Green River Study: Suspended Solids Characterization Sampling and Analysis Plan

January 2013

Final

King County

Department of Natural Resources and Parks
Water and Land Resources Division
Science and Technical Support Section
King Street Center, KSC-NR-0600
201 South Jackson Street, Suite 600
Seattle, WA 98104
206-296-6519 TTY Relay: 711
www.kingcounty.gov/environment/wlr/science-section.aspx

Alternate Formats Available

206-296-6519 TTY Relay: 711

Green River Study: Suspended Solids Characterization

Sampling and Analysis Plan

January 2013 - Final

Prepared for:

King County Department of Natural Resources and Parks

Wastewater Treatment Division Sediment Management Program

Submitted by:

Debra Williston and Deb Lester
King County Water and Land Resources Division
Department of Natural Resources and Parks

King County
Department of Natural Resources and Parks
Water and Land Resources Division
Science and Technical Support Section

Acknowledgements

We thank the Washington Department of Ecology for allowing us to use their filtered solids sampling equipment and SAIC for their guidance on the use and modification of the sampling equipment to meet our needs. We would also like to thank Foster Links Golf Course for allowing us site access and use of power.

.

Citation

King County. 2013. Green River Study: Suspended Solids Characterization – Sampling and Analysis Plan. Prepared by Debra Williston and Deb Lester, King County Water and Land Resources Division. Seattle, Washington.

Table of Contents

Figures

Tables

Acronyms

AXYS	AXYS Analytical Services Ltd.
COC	chain of custody
CVAA	cold vapor atomic absorbance
DQOs	data quality objectives
Ecology	Washington Department of Ecology
EIM	environmental information management
EPA	U.S. Environmental Protection Agency
FSU	Field Science Unit
GC/ECD	gas chromatography/electron capture detection
HPAH	high molecular weight PAHs
HRGC/HRMS	high-resolution gas chromatography/high-resolution mass spectroscopy
KCEL	King County Environmental Laboratory
LCS	laboratory control sample
LDW	Lower Duwamish Waterway
LIMS	Laboratory Information Management System
LMCL	lowest method calibration limits
LPAH	low molecular weight PAH
MDL	method detection limit
OPR	ongoing precision and recovery
PAHs	polycyclic aromatic hydrocarbons
PCB	polychlorinated biphenyls
RDL	reporting detection limit
PQL	practical quantitation limit
PSD	particle size distribution
PVC	polyvinyl chloride
QC	quality control
QA/QC	quality assurance/quality control
SAP	sampling and analysis plan
SCWC	Source Control Work Group
SDL	specific detection limit
SRM	standard reference material
SVOC	semivolatile organic compound
TOC	total organic carbon
TSS	total suspended solids

1 INTRODUCTION

This sampling and analysis plan (SAP) presents project information and sampling and analytical methodologies to better understand the relative contribution of polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), dioxins/furans and arsenic associated with suspended solids in the Green River and its major tributaries. Two sampling methods will be used to collect suspended solids samples for this characterization effort: sediment traps and suspended solids collected on filters. This project will provide additional context to better understand the potential for PCBs, PAHs, dioxin/furans and arsenic to be transported from the Green River basin to the Lower Duwamish Waterway; this project is not intended as a formal loading analysis.

1.1 Project Background

The Duwamish River originates at the confluence of the Green and Black Rivers near Tukwila, Washington, and flows northwest for approximately 19 km (12 mi), splits at the southern end of Harbor Island to form the East and West Waterways, and then discharges into Elliott Bay in Puget Sound, Seattle, Washington. The Lower Duwamish Waterway (LDW) is approximately 5 miles long and consists of the downstream portion of the Duwamish River, excluding the East and West Waterways.

King County is a member of the Source Control Work Group (SCWG) for the Lower Duwamish Superfund site. Other members include lead agency Washington Department of Ecology (Ecology), U.S. Environmental Protection Agency (EPA), City of Seattle and the Port of Seattle. The SCWG works to understand potential chemical sources within the LDW Superfund site and to control and reduce sources that can contaminate waterway sediments. King County Wastewater Treatment Division seeks to better understand the potential sources of contaminants of concern into combined sewer overflow basins which discharge to the LDW and also contaminant inputs to the LDW from upstream sources.

The LDW Remedial Investigation (RI) (Windward 2010) indicates that more than 99% of the new sediment deposited in the LDW each year originates upstream of the LDW in the Green/Duwamish River basin. Because of this, LDW surface sediment quality will be closely tied to the quality of incoming sediment from the Green/Duwamish River. Studies and sampling programs have evaluated the water chemistry of the Green/Duwamish River system (King County 2007; Windward 2010[1]) and the chemistry of suspended solids from the Green/Duwamish River system (Gries and Sloan 2009). In 2011, King County initiated an effort to characterize water chemistry in the Green River and four of its major tributaries to evaluate the relative contributions of PCBs, PAHs and arsenic to the LDW under both base and storm flow conditions (King County 2011). In summer 2012, King County also collected bulk sediment samples from tributaries to the Green River, as well as

[1] Whole water samples collected by King County from the Green River for total PCBs, PAHs and arsenic are summarized in this report.

four locations on the main-stem of the River. Sediment samples were analyzed for a number of of priority pollutants including dioxins/furans (King County 2012). The primary purpose of the sampling and analysis effort described here is to provide a better understanding of the relative concentrations of select contaminants in suspended solids from up to four tributaries to the Green River, as well as two main-stem river locations. The data collected by this study, along with previous water and sediment data collection efforts, will serve to better characterize contaminant conditions upstream of the LDW. This study will focus on PCBs, PAHs, dioxins/furans and arsenic because the LDW RI has identified these as human health contaminants of concern within the LDW and unacceptable residual risks are predicted to be present after cleanup. The data collected by the study described in this SAP, and previous efforts to characterize water and sediment in the Green River basin (King County 2011; 2012), are not intended to evaluate contaminant loading to the LDW. However, the data collected by these efforts may be used to assist in development of future studies to evaluate contaminant loading to the LDW.

1.2 Scope of Work

Suspended solids samples will be collected from up to four major tributaries to the Green River and two locations on the main-stem of the River. Samples will be collected using two different methods: sediment traps and suspended solids collected on filters (herein referred to as filtered solids).

Sediment traps will be deployed for approximately 2 to 3 months and will represent suspended solids collected over a defined time frame. Two sediment trap deployment periods are targeted during the wet season (October–April); due to the relatively low suspended solids concentrations at most sampling locations during the dry season, it is not anticipated that a sample mass sufficient for the desired analytes can be collected during this time period. However, if the initial trap deployment indicates sufficient sample mass could be collected under baseflow conditions, the samplers may also be deployed during the dry season (July through September) in 2013. Sediment traps will be deployed at upper and lower boundary locations along the main-stem of the Green River, and in three major tributaries: Soos, Newaukum, and Mill Creeks. Sediment traps will not be deployed below the Black River pump station due to the lack of a suitable sampling location. This area experiences limited flow due to pump station operations and can also experience back-water conditions from the Duwamish River. The upper main-stem river boundary location (upriver of the major tributaries to be sampled) will be the entrance bridge to Flaming Geyser State Park, while the lower boundary location (downstream of the tributaries) will be at the Foster Links Golf Course in Tukwila. All samples will be analyzed for PCB Aroclors®, PAHs[2], dioxins/furans and arsenic (and other metals[3]), in addition to total

[2] Because the analytical method expected to be used for PAHs also gives results for other semi-volatile organic compounds, data for additional compounds will be available (see Section 4.2 for full analyte list).

[3] Because the sample mass required for arsenic analysis is sufficient to analyze for additional metals by the same analytical method used for arsenic, results for the metals listed in Section 4.3 will also be acquired and reported.

organic carbon (TOC), total solids and particle size distribution (PSD). If sufficient sample mass is collected, additional analyses may be conducted (e.g., mercury).

Filtered solids samples will be collected by pumping water through a pair of 19-inch 5-micron bag filters over a set time period (e.g., 6 to 20 hours) trapping the suspended solids onto the filter. Filtered solids samples will be collected during both dry season (base flow) and storm flow conditions. One base flow sample and five wet season/storm flow events will be targeted. Collection of filtered solids samples will be targeted at the same upper and lower boundary locations along the main-stem of the Green River as described above, in addition to the Black River pump station and Soos, Newaukum, and Mill Creeks. If sufficient sample mass is collected, all samples will be analyzed for PCB Aroclors®, PAHs, dioxins/furans and arsenic (and other metals) in addition to, total solids and PSD. In the case of limited sample mass, lower priority will be given to analysis of PAHs. Due to the analytical interference associated with the filter material, TOC cannot be measured in the filtered solids samples.

1.3 Study Schedule

The initial sediment trap deployment will occur between late October and mid-November of 2012. Trap retrieval will be targeted following a two to three month deployment period. Assuming a late fall deployment, the traps will be retrieved in January 2013. However, if a two to three month deployment period results in a sample mass that is insufficient to conduct the desired analyses, the second trap deployment period will be extended beyond the targeted two to three month deployment period. A second trap deployment is estimated to take place between approximately February and April 2013. Analysis of sediment trap samples is expected to continue through June 2013. If the initial trap deployment does not result in a sample mass sufficient to conduct the desired analyses, it may be necessary to combine the sample mass from two deployment periods. If sediment traps are deployed during baseflow conditions in 2013 the analysis schedule is anticipated to continue through November 2013.

The filtered solids sampling will occur between January and May 2013 for storm sampling and between August-September 2013 for dry season sampling. Storm sampling maybe extended to October-December 2013 if the desired number of samples is not collected by May 2013. It is anticipated that sampling will be complete at the end of 2013 and sample analysis will continue into early 2014. Data from both sediment trap and filtered solids sampling events are anticipated to be validated, reviewed and ready for release in a draft data report by August 2014.

1.4 Project Staff

The following staff members are responsible for project execution:

Jeff Stern, LDW Project Manager.....206-263-6447

Wastewater Treatment Division Manager and Technical lead for all Lower Duwamish River studies.

