to jar

- The centrifuge runs happily until there is too much sediment in the bowl (~20 g), then it starts to make a louder noise. The run time until this happens depends on the SSC. For turbidity < 200 NTU, empty the bowl(s) into new amber glass jar(s) at least each evening. For higher turbidity waters, empty more frequently. To do this:
  - Turn off the peristaltic pump.
  - Push the round black button on the front of the centrifuge to stop the rotor.
  - Once the rotor is stopped, turn the knob from “locked” to “unlocked” and push to open the doors.
  - Gently remove the Effluent tubing from the Effluent port, replace the port cap, and bag the tip of the C-FLEX in a clean bag.
  - Gently remove the Influent tubing from the Influent port, replace the port cap, and bag the tip of the C-FLEX in a clean bag.
  - Remove the bowl.
  - Vortex and manually agitate the sediment in the bowl
  - Take port caps off and invert the bowl

- Pour the water out of the effluent port into a new pre-weighed amber glass jar. Periodically resuspend the sediment in the bowl to get as much sediment out during the first pour.
- Squirt a few mLs of organic-free water into the bowl through the influent port.
- Manually agitate and repeat pouring steps.
- If you are going to continue centrifuging, no need to get every last bit of sediment out of the bowl (we're trying to minimize water in the jar).
- Inspect the bowl. If it looks fine, put it back in the centrifuge, and follow steps to start centrifuging again. Or replace with a new bowl.
- Refill the 30-gallon drum with river water as needed.
- Add ice to garbage can (and pump out excess water in can) as needed.
- Restart centrifuge.
- Cap, label, and store jar(s) at 4°C overnight.
- NOTE: If the centrifuges will be running for multiple days, decant the overlying water in the jar(s) from the previous day just before emptying the current day's bowl into the jar (otherwise the jar will overflow).
  - Very carefully and slowly carry the quiescent jar from the fridge to the lab.
  - Use a clean, methanol-rinsed glass pipette (50- or 100-mL) and bulb to decant the overlying water from the jar(s).
  - Add decant water back into 30-gal Teflon bag to be centrifuged again.
  - Tip: carefully raise one side of the jar (sitting on its lid) to pipette as much water and disturb as little sediment as possible.

### 3.5 Finish pumping

- As the last of the sample is being pumped into the centrifuge (include the previous day's jar decant water), rinse the Teflon bag with OBW water and agitate to pump any remaining sediment from the bottom of the bag.
- Once the bag is clean and empty, follow steps in Section 3.4 to turn off the centrifuge and empty the bowl contents into the jar(s).
- This time, rinse the bowl to get as much sediment out as possible (without overflowing the jar).
- Store the jar(s) at 4°C overnight to settle.
- Flip off the power switch on the centrifuge (bottom left side).

### 3.6 Replacing the fuse, if blown

- Locate the fuse on the bottom right side of the centrifuge (in a mini drawer in the black part above the plug)
- Replace it with a new fuse (there is a bag taped to the power cord) and power unit on

### 3.7 Dewatering the jar sample

- After the sample has settled quiescently for at least 12 hours at 4°C, and being very careful not to disturb the settled sediment, pipette the overlying water into Teflon or glass centrifuge tubes
- Spin in Dynac centrifuge for 20 minutes at 1000 x g
- Transfer by pipette any centrifuged sediment in the bottom of tubes to the amber jar containing the rest of the sample
- Weigh the sample + jar; subtract empty jar weight to get wet sample weight
- Store concentrated suspended sediment sample in amber jar at 4°C until analysis

### 3.8 Other sample processing

- TPCN (see USGS National Field Manual for protocol), send to USGS National Water Quality Laboratory for particulate carbon and nitrogen analysis
- Measure centrifuge influent and effluent for TSS using standard methods
- Send polyethylene bottles of centrifuge influent and effluent to lab for PSD by laser diffraction

## 4. Preparation for Subsequent Sampling

- Wash all 5-gallon Teflon bags, 30-gallon Teflon bags, ISCO and centrifuge Teflon tubing and C-FLEX tubing as follows:
  - Wash and scrub using phosphate-free soap and warm tap water
  - Rinse with tap water
  - Soak for at least 30 minutes in 5% hydrochloric acid
  - Rinse with deionized water
  - Rinse with trace-grade methanol.
  - Allow to air-dry, then bag.
- Rinse river water and mud from other field equipment; air-dry
- Charge batteries
- Store cleaned equipment for next sampling event