Deb Lester, Green River Study Project Manager.....206-296-8325

Responsible for basin study project execution and adherence to SAP and schedule.

Debra Williston, Water and Land Resources Division (WLRD) Technical Lead.....206-263-6540

Technical Support for all Lower Duwamish River studies including study project.

Jim Devereaux, Field Science Unit Field Lead.....206- 684-2398

Responsible for sediment trap sample collection.

Jean Power, Field Science Unit Field Lead.....206-684-2393

Responsible for filtered solids sample collection.

Fritz Grothkopp, King County Environmental Lab (KCEL) Project Manager.....206-684-2327

Manages sample analysis, sample shipment, and data delivery.

Scott Mickelson, Data Validation Lead.....206-296-8247

Responsible for data validation of KCEL data.

2 STUDY DESIGN

The goal of this study is to collect representative samples that reflect chemical concentrations associated with suspended solids (sediments) within the Green River and its major tributaries. Resulting data will allow King County to begin to estimate relative contributions of these contaminants to the LDW from the Green River basin. As previously discussed, these data are not intended to quantify contaminant loading to the LDW.

2.1 Data Quality Objectives

The data quality objectives (DQOs) for this project are to collect data of known and sufficient quality to meet the study goals. Validation of project data will assess whether the data collected are of sufficient quality to meet the study goals. The data quality issues of precision, accuracy, bias, representativeness, completeness, comparability, and sensitivity are described in the following sections. Data validation is discussed in Section 5.1.

2.1.1 Precision, Accuracy, and Bias

Precision is the agreement of a set of results among themselves and is a measure of the ability to reproduce a result. Accuracy is an estimate of the difference between the true value and the measured value. The accuracy of a result is affected by both systematic and random errors. Bias is a measure of the difference, due to a systematic factor, between an analytical result and the true value of an analyte. Precision, accuracy, and bias for analytical chemistry may be measured by one or more of the following quality control (QC) procedures:

- Analysis of various laboratory QC samples such as method blanks, spiked blanks, matrix spikes, laboratory control samples and laboratory duplicates or triplicates

Accuracy is assessed through matrix spikes and spike duplicates along with the ongoing precision and recovery sample control charts. Additionally, the isotopic dilution method chosen for this study is the most rigorous method for dioxin/furan congener analysis. This method uses isotopically labeled congeners, to track the recovery performance of the range of congeners. Thus, each congener concentration is theoretically adjusted for the extraction efficiency and analytical performance of that specific sample.

2.1.2 Representativeness

Representativeness expresses the degree to which sample data accurately and precisely represent a characteristic of a population, parameter variations at the sampling point, or an environmental condition. Suspended solid samples will be collected from stream or river locations to represent sediment quality during defined deployment periods for sediment trap samples and flow conditions for filtered solids samples. The samples are intended to generate data of sufficient quality to provide estimates of the chemical characteristics of PCBs, PAHs, dioxins/furans and arsenic in suspended solids from the major tributaries and the main-stem Green River. The sampling methodologies are not intended to capture the

entire distribution of suspended solids in tributaries or the main-stem river. Sediment traps may for example, collect some small percentage of bed load and may not capture the very fine grain size particles suspended in the water column. The bag filters used to collect the filtered solids are not expected to capture much, if any, of the fine grained material that is smaller than the pore size of the bag filters (i.e., 5-microns). PSD will be analyzed in samples collected using both sampling methods (i.e., sediment trap and filtered solids) to characterize the grain size distribution. In addition, to better understand the ability of the filtered solids sampling equipment to collect samples representative of stream/river conditions water samples will be collected at the inlet of the sampler. These samples will be analyzed for total suspended solids (TSS) and PSD and will provide ancillary information for qualitative data evaluations.

Samples will be collected in a manner that minimizes potential contamination and other types of degradation to the chemical and physical composition of the sediment. This can be achieved by following guidelines for sampler decontamination, sample acceptability criteria, sample processing, observing proper hold-times, preservation, storage and preparation of samples.

2.1.3 Completeness

Completeness is defined as the total number of samples analyzed for which acceptable analytical data are generated, compared to the total number of samples submitted for analysis. Sampling that adheres to standardized sampling and testing protocols will aid in providing a complete set of data for this study. The goal for completeness is 90%. If 90% completeness is not achieved, the project team will determine if the DQOs can still be met, or if it is necessary to collect and analyze additional samples.

2.1.4 Comparability

Comparability is a qualitative parameter expressing the confidence with which one data set can be compared with another. This goal is achieved through the use of standard techniques to collect and analyze representative samples, along with standardized data validation and reporting procedures. By following the guidance of this SAP, the goal of comparability between this and future sampling events will be achieved. The sampling techniques (i.e., sediment traps and filtered solids apparatus) described here have not been previously used in the Green River system, but similar techniques have been used elsewhere. Only data collected using the same (or similar) techniques will be compared.

2.1.5 Sensitivity

Sensitivity is a measure of the capability of analytical methods to meet the study goal. The analytical method detection limit (MDL) goals presented in Section 4 should be sufficiently sensitive to detect contaminants at concentrations of interest to understand the chemical characteristics of the suspended solids within the Green River and its tributaries.

2.2 Sampling and Analytical Strategy

The sampling strategy is designed to result in a data set sufficient to provide general chemical characterization of suspended solids within the Green River and its major tributaries. These data will be used to make relative comparisons of chemical characteristics between locations and to provide information, along with other datasets (e.g., whole water) to estimate their relative chemical contributions to the LDW. The study is not intended to quantify contaminant loading from the Green River basin to the LDW, , but to provide information on the relative differences between locations. This information may also be used in the future to focus more detailed loadings assessments and/or to assist in source control studies in identifying subbasins/areas in the Green River that are contributing significant levels of contaminants to the Green River. The study is designed to address the following questions:

1) Sediment Traps and Filtered Solids Samples - What are the general chemical characteristics of suspended solids collected over the study period in three major tributaries to the Green River and from upper and lower boundary conditions in the main-stem Green River?
2) Filtered Solids Samples - How do concentrations of PCBs, PAHs, dioxins/furans and arsenic associated with suspended solids within the Green River Basin differ between locations during dry season/base flow and wet season/storm conditions?
3) Sediment Traps and Filtered Solids Samples - What are initial estimates of the relative contributions of PCBs, PAHs, dioxins/furans and arsenic from the major tributaries and the Green River to the LDW?

To answer these questions, sediment trap and filtered solids samples will be collected. Both sample types will be collected from the following locations: upper boundary sampling location in the Green River (upstream of the Newaukum Creek confluence at Flaming Geyser State Park); downstream boundary location (in Foster Links Golf Course in Tukwila); and Mill, Newaukum, and Soos Creeks. Filtered solids samples will be collected at the Black River Pump station; however, sediment traps will not be deployed at this location due to the lack of appropriate collection location. Sample collection at the Black River pump station may be limited due to logistical challenges associated with deployment of sampling equipment; see Section 2.2.4 for further discussion.

Information generated from both sampling techniques will provide data to supplement the whole water (King County 2011) and bulk stream sediment data (King County 2012) to help characterize the relative differences between inputs from the major tributaries to the Green River and subsequent inputs from the Green River to the LDW.

The sampling methodologies described in this SAP have not been previously used in the Green River basin. As such, although sampling goals have been established for all locations, the ability to collect sample mass sufficient for analysis of all desired parameters is uncertain. Any issues associated with insufficient sample mass or the inability to analyze the desired number of samples will be documented in the data report. In addition, sampling

will be continued as deemed necessary based on results of current proposed sampling and consideration of the project schedule.

2.2.1 Sediment Traps

The sediment trap sampling strategy is designed to cumulatively collect suspended solids samples over a variety of flow and storm event conditions. The targeted sampling period is 2-3 months. All samples will be analyzed for PCB Aroclors®, PAHs (and other SVOCs), dioxins/furans and arsenic (and other metals) in addition to TOC, total solids and PSD. If sufficient sample mass is collected, additional analyses may be conducted (e.g., mercury). Any excess sample mass will be archived and frozen. If insufficient sample mass is collected to complete all analyses, the following analytical prioritization will be followed: PCBs, total solids, TOC, dioxins/furans, PSD, arsenic and PAHs. The following list outlines the sediment mass necessary for analysis of the target parameters (including quality control samples): PCBs-90 g; PAHs (includes other SVOCs)-90 g; dioxins/furans-10 g; arsenic (includes other metals)-4 g; mercury-4 g; TOC-30 g; total solids-30 g; PSD-30-300 g, depending on the analytical method (see Section 4.4). Approximately one-third of the sample mass shown above can be used for samples not being used for quality control analyses (if less than one-third of the sample mass is available, sample specific detection limits will likely increase; see Section 4).

At the Mill Creek sampling location, two types of sediment traps will be deployed to evaluate the influence of trap design on the type and chemical composition of the material collected (see Section 3.1.1 for an explanation of the trap types).

2.2.2 Filtered Solids

The filtered solids samples will be collected with purpose-built devices that pump water through 19 inch 5 micron bag type filters to trap suspended solids. The volume of water pumped through the filter over the sampling period will be estimated and recorded. One dry season and up to 6 wet season/storm condition events will be targeted. The wet season/storm condition events will be triggered by a minimum of 0.25 inches of rain without an antecedent dry period. To the extent possible, storms of varied intensity will be targeted. If sufficient sample mass is collected, all samples will be analyzed for PCB Aroclors®, PAHs, dioxins/furans and arsenic in addition to total solids and PSD. Any excess sample mass will be archived and frozen. The targeted sample mass necessary for analysis of these parameters is the same as that listed above in Section 2.2.1 for sediment trap samples, with the exception of PSD; which will be analyzed using only the laser diffraction method and requires 30 g of sample (see Section 4.4). As described above for the sediment trap samples, less sediment mass is required for samples not being used for QC analyses. If insufficient sample mass is collected to complete all analyses, the following analytical prioritization will be followed: PCBs, total solids, dioxins/furans, PSD, arsenic and PAHs. If individual storm samples do not result in a sample mass sufficient for most analyses, samples from multiple storms may be combined. Due to the complexity and logistical restraints associated with this sampling method, field replicates will not be collected.

To better understand the relative filtration efficiency of the filtered solids apparatus and to compare grain size distribution in the water passing through the filtered solids sampler and the solids retained on the filter, one set of grab samples collected from the inlet and outlet of the sampler will be collected at each location and analyzed for TSS and PSD (see Section 3.2.1 for a more detailed description of this sampling effort).

2.2.3 Sampling Station Locations and Sample Identification

Sample locations will be identified using a unique locator name. The locator name, collection date and the unique sample identification number generated by KCEL will identify individual samples collected at each location. The six sampling locations are listed in Figure 1. The corresponding locator numbers and sample coordinates are shown in Table 1.

Table 1. Green River and Tributary Sampling Locations and Locator Names.

Locator		Locator Description	Northing[a]	Easting[a]
Sediment Trap	Filtered Solids			
FG319_ST_BAF	FG319_FS	**Green River** – Flaming Geyser State Park Upstream of Newaukum Creek	104038	1341097
FL319_ST_BAF	FL319_FS	**Green River** – Foster Links Golf Course Downstream of Confluence with Black River	177997	1288012
0322_ST_BAF	0322_FS	Mouth of **Newaukum Creek**	102390	1336841
A320_ST_BAF	A320_FS	Mouth of **Soos Creek**	116821	1309972
A315_ST_BAF A315_ST_J[b]	A315_FS	Mouth of **Mill Creek**	137218	1289725
None	PS317_FS	**Black River** @ Black River Pump Station	176593	1291222

Note: "ST_BAF" refers to the baffle type sediment trap, "ST_J" refers to the jar type sediment trap and "FS" refers to filtered solids samples; see Section 3.1.1 for descriptions of the two types of traps.

[a] State plane coordinates in North American Datum 1983 (NAD983) Washington State Plane North (4601)

[b] Two types of sediment traps will be deployed at this location

2.2.4 Sample Acquisition and Analytical Parameters

King County Field Science Unit (FSU) staff will primarily conduct sampling; however, other King County WLRD staff may provide assistance as needed. Sampling techniques are discussed in Section 3. Table 2 summarizes the number of samples targeted for collection at each location. Due to low suspended solids concentrations at some locations it is possible that the filtered solids apparatus may not collect a sample mass sufficient for analysis of the desired parameters during the dry season and some wet season/storm conditions. Therefore, the targeted number of samples listed in Table 2 are proposed study goals (see Section 3.2 for further discussions). As previously discussed, both sediment trap and filtered solids samples will be analyzed for PCB Aroclors®, 17 dioxin/furan congeners, PAHs (along with other SVOCs), arsenic (and other select metals), total solids and PSD; the sediment trap samples will also be analyzed for TOC. If sufficient sample mass is collected in the sediment traps, additional analyses may be conducted (e.g., mercury). The specific SVOCs (including PAHs) and metals to be analyzed are listed in Sections 4.2 and 4.3, respectively. Dioxin/furan congener analysis will be conducted by AXYS Analytical Services (hereinafter AXYS) in Sidney, British Columbia. All other chemical and conventional analyses will be conducted by the KCEL, an Ecology Accredited Laboratory.

Two sets of sediment trap samples are targeted for collection at each location (See Section 3.1.1). As previously discussed, low suspended solids concentrations at some locations may result in the inability to collect sample mass sufficient to analyze all or part of the desired analyte list. All changes to the target sampling plan will be documented in the final data report.

Due to logistical challenges at the Black River Pump Station sampling location and associated difficulty collecting samples representative of storm conditions, a limited number of wet season filtered solids sampling events are targeted at this site. Because the accessible sampling locations at this site are located on the upstream side of the pump station structure/dam in the "ponded" area (where TSS is very low during dry conditions), it may not be feasible to collect a baseflow sample from the Black River site; however, at least one attempt will be made to so.

Table 2. Number of Samples Targeted by Sample Type and Sampling Locations

Sample Locations	Sediment Trap Samples	Filtered Solids Samples	
		Dry Season Base Flow	Wet Season/Storm Flow
Green River – Flaming Geyser State Park (Upstream of Newaukum Creek)	2	1	5
Green River – Foster Links Golf Course (Downstream of Confluence with Black River)	2	1	5
Newaukum Creek	2	1	5
Soos Creek	2	1	5
Mill Creek	4[a]	1	5
Black River @ Black River Pump Station	0	1	3[b]
Total Number of Samples	**11**	**5**	**28**

[a] Two different sediment trap designs will be used with 2 sampling events for each targeted; see Section 3.1.1.

[b] Tentative number of samples to be collected

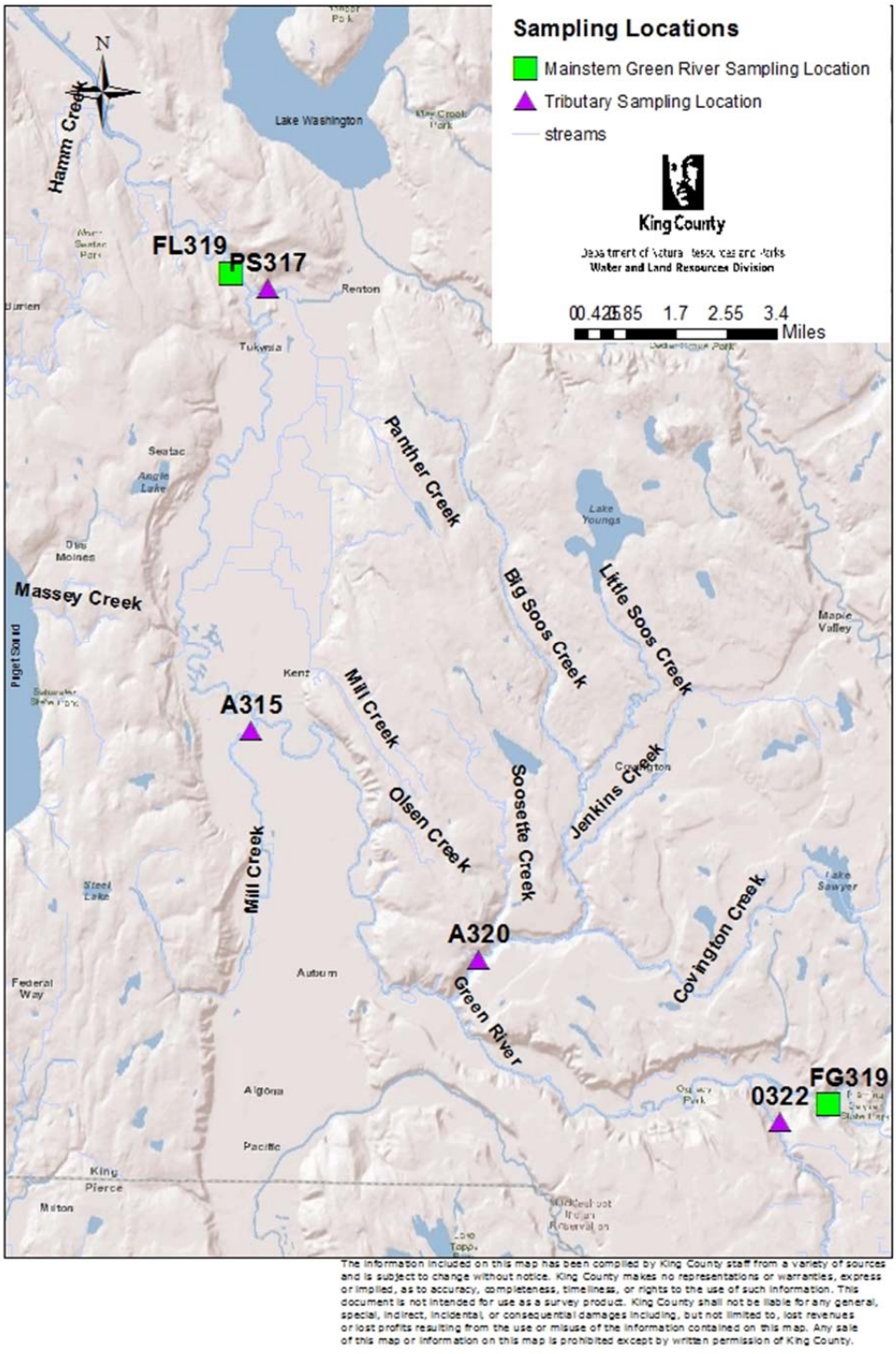

Figure 1. Sampling locations

3 SAMPLING PROCEDURES

This section describes field procedures that will be used to collect the sediment trap and filtered solids samples. Procedures are described for collecting samples including equipment used, decontamination of sampling equipment, and recording field measurements and conditions. Requirements for sample containers and preservation, and sample custody procedures are also described.

3.1 Sediment Traps

3.1.1 Sampling Methods

Suspended solids will be collected using sediment traps designed to capture sediment particles that have been suspended in the water column of the Green River or associated tributary. These sediment particles may originate from the stream/river bed or from stormwater/overland flow into the stream. A "Baffle Sediment Trap" is the primary sampling device used in this study. The baffle trap is composed of PVC material with an overall length of 42 inch (includes reducers on both ends) with a central 6 inch diameter pipe that is 24 inch long. The inlet diameter is 1-1/2 inch and outlet diameter is 3 inch; the differing inlet/outlet diameters are intended to slow water flow within the trap. A 24 inch baffle within the trap is designed to help entrain solids within the trap (Figure 2). The baffle trap is deployed by attaching it to a set of cement blocks (approximately 8 inches in height) placed on the stream bed. The bottom of the trap inlet is 3 inches above the base of the trap. When the trap is attached to the blocks, the base of the sampler inlet is approximately 11 inches above the stream bed. As a result, the trap is not likely to collect much, if any, bed load material. With the exception of the baffle insert, the traps were fabricated by Jim Devereaux, King County FSU. The baffle insert was fabricated by Ballard Sheet Metal based on a functional prototype designed and built by Jim Devereaux.