# Appendix C. Example USGS field form.

November 2013



## U. S. GEOLOGICAL SURVEY SURFACE-WATER QUALITY NOTES

Station No. 12113390

NWIS Record No. \_\_\_\_\_

Station No. 12113390 Station Name Duwamish River at Golf Course nr Tukwila, WA Field ID \_\_\_\_\_  
 Sample Date \_\_\_\_\_ Mean Sample Time \_\_\_\_\_ Time Datum \_\_\_\_\_ (eg. PST, PDT)  
 Sample Medium: SS (susp. sed) \_\_\_\_\_ SSQ (QC-SS) \_\_\_\_\_ WS (SW) \_\_\_\_\_ WSQ \_\_\_\_\_ Sample Type: 9 (regular) 7 (replicate) 1 (spike)  
 QC Samples Collected? Y N Blank Replicate Spike Other \_\_\_\_\_  
 Project No. GC14YG00F6E0000 / GC14YG00F6EGS00 Project Name Green River Toxic Loads  
 Sampling Team \_\_\_\_\_

### FIELD MEASUREMENTS

Property	Parm Code	Method Code	Result	Units	Remark Code	Value Qual.	Null Value Qual.	NWIS Result-Level Comments
Gage Height	00065			ft				
Discharge, instantaneous	00061			cfs				
Turbidity (DTS-12)	63680	TS032		FNU				
Turbidity (hand-held)	63680	TS087		FNU				
Temperature, Air	00020	THM04 (thermister) THM05 (thermometer)		°C				
Temperature, Water	00010	THM01 (thermister) THM02 (thermometer)		°C				
Specific Conductance	00095	SC001 (contacting sensor)		µS/cm				
Dissolved Oxygen	00300	MEMBR (amperometric)		mg/L				
Barometric Pressure	00025	BAROM		mm Hg				
pH	00400	PROBE (electrode)		units				
Alkalinity, filtered, incr.	39086	TT061		mg/L				
Carbonate, ftt, incr.	00452	SSM01		mg/L				Advanced Speciation Method
Bicarbonate, ftt, incr.	00453	SSM01		mg/L				Advanced Speciation Method
Suspended Sediment	80154			mg/L				
Susp. Sed., < 62.5 µm	70331			%				
QC Sample Collected	99111							See Page 7 for Codes
Type of Replicate	99105							See Page 7 for Codes
Purpose, topical QC	99112							For Cross-Sections: Variability

### SAMPLING INFORMATION

Parameter	Pcode	Value	Information
Sampler Type—for suspended sediment chemistry	84164	3044 DH-81 3051 DH-95 Teflon 3053 D-95 Teflon 3055 D-96 Bag Sampler 3058 DH-2 Bag Sampler 3070 Grab 3045 DH-81 Teflon 3052 DH-95 Plastic 3054 D-95 Plastic 3057 D-99 Bag Sampler 3060 Weighted-Bottle Sampler 4115 Sampler, point, automatic	Sampler ID: _____ Sampler bottle/bag material: plastic (teflon) other _____ Nozzle material: plastic teflon other _____ Nozzle size: 3/16" 1/4" 5/16"
Sampler Type—for water chemistry and suspended sediment physical parameters	84164	3044 DH-81 3051 DH-95 Teflon 3053 D-95 Teflon 3055 D-96 Bag Sampler 3058 DH-2 Bag Sampler 3070 Grab 3045 DH-81 Teflon 3052 DH-95 Plastic 3054 D-95 Plastic 3057 D-99 Bag Sampler 3060 Weighted-Bottle Sampler 4115 Sampler, point, automatic	Sampler ID: _____ Sampler bottle/bag material: plastic (teflon) other _____ Nozzle material: plastic (teflon) other _____ Nozzle size: 3/16" 1/4" (5/16)
Sampling Method—for physical parameters	82398	10 EWI; (20) EDI; 30 single vertical; 40 multiple vertical; 50 Point Sample; 70 Grab (dip sample)	Bottle size: pint quart 1 L bottle 1 L bag (3 L bag) 6 L bag
Transit Rate	50015	ft/sec	
Hydrologic Condition	N/A	X Not applicable; 4 Stable, low stage; 5 Falling stage; 6 Stable, high stage; 7 Peak stage; 8 Rising stage; 9 Stable, normal stage	
Observations [Codes: 0=none; 1=mild; 2=moderate; 3=serious; 4=extreme]		Oil-grease (01300) _____ Delergent suds (01305) _____ Alm. Odor (01330) _____ Fish kill (01340) _____	Floating garbage (01320) _____ Floating algae mats (01325) _____ Floating debris (01345) _____ Turbidity (01350) _____

COMPILED BY: \_\_\_\_\_ DATE \_\_\_\_\_ CHECKED BY: \_\_\_\_\_ DATE \_\_\_\_\_ LOGGED INTO NWIS BY: \_\_\_\_\_ DATE \_\_\_\_\_

Station No. \_\_\_\_\_

**SAMPLING CONDITIONS**

Stream width: \_\_\_\_\_ ft Notes: \_\_\_\_\_  
Sediment Sampling points: \_\_\_\_\_  
Sediment Sampling location: wading bridge upstream downstream side of bridge 0.8 mi below gage  
Total number of sediment bottles: \_\_\_\_\_ A and B set?: \_\_\_\_\_ Sediment mean time: \_\_\_\_\_ (attach sediment field sheet)  
Chemistry Sampling location (tubing intake): \_\_\_\_\_ (ft from REW) \_\_\_\_\_ (ft below water surface)  
Sonde Location: \_\_\_\_\_ (ft from REW) \_\_\_\_\_ (ft below water surface)  
Sonde No. \_\_\_\_\_ Calibrated by: \_\_\_\_\_ Calibration Location: \_\_\_\_\_ (attach calibration information)  
Turbidity Meter: make/model: \_\_\_\_\_ S/N: \_\_\_\_\_ ID: \_\_\_\_\_  
Probe: make/model: \_\_\_\_\_ S/N: \_\_\_\_\_ ID: \_\_\_\_\_  
Calibration information: \_\_\_\_\_  
Sampling site: pool riffle open channel braided backwater Bottom: bedrock rock cobble gravel sand silt concrete other \_\_\_\_\_  
Stream color: brown green blue gray clear other \_\_\_\_\_ Stream mixing: well-mixed stratified poorly-mixed unknown other \_\_\_\_\_  
Weather: *sky*- clear partly cloudy cloudy **precipitation**- none light medium heavy snow sleet rain mist \_\_\_\_\_  
**wind**- calm light breeze gusty windy est. wind speed \_\_\_\_\_ mph **temperature**- very cold cool warm hot \_\_\_\_\_  
No. days since last significant rainfall \_\_\_\_\_  
Field Observations: \_\_\_\_\_  
Sample Comments (for NWMS; 300 characters max.): \_\_\_\_\_

**LABORATORY INFORMATION** *Sample Set ID* \_\_\_\_\_

**SAMPLES COLLECTED:** *If Pesticides are collected, circle Organics bottle type and Laboratory Schedule number.*  
Nutrients:  WCA  FCC  FCA  CC Major cations:  FA  RA Major anions:  FU Trace elements:  FA  RA  CU  
Mercury:  FAM  RAM  Wis. Hg Lab Lab pH/SC/ANC:  RU  
VOC: GCV ( vials) Organics:  GCC filtered  unfiltered  BGC  C18  Kansas OGRG Lab  
Suspended solids:  SUSO Turbidity:  TBY  
Phenols:  PHE Oil&Grease:  OAG Methylene Blue Active Substances:  MBAS Color:  RCB  
Carbon:  TPCN  PIC filter1-vol filtered \_\_\_\_\_ mL filter2-vol filtered \_\_\_\_\_ mL filter3-vol filtered \_\_\_\_\_ mL  DOC  DIC  
Stable isotopes:  FUS  RUS Radiochemicals:  FUR  RUR  SUR  FAR  RAR  CUR  RURCT  RURCV  
 BOD  COD Chlorophyll:  CHL Algae: \_\_\_\_\_ Invertebrates:  IQE  IQL  IQM  IRE Fish tissue:  TBI  
Ultraviolet Absorbing Substances:  UAS  
Other: \_\_\_\_\_ (Lab \_\_\_\_\_) Other: \_\_\_\_\_ (Lab \_\_\_\_\_) Other: \_\_\_\_\_ (Lab \_\_\_\_\_)  
Other: \_\_\_\_\_ (Lab \_\_\_\_\_) Other: \_\_\_\_\_ (Lab \_\_\_\_\_) Other: \_\_\_\_\_ (Lab \_\_\_\_\_)  
Suspended sediment:   CONC.  S/P  FINES [No. bottles 1] **NOTE: from pumped sample, see attached field notes for bridge sample info**  
Microbiology: \_\_\_\_\_ (Lab \_\_\_\_\_)  
Laboratory Schedules: \_\_\_\_\_ see analytical lab contract \_\_\_\_\_  
Lab Codes: \_\_\_\_\_ add/delete \_\_\_\_\_ add/delete \_\_\_\_\_ add/delete \_\_\_\_\_ add/delete \_\_\_\_\_ add/delete  
Comments: \_\_\_\_\_  
Date shipped: \_\_\_\_\_ Lab(s): \_\_\_\_\_  
Date sediment sample shipped: \_\_\_\_\_ Sediment Lab: **CVO**  
**\*\*Notify the NWQL in advance of shipment of potentially hazardous samples—phone 1-866-ASK-NWQL or email LabLogin@usgs.gov**