A second type of sediment trap will be targeted for deployment in Mill Creek. This type of trap will consist of two wide-open mouth 1000 mL Teflon® bottles with the following dimensions: 3.5 inch diameter, 7.75 inch tall (7 inches to shoulder) with an opening of 1 5/8 inch. The bottles are attached to a concrete block (6" in height) and referred to as the "Jar Sediment Trap" (Figure3). The top of the collection bottle once inserted into the concrete block will be approximately 9 inches from the bottom of the stream bed.

Pilot testing of the two trap types in Mill Creek in the spring/summer of 2012 suggested that the baffle type trap was more efficient at collecting material than the simple, but more traditionally used jar trap. Deployment of both types of traps at one location will allow for a more systematic comparison of the type of material captured by the two sediment trap designs.

Sediment traps deployed in tributary streams will be placed as close as possible to the center of the stream within a depositional area. Traps deployed in the main-stem Green River will be placed closer to the river bank based on both consideration of field crew safety and due to the

difficulties associated with deploying and retrieving equipment in these locations. The traps will be anchored in place with concrete blocks.

Sediment traps will be deployed for approximately 2- to 3-months to allow sufficient sample mass to accumulate. If the sample mass collected during this deployment period results in a sample mass insufficient for analysis of the desired analytes, , the second deployment period will be extended (e.g., 4 months).

Over the course of their deployment the sediment traps will be periodically inspected to assure that they have retained their position and/or have not been vandalized. The traps will be inspected approximately once a month.

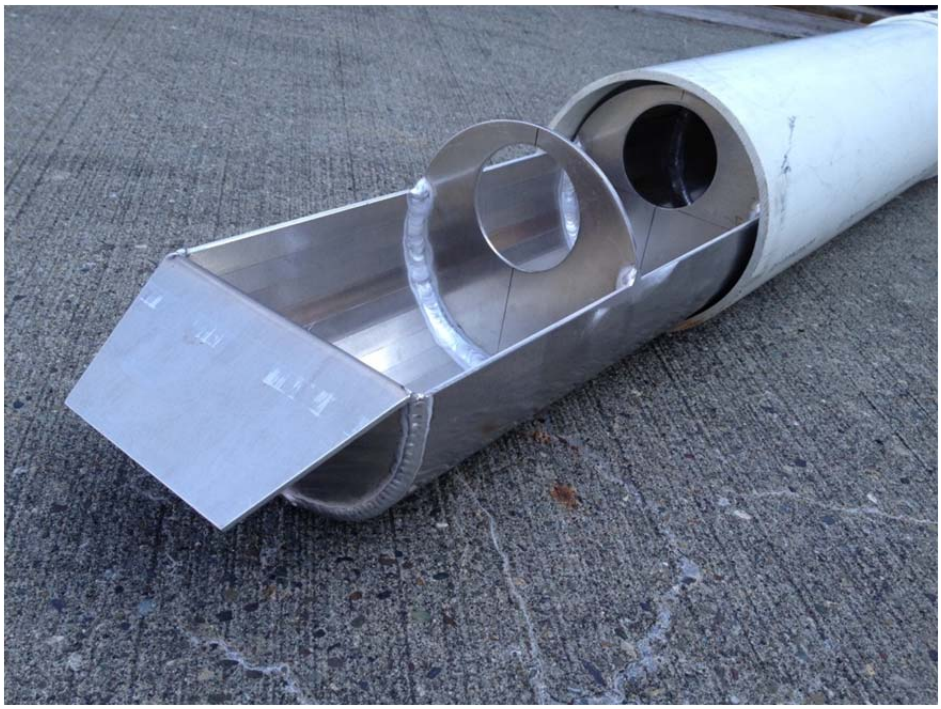

Figure 2. Baffle-Style Sediment Trap

Figure 3. Jar-Style Sediment Trap

Before removing the baffle trap from the water, caps will be screwed into both ends of the PVC tube. The tube will be released from the concrete anchors via quick releases. The PVC tube containing the baffle and sample will be moved to a temporary workspace on the bank. Water remaining in the tube will be allowed to slowly drain by gradually loosening one of the caps. Once all water has drained, the cap will be removed and the baffle tray slowly removed from the PVC tube. The sediment in the tray will then be transferred into a pre-cleaned 2.5-gallon-size glass jar via a large stainless steel funnel using a stainless steel spoon. The stainless steel funnels and spoons will be pre-cleaned at the KCEL and will be transported back to the laboratory for cleaning before any additional field use. A pre-cleaned squirt bottle filled with ambient water from the sampling location will be used to wash any remaining sediment from the tray into the sample jar. The sample jar will be capped with a Teflon lined lid, labeled with the appropriate location information and put in a cooler with ice and a plastic barrier for delivery to KCEL.

Upon retrieval of the jar-style sediment trap, the sample containers will be capped and removed from the concrete block and put on ice in a cooler for delivery to KCEL. Once the sample containers (jar-style traps) have been transported to KCEL, they will be allowed to sit so that fines are allowed to settle; excess water will be decanted and siphoned off. If necessary, the sample maybe centrifuged to further reduce the water content. A laboratory SOP (109) is being developed to outline the laboratory sample handling procedures for these samples. Once the overlying water has been removed, a pre-cleaned stainless steel spoon or spatula will be used to homogenize the sample. The sediment will then be transferred into the appropriate analyte containers and stored as noted in Section 3.3.

Samples will be analyzed for the parameters outlined in Section 2.2.2. Any excess sample mass will be archived frozen for potential future analysis.

The mass of sediment required for analysis of all parameters, including QC samples, is approximately 560 g (see Section 2.2.1). If necessary, samples (of the same type; i.e., sediment traps or filtered solids) from different deployment periods from the same location will be combined to provide sufficient mass for analysis. If this occurs, sediment from the first deployment will be homogenized and split into one jar for PSD analysis and a second jar for all other analysis. The jar for PSD analysis will be refrigerated at 4°C and the other jar will be frozen (see Section 3.3). Once the second deployment is complete and the sample has been processed as described above, the sediment will be combined with the material collected during the first deployment. The frozen sediment will be thawed prior to combining with a subset of sediment from the second deployment. The sediment from the two deployments will then be thoroughly mixed in a pre-cleaned stainless steel bowl prior to adding to appropriate pre-cleaned sample containers for chemical analysis. The other archived sample held at 4°C for PSD analysis will be combined with a subset of sediment from the second deployment and thoroughly mixed prior to analysis. Samples will be analyzed for the parameters outlined in Section 2.2.2. Any excess sample mass will be archived frozen for potential future analysis.

3.1.2 Sampling Equipment`

1) Deployment Equipment:
   a) Sediment Traps
   b) Concrete blocks
   c) Harnesses
2) Retrieval Supplies:
   a) Baffle-style sediment trap caps and jar-style sediment trap lids
   b) 2.5 gallon-size Glass jars with lids
   c) Stainless steel spoons and funnels
   d) Coolers with ice
   e) Nitrile gloves
   f) Squirt bottles
3) Safety equipment:
   a) Safety vest
   b) Personal floatation device, as needed
   c) Safety shoes and glasses
   d) Appropriate traffic control equipment and personnel where applicable (FSU supervisor will approve safety plan)
4) Documentation supplies:
   a) Field notebook

b) Sample labels
c) Chain-of-custody forms
d) Digital Camera

When visiting the sampling station, field personnel will record the following information on field forms that are maintained in a waterproof field notebook.

- Date
- Time of sample collection or visit
- Name(s) of sampling personnel
- Description of sampling location
- Weather conditions
- Number and type of samples collected
- Field notations/observations
- Comments on the working condition of the sampling equipment
- Deviations from sampling procedures
- Unusual conditions (e.g., water color or turbidity, presence of oil sheen, odors, and land disturbances)

3.1.3 Equipment Decontamination

All sampling equipment, including the sediment trap and stainless-steel bowl, funnel and spoon for sample retrieval from sediment trap will be decontaminated after each sampling event. The following decontamination procedures will be followed:

- Phosphate-free detergent wash and tap water rinse
- Reverse Osmosis laboratory water rinse
- Air dry

After the decontamination procedures have been completed, the sampling equipment and sample processing material will be capped or sealed with new uncoated aluminum foil to be protected and kept clean until needed.

3.2 Filtered Solids Sampling Methods

3.2.1 Sampling Equipment and Methods

A filtered solids collection system will be installed at sampling locations during sampling events; at some locations it may be necessary to deploy two samplers to ensure that sufficient sample mass is collected. The design of the filtration system is similar to that used by SAIC for collecting stormwater filtered solids at the North Boeing Field/Georgetown Steam Plant Site

(SAIC 2009). The system consists of a DC-powered bilge pump connected to a frame which supports two parallel filtration housings and batteries. The weighted pump will sit on a concrete paver (or similar) above the bottom of the stream/bed or it will be suspended from an existing structure (such as a bridge or railing). The pump unit will be secured to prevent movement during high flow events.

Water will be pushed through the pump hose where the flow is split and forced through two independent filter canisters. Flow totalizers connected to the outflow side of each filter canister will measure the volume of water passing through each filter. If the flow totalizers do not function properly during the collection event, an alternative method (e.g., 5-gal bucket and stop watch) will be used to estimate flow at the beginning and end of the collection period. Filtered water exits the system through outlet hoses positioned several feet downstream of the pump to avoid resampling water. As the filter bags accumulate solids, flow velocity through the system may decrease. To prevent damage to the filter unit in the event of clogging an in-line pressure relief valve is used and located upstream of the filtration housings.

The filtration housings are each equipped with a 20-inch long, 4-inch diameter filter bag. All bags are made of 5 micron polypropylene felt, pressure rated to 15 psi. This parallel system allows for the concurrent collection of two discrete suspended solids samples representative of the sampling event.

Prior to each sampling event, a suspended solids filtration system will be deployed at each location to be sampled. The frame containing the two filter housings will be loaded with two fully-charged 12 volt batteries. Pre-weighed and numbered filter bags and associated gaskets will be installed in each of the filter housings and digital flow totalizers will be zeroed immediately before deployment.

At the end of the sampling period, the filtration units will be retrieved from the site. Once the batteries and hoses have been disconnected, valves in the bottom of the filtration housings will be opened to allow remaining filtrate to drain. The entire unit will then be removed and secured in the field vehicle for transport back to KCEL. At the laboratory, filter bags will be removed from the filter housings, gently squeezed of their excess water, and placed into Ziploc® plastic bags and labeled with the sample location name, filtered volume, and date. All information will be recorded in the field logbook. At KCEL, the solids captured on the filter will be removed by cutting the filter open and gently scraping the solids from each filter using a pre-cleaned stainless steel spoon or spatula. Solids from all filter bags associated with the sampling location and sampling event will be combined into a pre-cleaned, pre-weighed (or tared) clear glass wide-mouth jar and thoroughly mixed. After the solids have been scraped off the filter (without damaging filter), and placed into the jar, the jar and its content will be weighed to determine the mass of collected material. The scraped filters will also be weighed. The solids weight will be recorded in the notebook. Once homogenized, the solids will be split into appropriate pre-cleaned sample containers for chemical analysis. The containers will be labeled with sample locator, sample identification number, sample date, and analysis type.

In the event that a sufficient mass of solids is not expected to be collected from carefully scraping the filters based on a visual inspection, one filter will be scraped and processed as above

and the other filter will be prepared as follows. An unscraped filter from the sampling event will be dried at 40°C for 24 hours, weighed and then the filter will be wrapped in foil and double bagged in in a clean zip lock bags for storage and shipment to AXYS for dioxin/furan analysis (see Section 3.3). The weight measurement before the filter bag was used will be compared to the dried filter bag weight (containing solids) in order to estimate the mass of the solids on the filter. The project manager will be consulted to determine whether to use this procedure and also to prioritize the parameters to be analyzed.

If insufficient mass is collected from one sampling event, sample from a subsequent sampling event may be combined with the prior event to allow for analysis of all desired parameters. If this occurs, the frozen solids will be thawed prior to combining with a subset of solids from a separate sampling event. The solids from the two events will then be thoroughly mixed in pre-cleaned stainless steel bowl prior to splitting into appropriate pre-cleaned sample containers for chemical analysis. The PSD archived sample held at 4°C will be combined with a subset of solids from the separate sampling event and thoroughly mixed prior to analysis. Samples will be analyzed for the parameters outlined in Section 2.2.2. Any excess sample mass will be archived frozen for potential future analysis.

As previously indicated, water samples will be collected at the inlet and outlets of the filtered solids sampling apparatus to provide a rough estimate of the filtration efficiency and to compare grain size distribution of water passing through the sampler and the material retained on the filter. At each location, one event will be targeted for assessment of TSS and PSD. Grab samples will be collected during the first 1-2 hours of sample collection and again at the end of the collection period. Grab samples will be collected adjacent to the sample intake line and at the outlets after the water has passed through the filter unit. Samples will be collected in high density polyethylene (HDP) jars. To ensure sufficient sample volume for analysis of QC analysis a minimum of 3 liters will be collected at the intake and each outlet both at the beginning and before the end of the filter solids collection period. It is important to collect TSS and PSD measurements at both the start and end of the sample collection period because as solids collect on the filter the finer material will become embedded on the filter and likely influence the particle size of suspended solids captured on the filter (i.e., as the filter pores are filled, a larger mass of finer particulates may be retained on the filter over time).

3.2.2 Sampling Equipment

1) Sampling Equipment:
   a) Filtration system units (pump, intake hose, filter unit)
   b) Outlet hoses
   c) Batteries, battery boxes and wiring harnesses
   d) Pre-weighed and numbered filter bags plus gaskets
   e) Concrete tiles/blocks
   f) Rope
   g) Gloves

h) Plastic wrench for cartridge units
i) 5-gal bucket
j) Stop Watch
k) Duct tape
l) Hand truck or cart (if practical)

2) Safety equipment:
   a) Safety vest
   b) Personal floatation device, as needed
   c) Safety shoes and glasses
   d) Appropriate traffic control equipment and personnel where applicable (FSU supervisor will approve safety plan)
   e) Waders and wading shoes
3) Documentation supplies:
   a) Field notebook
   b) Write in the rain pen/sharpies
   c) Sample labels
   d) Chain-of-custody forms
   e) Digital Camera

When visiting the sampling station, field personnel will record the following information on field forms that are maintained in a waterproof field notebook.

- Date
- Time of sample collection or visit
- Name(s) of sampling personnel
- Description of sampling location
- Weather conditions
- Number and type of samples collected
- Field notations/observations
- Comments on the working condition of the sampling equipment
- Deviations from sampling procedures
- Unusual conditions (e.g., water color or turbidity, presence of oil sheen, odors, and land disturbances)

3.2.3 Equipment Decontamination

All sampling equipment, including the hoses and filter housing will be decontaminated after each sampling event. The following decontamination procedures will be followed:

- Phosphate-free detergent wash and tap water rinse

- Reverse Osmosis laboratory water rinse
- Air dry

Following sampling, the filtered solids samplers will be taken back to KCEL to be cleaned. Batteries will be recharged between events.

3.3 Sample Delivery and Storage

No additional preservative is required for solids samples. Tables 3 and 4 provide sample handling and storage requirements for all possible analyses. Archived solids will be placed in glass jars and held frozen at –18°C. Dioxin/furan glass jars will be wrapped in individual zip lock bags and shipped frozen in coolers with ice or frozen gel packs to AXYS via overnight delivery within four weeks of sample collection. If filter bags are sent to AXYS for analysis, the bags will be kept frozen at -18°C until shipped to AXYS. The filters will be stored wrapped in foil and then double bagged in Ziploc® plastic bags. The samples would then be shipped in the same manner as if sample were in glass jars. The temperature inside the cooler(s) containing dioxin/furan samples will be checked upon receipt at AXYS. AXYS will also assign each dioxin/furan sample with a unique laboratory number for tracking within their system.

Table 3. Solids Sample Container, Preservation, Storage, and Hold Time Requirements for Samples

Analyte in priority	Container [a]	Preferred Storage Conditions	Hold Time [b]	Acceptable Storage Conditions	Hold Time
PCBs	16-oz. glass	freeze at -18°C	1 year to extract 40 days to analyze	refrigerate at 4°C	14 days to extract 40 days to analyze
Dioxins/furans	8-oz. glass	freeze at -18°C	1 year to extract 1 year to analyze	N/A	N/A
Total Organic Carbon (TOC)	4-oz. glass or polypropylene	freeze at -18°C	6 months to analyze	refrigerate at 4°C	14 days to analyze
Total Solids (collect with TOC)	4-oz. glass or polypropylene	freeze at -18°C	6 months to analyze	refrigerate at 4°C	14 days to analyze
Mercury	4-oz polypropylene	freeze at -18°C	28 days to analyze	N/A	N/A
PAHs/Semi-Volatile Organic Compounds	16-oz. glass	freeze at -18°C	1 year to extract 40 days to analyze	refrigerate at 4°C	14 days to extract 40 days to analyze
Arsenic/Other Metals	4-oz polypropylene	freeze at -18°C	2 years to analyze	refrigerate at 4°C	6 months to analyze
Archive jar	16-oz. glass	freeze at -18°C	Analyte specific		
Particle Size Distribution	16-oz. glass or polypropylene	refrigerate at 4°C	6 months to analyze	N/A	N/A

[a] Containers to be filled approximately ¾ full to allow space for expansion upon freezing (except for Particle Size Distribution).
[b] Holding time begins the date the sample is removed from the collection device.

Table 4. Water Sample Container, Preservation, Storage, and Hold Time Requirements for Samples

Analyte in priority	Container	Preferred Storage Conditions	Hold Time [b]	Acceptable Storage Conditions	Hold Time
Total Suspended Solids	1-liter WM HDPE	Refrigerate at <6° C	7 days to analyze	N/A	N/A
Particle Size Distribution	1-liter WM HDPE	Refrigerate at <6° C	7 days to analyze	N/A	N/A

WM HDPE – Wide mouth high density polyethylene

3.4 Chain of Custody

Chain of custody (COC) will commence at the time the traps/filter units are removed from the stream or river location. Thereafter, all samples will be under direct possession and control of King County FSU staff. All sample information will be recorded on a COC form (Appendix A). This form will be completed in the field and will accompany all samples during transport and delivery to KCEL. Upon arrival at the KCEL, the date and time of sample delivery will be recorded and both parties will then sign off in the appropriate sections on the COC form at this time. Copies of COC forms will accompany dioxin/furan samples to be shipped to AXYS. Once completed, original COC forms will be archived in the project file at KCEL.

Samples delivered to KCEL after regular business hours will be stored in a secure refrigerator after hours until the next day using established procedures for delivery.

3.5 Sample Documentation

Sampling information and sample metadata will be documented using the methods noted below.

- Field sheets generated by King County's Laboratory Information Management System (LIMS) will be used at all stations and will include the following information:
    1. sample ID number
    2. station name
    3. date and time of sample collection (i.e., when samples are retrieved from sampling location)
    4. sampling time or time span (i.e., the duration of the collection period as recorded by date and time of start and end times)
    5. general weather conditions at start and end times
    6. initials of all sampling personnel
    7. any deviations from these sampling procedures

- LIMS-generated container labels will identify each container with a unique sample number, station and site names, collect date, analyses required, and preservation method.
- COC documentation will consist of KCEL COC form, which is used to request analyses and track release-receipt of each sample from collection to arrival at the lab.