Station No. \_\_\_\_\_

**SAMPLE TIMES:**

Instantaneous Discharge Measurement: \_\_\_\_\_ Time: \_\_\_\_\_ Initials: \_\_\_\_\_

Water Sample Start Time: \_\_\_\_\_ End Time: \_\_\_\_\_ Mean Time: \_\_\_\_\_

Suspended Sediment Physical Parameters Start Time: \_\_\_\_\_ End Time: \_\_\_\_\_ Mean Time: \_\_\_\_\_

Suspended Sediment Chemistry Pump Start Time: \_\_\_\_\_ End Time: \_\_\_\_\_ Mean Time: \_\_\_\_\_

**From pump:**

1-L amber glass bottle for TPCN: \_\_\_\_\_

1-L poly bottle for TSS: \_\_\_\_\_

3-L poly bottle for SSC/PSD: \_\_\_\_\_

**BED SEDIMENT SAMPLING**

Bed Sediment Sample Start Time: \_\_\_\_\_ End Time: \_\_\_\_\_ Mean Time: \_\_\_\_\_

**Bed Sediment Sample GPS Locations:**

- 1. \_\_\_\_\_
- 2. \_\_\_\_\_
- 3. \_\_\_\_\_
- 4. \_\_\_\_\_
- 5. \_\_\_\_\_
- 6. \_\_\_\_\_
- 7. \_\_\_\_\_
- 8. \_\_\_\_\_
- 9. \_\_\_\_\_
- 10. \_\_\_\_\_

**GENERAL WATER QUALITY**

Time	Water Temp (°C)	pH	Specific Cond. (uS/cm)	DO (mg/L)	Turbidity (NTU)	Air Temp (°C)	Barometric Pressure (mm Hg)	Notes

**OTHER FIELD NOTES:**

**QUALITY-CONTROL INFORMATION**

**PRESERVATIVE LOT NUMBERS**

4.5N H <sub>2</sub> SO <sub>4</sub> (NUTRIENTS&DOC)	4.5N H <sub>2</sub> SO <sub>4</sub> (NUTRIENTS&DOC)	4.5N H <sub>2</sub> SO <sub>4</sub> (NUTRIENTS&DOC)	7.5N HNO <sub>3</sub> (METALS&CATIONS)	7.5N HNO <sub>3</sub> (METALS&CATIONS)
--	--	--	---	---

1:1 HCl \_\_\_\_\_ Number of drops of HCL added to lower pH to ≤ 2 \_\_\_\_\_ (NOTE: Maximum number of drops = 5)  
(voc)

**BLANK WATER LOT NUMBERS**

Inorganic (99200) \_\_\_\_\_ 2nd Inorganic (99201) \_\_\_\_\_  
 Pesticide (99202) \_\_\_\_\_ 2nd Pesticide (99203) \_\_\_\_\_  
 VOC/Pesticide (99204) \_\_\_\_\_ 2nd VOC/Pesticide (99205) \_\_\_\_\_

**SPIKES**

<b>99106 Spike-sample type</b> 10 Field 20 Lab	<b>99107 Spike-solution source</b> 10 NWQL
<b>99108 Spike-solution volume, mL</b> _____	
<b>99104 Spike-vial lot number</b> _____	
<b>Expiration Date</b> _____	

**FILTER LOT NUMBERS**

capsule \_\_\_\_\_ pore size \_\_\_\_\_ brand \_\_\_\_\_  
 142mm GFF (organics) \_\_\_\_\_ pore size \_\_\_\_\_ brand \_\_\_\_\_  
 25mm GFF (organic carbon) \_\_\_\_\_ pore size \_\_\_\_\_ brand \_\_\_\_\_