3.6 Equipment Blanks

One equipment blank will be collected for the baffle-style sediment trap. The equipment blank will be collected by filling the polyvinyl chloride (PVC) housing containing the trap with reverse osmosis (RO) laboratory water. The trap will be sealed with caps placed on the inlet and outlet openings. This will be allowed to sit for 2 to3 days. The laboratory water will then be collected into appropriate sample jars and analyzed for PCB Aroclors®, SVOCs, metals and mercury (see Section 4 for specific analytes).

Collection and analysis of one equipment blank at KCEL will be required for the filter bags used to collect filtered solids. Analysis of the equipment blank will be used to evaluate levels of contamination that might be associated with the filter bags. The filter bag will be soaked in RO laboratory water for2 to 4 days. The water will be placed into appropriate sample jars and analyzed for PCB Aroclors®, SVOCs and metals (see Section 4 for specific analytes).

As described for regular samples, equipment blank samples will be stored and analyzed in the same manner as environmental liquid samples. The equipment blank methods and associated detection limits are listed in Appendix C.

4 ANALYTICAL METHODS AND DETECTION LIMITS

Analytical methods are presented in the following subsections, along with analyte-specific detection limit goals. For the PCB Aroclors®, SVOCs (including PAHs), metals and selected conventional analytes, the terms MDL and RDL, used in the following subsections, refer to method detection limit and reporting detection limit, respectively.

EPA's Office of Wastewater generally defines the MDL as the minimum concentration of a chemical constituent that can be detected, while the practical quantitation limit (PQL) is the minimum concentration of a chemical constituent that can be reliably quantified.

The KCEL utilizes a LIMS to enter analytical data and generate laboratory review reports. KCEL defines the LIMS Method Detection Limit (LIMS MDL) as the lowest detectable concentration of a chemical constituent that will be reported.

For the majority of trace metals, conventionals and trace organic PCB Aroclor® (gas chromatography/electron capture detection[GC/ECD]) analyses, KCEL LIMS MDLs are typically two to five times higher than the statistically derived MDLs that are calculated by the 40 CFR Part 136, Appendix B procedure (Federal Register, Appendix B. 2007).

In the case of some trace metals and conventionals tests, MDLs are evaluated by the procedure listed in Appendix D of 40 CFR Part 136. The detection limits derived from this approach are also typically two to five times the statistically derived MDLs that are calculated by the 40 CFR Part 136, Appendix B procedure.

In the case of organic mass spectral analyses (including PAHs and other SVOCs), a standard analyzed near the MDL concentration during calibration must produce a valid mass spectra and this standard may be used to define the MDL.

The KCEL defines the LIMS RDL as the minimum concentration of a chemical constituent that can be reliably quantified. The LIMS RDL is analogous to the PQL for all analyses. The LIMS RDL is verified either by including it on the calibration curve or by running a low level standard near the PQL value during the analytical run.

KCEL reports both the LIMS RDL and the LIMS MDL for each sample and parameter, where applicable. Actual KCEL MDLs and RDLs may differ from the target detection limit goals as a result of necessary analytical dilutions or a reduction of extracted sample amount based on a preliminary examination of the sample (including total solid and TOC values). Sample extracts may require dilution due to: (i) the concentrations of one or more target analytes exceeding the upper end of the calibration curve, (ii) the presence of parameter-specific interferences impacting one or more target analytes, or (iii) unacceptable run QC (e.g., internal standard failures). In these cases, MDLs and RDLs from the original, undiluted extract will be reported for all parameters other than the specific parameters that trigger the required dilution.

For those specific parameters that trigger the required dilution, the dilution chosen for reporting data must minimize interferences and, wherever possible, demonstrate passing run QC. While every effort will be made to meet the target MDL/RDL goals listed in tables below, required dilutions may result in reported MDL/RDL values which exceed the target goals with target analytes not detected. In these cases the target analyte will be reported from the lowest acceptable dilution in order to minimize the MDL/RDL exceedance.

For dioxin/furan high resolution isotopic dilution based methods, the MDL and RDL terms are less applicable because limits of quantitation are derived from calibration capabilities and ubiquitous but typically low level equipment and laboratory blank contamination. Additional reporting limit terms used particularly for dioxin/furan congener analyses are sample specific detection limits and lowest method calibration limits. Sample specific detection limit (SDL) is determined by converting the area equivalent to 2.5 times the estimated chromatographic noise height to a concentration. SDLs are determined individually for every congener of each sample analysis run and accounts for any effect of matrix on the detection system and for recovery achieved through the analytical work-up. Lowest method calibration limits (LMCL) are based on calibration points from standard solutions. They are prorated by sample size and are supported by statistically derived method reporting limit values. The dioxin/furan congener data will be reported to LMCL and flagged as estimates down to the SDL value. In many cases the SDL may be below the LMCL.

Details regarding the frequency of required QC samples are provided in the individual analytical sections shown below. In general for all methods, this frequency is 1 in 20 samples or 1 per batch whichever is more frequent.

Below are general descriptions of types of laboratory QC samples:

- A method blank is an aliquot of clean reference matrix that is generally processed through the entire analytical procedure. Analysis of the method blank is used to evaluate the levels of contamination that might be associated with the processing and analysis of samples in the laboratory. All method blank results should be less than the method detection limit.
- A laboratory duplicate is a second aliquot of a sample, processed concurrently and in an identical manner with the original sample. The laboratory duplicate is processed through the entire analytical procedure along with the original sample in the same quality control batch. Laboratory duplicate results are used to assess the precision of the analytical method and the relative percent difference between the results should be within method-specified, SAP-specified or performance-based quality control limits. In the case of SVOCs and mercury, a matrix spike duplicate (see below) may be used in lieu of a laboratory duplicate due to the large number of non-detects frequently encountered in these analyses.
- A spike blank is a spiked aliquot of clean reference matrix used for the method blank. The spiked aliquot is processed through the entire analytical procedure. Analysis of the spike blank is used as an indicator of method accuracy. It may be conducted in lieu of a laboratory control sample/standard reference material

(LCS/SRM). A spike blank duplicate should be analyzed whenever there is insufficient sample volume to include a sample duplicate or matrix spike duplicate in the batch.

- A matrix spike is a spiked aliquot of sample fortified with a known concentration of target analyte(s). The matrix spike sample is processed through the entire analytical procedure. Analysis of the matrix spike is used as an indicator of sample matrix effect on the recovery of target analyte(s). In conjunction with the spike blank, the matrix spike is also used as an indicator of method accuracy subject to the influence of the sample matrix. A matrix spike duplicate may also be prepared as an indication of the precision of the analytical method under the influence of the sample matrix.
- A laboratory control sample (LCS) is a sample of known analyte concentration(s) that is prepared in the lab from a separate source of analyte(s) relative to the calibration standards. Since the LCS analysis should follow the entire analytical process, it should be stored and prepared following the same procedures as a field sample. Analysis of a LCS is used as an indicator of method accuracy and long-term analytical precision.
- The ongoing precision and recovery (OPR) samples should show acceptable recoveries, according to the respective methods for data to be reported without qualification. The OPR sample is typically an LCS or Spiked Blank is LIMS.
- A Standard Reference Material (SRM) is a specific certified reference material that is generally obtained from the National Institute of Standards and Technology (NIST) or the National Research Council Canada (NRCC). A SRM reference material is a matrix-specific material of known analyte concentration(s) or properties that are certified by an outside agency. The SRM must match the general matrix of the batch of samples being analyzed. An aliquot of the certified reference material, as received, is processed as a sample through the complete analytical procedure. A certificate or other official document defining the certified value(s) should be kept for each lot of an SRM. An SRM duplicate may be prepared to provide further indication of the precision of the analytical method.

4.1 PCB Aroclors®

Samples in this study will be analyzed for PCBs as Aroclors®. PCB analysis will be performed according to EPA methods 3550B/8082A (SW846), which employ solvent extraction with sonication and analysis by GC/ECD and dual column confirmation, KCEL SOP 757. The LIMS product name is PCB.

The detection limits for PCB Aroclors® are summarized in Table 5. These MDLs and RDLs are presented on a wet-weight basis and are based on extraction of a 30 g sample, gel permeation cleanup (GPC), and concentration to a final volume of 1 ml. Every effort will be made to meet these limits, however depending upon the organic content of the samples it may not be possible to obtain this concentration factor. When reporting PCB results, the KCEL will report each individual Aroclor result and calculate Total Aroclors® as the sum of

detected Aroclors®[4]. If no individual Aroclors® are detected in a sample, the reported MDL/RDL for the Total Aroclors® parameter will be set equal to the highest MDL/RDL among the individual Aroclors® reported for the sample. The detection limits can vary if limited sample is available for extraction (less than 30 g) or if dilution is required due to elevated analyte concentration(s).

Table 5. PCB Aroclor® Detection Limit Goals (µg/kg wet weight)

Analyte	MDL	RDL
Aroclor 1016	1.3	5.33
Aroclor 1221	2.7	5.33
Aroclor 1232	2.7	5.33
Aroclor 1242	1.3	5.33
Aroclor 1248	1.3	5.33
Aroclor 1254	1.3	5.33
Aroclor 1260	1.3	5.33
Total Aroclors® [a]	1.3 [a]	5.33 [a]

MDL - Method detection limit
RDL - Reporting detection limit

[a] When Aroclors® are detected, the reported MDL/RDL for the Total Aroclors® parameter will be lowest MDL/RDL of the individual Aroclors®. If Aroclors® are not detected; the reported MDL/RDL for the Total Aroclors® parameter will be the highest MDL/RDL of the individual Aroclors®.

In addition to the surrogates which assess sample accuracy and bias, a method blank, laboratory duplicate, spike blank, matrix spike, matrix spike duplicate, SRM and SRM duplicate sample will be analyzed with each set of 20 samples, or one per batch. Quality assurance/quality control (QA/QC) frequency and acceptance criteria for Aroclor® analysis are as shown in Table 6. Performance-based control limits are statistically derived, reviewed and potentially updated on an annual basis. The limits for the 2012 calendar year are shown in Appendix B.