**QC SAMPLES**

**Starting date for set of samples (99109) (YMMDD)** \_\_\_\_\_ **Ending date for set of samples (99110) (YMMDD)** \_\_\_\_\_  
**Starting time for set of samples (82073) (2400 hours)** \_\_\_\_\_ **Ending time for set of samples (82074) (2400 hours)** \_\_\_\_\_

<b>Sample Type</b>	<b>NWIS Record No.</b>	<b>Sample Type</b>	<b>NWIS Record No.</b>	<b>Sample Type</b>	<b>NWIS Record No.</b>
Equip Blank _____	_____	Sequential _____	_____	Trip Blank _____	_____
Field Blank _____	_____	Spike _____	_____	Other _____	_____
Split _____	_____	Concurrent _____	_____	Other _____	_____

NWQL Schedules/lab codes (QC Samples) \_\_\_\_\_

COMMENTS: \_\_\_\_\_

<p><b>Sample Medium Codes</b></p> <p>WS Surface water                  WSQ Quality-control sample                  OAQ Artificial</p>	<p><b>Sample Type Code</b></p> <p>9 Regular                  7 Replicate                  2 Blank                  1 Spike                  5 Duplicate</p>	<p>(Circle appropriate selections)</p> <p><b>99111 QC sample associated with this environmental sample</b></p> <p>1 No associated QA data                  10 Blank                  30 Replicate Sample                  40 Spike sample                  100 More than one type of QA sample                  200 Other</p>	<p><b>99102 Blank-sample type</b></p> <table style="width: 100%;"> <tr> <td>1 Source Solution</td> <td>90 Ambient</td> </tr> <tr> <td>30 Trip</td> <td>100 Field</td> </tr> <tr> <td>40 Sampler</td> <td>200 Other</td> </tr> <tr> <td>50 Splitter</td> <td></td> </tr> <tr> <td>60 Filler</td> <td></td> </tr> <tr> <td>70 Preservation</td> <td></td> </tr> <tr> <td>80 Equipment (done in non-field environment)</td> <td></td> </tr> </table>	1 Source Solution	90 Ambient	30 Trip	100 Field	40 Sampler	200 Other	50 Splitter		60 Filler		70 Preservation		80 Equipment (done in non-field environment)	
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<p><b>99105 Replicate-sample type</b></p> <table style="width: 100%;"> <tr> <td>10 Concurrent</td> <td>40 Split-Concurrent</td> </tr> <tr> <td>20 Sequential</td> <td>50 Split-Sequential</td> </tr> <tr> <td>30 Split</td> <td>200 Other</td> </tr> </table>	10 Concurrent	40 Split-Concurrent	20 Sequential	50 Split-Sequential	30 Split	200 Other	<p><b>99100 Blank-solution type</b></p> <p>10 Inorganic grade (distilled/deionized)                  40 Pesticide grade (OK for organics and organic carbon)                  50 Volatile-organic grade (OK for VOCs, organics, and organic carbon)                  200 Other</p>	<p><b>99112 Purpose, Topical QC data</b></p> <p>1 Routine QC (non-topical)                  10 Topical for high bias (contamination)                  20 Topical for low bias (recovery)                  110 Topical for variability (field collection)</p>	<p><b>84164 Sampler Type</b></p> <p>3044 US DH-81                  3045 US DH-81 With Teflon Cap And Nozzle                  3051 US DH-95 Teflon Bottle                  3052 US DH-95 Plastic Bottle                  3053 US D-95 Teflon Bottle                  3054 US D-95 Plastic Bottle                  3055 US D-96 Bag Sampler                  3057 US D-99 Bag Sampler                  3070 Grab Sample                  3071 Open-Mouth Bottle                  3080 VOC Hand Sampler                  8000 None                  8010 Other</p>								
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<p><b>99101 Source of blank water</b></p> <p>10 NWQL                  55 Wisconsin Mercury Lab                  140 EMD Chemicals                  150 Ricca Chemical Company                  200 Other</p>	<p><b>82398 Sampling Method</b></p> <p>10 Equal Width Increment (EWI)                  20 Equal Discharge Increment (EDI)                  30 Single Vertical                  40 Multiple Verticals                  50 Point Sample                  70 Grab Sample (Dip)                  8010 Other                  8030 Grab Sample At Water-Supply Tap</p>	<p>A complete set of fixed-value codes can be found online at:  <a href="http://www.nwis.er.usgs.gov/currentdocs/index.html">http://www.nwis.er.usgs.gov/currentdocs/index.html</a></p>															