Table 6. PCB Aroclor® QA/QC Frequency and Acceptance Criteria

	Method Blank	Spike Blank (% Recovery)	Matrix Spike (% Recovery)	Matrix Spike or Spike Blank Duplicate (RPD)	Lab Duplicate (RPD)	Standard Reference Material and SRM Dup (% Recovery)
Analyte/ Frequency	**1 per Extraction batch [a]**	**1 per Extraction batch [a]**	**1 per QC batch**	**1 per QC batch**	**1 per QC batch**	**1 per QC batch**
Aroclor 1016	<MDL	NA	NA	NA	35	NA
Aroclor 1221	<MDL	NA	NA	NA	35	NA
Aroclor 1232	<MDL	NA	NA	NA	35	NA
Aroclor 1242	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	NA
Aroclor 1248	<MDL	NA	NA	NA	35	NA
Aroclor 1254	<MDL	NA	NA	NA	35	NA
Aroclor 1260	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	38 – 167 (EPA Puget Sound Sediment Reference Material)
Surrogates - Added to all samples and QC		**Surrogate (% Recovery)**				
2,4,5,6-Tetrachloro-m-xylene		Laboratory QC Limits [b]				
Decachloro-biphenyl		Laboratory QC Limits [b]				

< MDL - Method Blank result should be less than the *method detection limit*.

RPD - Relative Percent Difference

NA - Not Applicable

[a] QC Extraction batch - 20 samples or less prepared within a 12 hour shift

[b] These are empirically derived performance-based laboratory control limits. These limits may be updated once per calendar year and the limits it in effect at the time of analysis will be used as accuracy limits.

Note: SRM will be run in duplicate to provide information on the analytical precision of the method. The RPD limit is 35%.

4.2 Semivolatile Organic Compounds

The primary semivolatile organics analyzed in this study will consist of PAH compounds as shown in Table 7. For the sediment trap samples, where sufficient sample mass is available, the semivolatile organics analyzed will be KCEL Base-Neutral-Acid-Sediment Management Standards (BNASMS) list type (see Table 8). The LIMS product name is BNASMS. The

samples will be prepared by sonication extraction as detailed in method SW846 3550B, and analyzed by method SW846 8270D, KCEL SOP 731. Wet weight MDL and RDL goals are as shown and are based upon taking 30 g of sample to 1 mL with a 3/8 loss due to a GPC cleanup. Every effort will be made to meet these limits, however depending upon the organic content and total solids of the samples; it may not be possible to obtain this concentration factor. KCEL will report individual PAH results.

For filtered solids samples, PAHs will be analyzed by a PAH- Selected Ion Monitoring (SIM) method. The extraction method is the same as for BNASMS listed above and the analytical method is SW846 8270 D SIM, KCEL SOP 731. The target PAH compounds are the same parameters listed in Table 6. The MDL and RDL goals will be established following a MDL test performed before sample analysis begins. A SAP appendix will be created with the SIM detection limits. The QC limits will be identical to the full scan limits for the PAH parameters. If sample mass is limited for sediment trap samples or if lower detection limits are needed, PAH-SIM method may be used. In this case, only PAHs in Table 7 would be reported.

In addition, KCEL will report total high molecular weight PAHs (HPAHs) and total low molecular weight PAHs (LPAHs) as the sum of detected HPAHs or LPAHs, respectively[5]. If no PAHs are detected within the LPAH or HPAH class, the reported MDL/RDL for these totals will be the highest MDL/RDL reported for the individual PAHs in that class. When individual PAHs in HPAH or LPAH are detected, the reported MDL/RDL for these totals will be the lowest MDL/RDL from the respective LPAH or HPAH class.

Table 7. PAH Target Compounds and Detection Limit Goals based on Method SW846 3550B/8270D (µg/kg, wet weight)

Analyte	MDL-FS	RDL-FS	MDL-SIM	RDL-SIM
2-Methylnaphthalene	5.3	10.7	TBD	TBD
Acenaphthene	5.3	10.7	TBD	TBD
Acenaphthylene	5.3	10.7	TBD	TBD
Anthracene	5.3	10.7	TBD	TBD
Benzo(a)anthracene	5.3	10.7	TBD	TBD
Benzo(a)pyrene	5.3	10.7	TBD	TBD
Benzo(b,j,k)fluoranthene	5.3	10.7	TBD	TBD
Benzo(g,h,i)perylene	5.3	10.7	TBD	TBD
Chrysene	5.3	10.7	TBD	TBD
Dibenzo(a,h)anthracene	5.3	10.7	TBD	TBD
Dibenzofuran	5.3	10.7	TBD	TBD
Fluoranthene	5.3	10.7	TBD	TBD

[5] When PAHs are detected, the reported MDL/RDL for the total LPAH or total HPAH parameter will be lowest MDL/RDL of the individual LPAHs or HPAHs, respectively.

Analyte	MDL-FS	RDL-FS	MDL-SIM	RDL-SIM
Fluorene	5.3	10.7	TBD	TBD
Indeno(1,2,3-Cd)Pyrene	5.3	10.7	TBD	TBD
Naphthalene	5.3	10.7	TBD	TBD
Phenanthrene	5.3	10.7	TBD	TBD
Pyrene	5.3	10.7	TBD	TBD

NOTE: The MDL/RDL limits are calculated on an extraction of 30 grams to a final volume of 1.0 mL with a 3/8 loss for GPC cleanup. MDL/RDL limits will vary depending on amount extracted and final volume.

FS-full scan
SIM- Selected Ion Monitoring

Table 8. Remaining SVOC Target Compounds and Detection Limit Goals (µg/kg, wet weight)

Analyte	MDL	RDL
1,2,4-Trichlorobenzene	0.53	1.07
1,2-Dichlorobenzene	5.33	5.33
1,4-Dichlorobenzene	8.00	8.00
2,4-Dimethylphenol	5.3	10.7
2-Methylphenol	5.3	10.7
3-,4-Methylphenol	27	53.3
Benzoic Acid	107	107
Benzyl Alcohol	13.3	13.3
Benzyl Butyl Phthalate[a]	8.00	8.00
Bis(2-Ethylhexyl)Phthalate[a]	11	21.3
Diethyl Phthalate[a]	11	21.3
Dimethyl Phthalate[a]	10.7	10.7
Di-N-Butyl Phthalate[a]	11	21.3
Di-N-Octyl Phthalate[a]	10.7	10.7
Hexachlorobenzene	0.53	1.07
Hexachlorobutadiene	2.7	5.33
N-Nitrosodiphenylamine	13.3	13.3
Pentachlorophenol	80.0	80.0
Phenol	27	80.0

NOTE: The MDL/RDL limits are calculated on an extraction of 30 grams to a final volume of 1.0 mL with a 3/8 loss for GPC cleanup. MDL/RDL limits will vary depending on amount extracted and final volume.

[a] Results from the two sediment trap collection methods will be compared to evaluate the potential of phthalate contamination from the PVC housing material used in the baffle-style sediment trap; depending on the outcome, phthalates may or may not be reported for the baffle-style sediment traps.

In addition to the surrogates and internal standards, which assess sample accuracy and bias, a method blank, laboratory duplicate, spike blank, matrix spike, matrix spike duplicate an SRM and an SRM duplicate sample will be analyzed with each set of 20 samples, or one per batch. QA/QC frequency and acceptance criteria for SVOC analysis are as shown in Table 9. Performance-based control limits are statistically derived, reviewed and potentially updated on an annual basis. The limits for the 2012 calendar year are shown in Appendix B.

Table 9. SVOC QA/QC Frequency and Acceptance Criteria

	Method Blank	Spike Blank (% Recovery)	Matrix Spike (% Recovery)	Matrix Spike or Spike Blank Duplicate (RPD)	Lab Duplicate (RPD)	SRM &SRM Dup (% Recovery)
Analyte/ Frequency	**1 per Extraction batch [a]**	**1 per Extraction batch [a]**	**1 per QC batch**	**1 per QC batch**	**1 per QC batch**	**1 per QC batch**
1,2,4-Trichlorobenzene	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	
1,2-Dichlorobenzene	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	
1,4-Dichlorobenzene	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	
2,4-Dimethylphenol	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	
2-Methylnaphthalene	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	
2-Methylphenol	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	
3-,4-Methylphenol	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	
Acenaphthene	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	
Acenaphthylene	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	
Anthracene	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	

	Method Blank	Spike Blank (% Recovery)	Matrix Spike (% Recovery)	Matrix Spike or Spike Blank Duplicate (RPD)	Lab Duplicate (RPD)	SRM &SRM Dup (% Recovery)
Analyte/ Frequency	**1 per Extraction batch [a]**	**1 per Extraction batch [a]**	**1 per QC batch**	**1 per QC batch**	**1 per QC batch**	**1 per QC batch**
Benzo(a)anthracene	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	Laboratory QC Limits [b]
Benzo(a)pyrene	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	Laboratory QC Limits [b]
Benzo(b,j,k) fluoranthene	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	Laboratory QC Limits [b]
Benzo(g,h,i)perylene	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	Laboratory QC Limits [b]
Benzoic Acid	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	
Benzyl Alcohol	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	
Benzyl Butyl Phthalate	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	
Bis(2-Ethylhexyl)Phthalate	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	
Chrysene	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	Laboratory QC Limits [b]
Dibenzo(a,h) anthracene	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	Laboratory QC Limits [b]
Dibenzofuran	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	
Diethyl Phthalate	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	
Dimethyl Phthalate	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	
Di-N-Butyl Phthalate	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	
Di-N-Octyl Phthalate	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	

	Method Blank	Spike Blank (% Recovery)	Matrix Spike (% Recovery)	Matrix Spike or Spike Blank Duplicate (RPD)	Lab Duplicate (RPD)	SRM &SRM Dup (% Recovery)
Analyte/ Frequency	**1 per Extraction batch [a]**	**1 per Extraction batch [a]**	**1 per QC batch**	**1 per QC batch**	**1 per QC batch**	**1 per QC batch**
Fluoranthene	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	Laboratory QC Limits [b]
Fluorene	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	
Hexachlorobenzene	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	
Hexachlorobutadiene	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	
Indeno(1,2,3-Cd)Pyrene	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	Laboratory QC Limits [b]
Naphthalene	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	
N-Nitrosodiphenylamine	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	
Pentachlorophenol	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	
Phenanthrene	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	Laboratory QC Limits [b]
Phenol	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	
Pyrene	<MDL	Laboratory QC Limits [b]	Laboratory QC Limits [b]	35	35	Laboratory QC Limits [b]
Surrogates - Added to all samples and QC		**Surrogate (% Recovery)**				
2-Fluorophenol		Laboratory QC Limits [b]				
D5-Phenol		Laboratory QC Limits [b]				
D5-Nitrobenzene		Laboratory QC Limits [b]				

	Method Blank	Spike Blank (% Recovery)	Matrix Spike (% Recovery)	Matrix Spike or Spike Blank Duplicate (RPD)	Lab Duplicate (RPD)	SRM &SRM Dup (% Recovery)
Analyte/ Frequency	**1 per Extraction batch [a]**	**1 per Extraction batch [a]**	**1 per QC batch**	**1 per QC batch**	**1 per QC batch**	**1 per QC batch**
D4-2-Chlorophenol		Laboratory QC Limits [b]				
D4-1,2-Dichlorobenzene		Laboratory QC Limits [b]				
2-Fluorobiphenyl		Laboratory QC Limits [b]				
2,4,6-Tribromophenol		Laboratory QC Limits [b]				
D14-Terphenyl		Laboratory QC Limits [b]				

< MDL - Method Blank result should be less than the *method detection limit*.
RPD - Relative Percent Difference
NA - Not Applicable
[a] QC Extraction batch - 20 samples or less prepared within a 12 hour shift
[b] These are empirically derived performance-based laboratory control limits. These limits may be updated once per calendar year and the limits it in effect at the time of analysis will be used.
Note: SRM will be run in duplicate to provide information on the analytical precision of the method. The RPD limit is 35%.

4.3 Arsenic and Other Metals

The primary inorganic element analyzed in this study will be arsenic. However, because the analytical method and sample mass is the same for other inorganic elements, the analysis will also include the metals listed in Table 10. Arsenic and other metals samples will be analyzed by EPA Method 3050B / 6020A (Inductively Coupled Plasma-Mass Spectrometry [ICP-MS]), KCEL SOP 624. If mercury is analyzed, it will be by EPA Method 7471B (Cold Vapor Atomic Absorption [CVAA]), KCEL SOP 604, mid-range (Table 11). The detection limit goals targeted for metals and mercury are shown in Tables 10 and 11, respectively. ICP-MS MDLs are based upon digesting a 1 g sample aliquot and diluting the resultant solution to a final volume of 250 mL. The CVAA MDL is based upon digesting a 1 g sample aliquot, resulting in a final volume of 100 mL. The MDL and RDL values for actual samples will be calculated based on exact amount of sample digested and will be reported to 2 and 3 significant figures, respectively.

Table 10. Trace Metals Target Analytes and Detection Limit Goals (mg/kg wet weight)

Analyte	MDL	RDL
Arsenic	0.025	0.125
Cadmium	0.013	0.0625
Chromium	0.05	0.25
Copper	0.1	0.500
Lead	0.025	0.125
Nickel	0.025	0.125
Silver	0.01	0.05
Vanadium	0.019	0.0938
Zinc	0.13	0.625

Table 11. Mercury Detection Limit Goals (mg/kg wet weight)

Analyte / Range	MDL	RDL
Mercury / Mid-Range	0.005	0.05

Sample accuracy and bias will be evaluated by a laboratory duplicates, spike blanks, and matrix spike/matrix spike duplicate samples and will be analyzed with each set of 20 samples, or one per batch. QA/QC frequency and acceptance criteria for metals and mercury analysis are as shown in Table 12. Performance-based control limits are statistically derived, reviewed and potentially updated on an annual basis. The limits for the 2012 calendar year are shown in Appendix B.

Table 12. Trace Metals and Mercury QA/QC Frequency and Acceptance Criteria

	Method Blank	Spike Blank (% Recovery)	Lab Duplicate	Matrix Spike Duplicate	Matrix Spike (% Recovery)	LCS (% Recovery)[a]
Analyte/ Frequency	**1 per batch***	**1 per batch [b]**	**1 per batch**	**1 per batch**	**1 per batch**	**1 per batch**
Total Metals by ICP-MS	< MDL	85 – 115%	RPD ≤ 20%	NA	75 - 125%	laboratory QC limits [c]
Total Mercury	< MDL	85 – 115%	RPD ≤ 20%	RPD ≤ 20%	75 - 125%	80-120%

[a] The LCS or SRM samples will be run in duplicate with an expected RPD <20%

[b] Batch - 20 samples or less prepared as a set

[c] These are empirically derived performance-based laboratory control limits. These limits may be updated once per calendar year and the limits it in effect at the time of analysis will be used.

< MDL - Method Blank result should be less than the *method detection limit*.

RPD - Relative Percent Difference

LCS - Lab Control Sample

NA - Not Applicable

4.4 Conventionals

The conventional parameters analyzed in this study for the solids matrix will be total solids, TOC and PSD; TSS and PSD will also be analyzed for the water matrix. Conventional analyses will follow Standard Methods (SM) (American Public Health Association [APHA] 1998), EPA, Puget Sound Estuary Program (PSEP), and/or American Society for Testing and Materials (ASTM) method protocols for all but one of the two PSD methods. For samples with insufficient mass to conduct standard PSD analyses (e.g., filtered solids samples) an alternative PSD method will be used. In these cases, the samples will be analyzed using laser diffraction method ISO 13320:2009(E). In this method, an aliquot of sample is dispersed in reverse osmosis water, laser light is passed through it, and the scattering of the light by the particles is measured and converted to particle size results. Table 13 presents the analytical methods, detection limits, and units for conventional analyses.

Table 13. Conventionals Target Analytes and Detection Limit Goals

Analyte	Method	KCEL SOP	Units	MDL	RDL
Total Suspended Solids	SM2540-D	309	mg/L	0.5	1.0
Total Organic Carbon	EPA 9060/PSEP 96	337	mg/kg wet weight	500	1000
Total Solids	SM 2540-G	307	% wet weight	0.005	0.01
Particle Size Distribution	ASTM D422	318	% dry weight	0.1 (gravel and sand) 0.5 (silt and clay)	1.0 (all)
	Laser Diffraction ISO 13320:2009(E)	350	% volume	0.1	0.1

PSEP - Puget Sound Estuary Program
SM - Standard methods
ASTM - American Society for Testing and Materials
ISO - International Standards Organization
MDL - Method Detection Limit
RDL - Reporting Detection Limit

Detection limits will vary slightly from sample to sample, depending on the exact amount of sample mass used for analysis. Table 14 describes the minimum QC required for the conventionals analysis. Conventional QC samples will be analyzed at the frequency of one per QC batch of 20 or less samples.

Table 14. Conventionals QA/QC Frequency and Acceptance Criteria

Analyte/ Frequency	Method Blank	Lab Triplicate (RSD)	Lab Duplicate (RPD)	Spike Blank (% Recovery)	Matrix Spike (% Recovery)	SRM/LCS (% Recovery)
	1 per batch[a]	1 per batch[a]	1 per batch[a]	1 per batch[a]	1 per batch[a]	1 per batch[a]
Total Suspended Solids	<MDL	N/A	25%	N/A	N/A	80-120%
Total Organic Carbon	<MDL	20%	N/A	80-120%	75-125%	80-120%
Total Solids	<MDL	20%	N/A	N/A	N/A	N/A
Particle Size Distribution (Solids)	N/A	20%	N/A	N/A	N/A	N/A
Particle Size Distribution (Water)	N/A	N/A	25%	N/A	N/A	N/A

[a] Batch - 20 samples or less prepared as a set
< MDL - Less than the Method Detection Limit.
RSD - Relative Standard Deviation
RPD – Relative Percent Difference
LCS - Lab Control Sample
SRM - Standard Reference Material
N/A - Not applicable

4.5 Dioxins/furans

Dioxin/furan congener analysis will be performed according to EPA Method 1613B (EPA 1994), which is a high-resolution gas chromatography/high-resolution mass spectroscopy (HRGC/HRMS) method using an isotope dilution internal standard quantification. This method provides reliable analyte identification and very low detection limits. Labeled native and surrogate standards (Table 15) are added before samples are extracted. Data are "recovery-corrected" for losses in extraction and cleanup, and analytes are quantified against their labeled analogues or a related labeled compound.

AXYS will perform this analysis according to their SOP MLA-017, which is based on EPA Method 1613b Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS. Sample will be extracted followed by standard method clean-up, which includes layered Acid/Base Silica, Florisil, and Alumina. Samples will be extracted using either sonication or soxhlet, depending on the state of the sample used for this analysis. Whenever possible, 5-10 g of solids from the filter bag will be sent to AXYS for analysis of dioxins/furans. In cases where there is insufficient mass from a scraped filter bag for this analysis, a dried and weighed filter bag will be used (see Section 3.2.1 for filter preparation prior to shipping to AXYS). AXYS will extract the filter bag to obtain sample for analysis in this case.

Table 15. Labeled Surrogates and Recovery Standards Used for EPA Method 1613b Dioxins/Furans Congener Analysis

^{13}C-labeled Congener Surrogate Standards	
Labeled analytes of interest are used for all dioxins and furans quantified except 1,2,3,7,8,9-HxCDD and OCDF	
^{37}Cl-labeled Cleanup Standards	
2,3,7,8 TCDD	
^{13}C-labeled Internal (Recovery) Standards	
1,2,3,4 TCDD	1,2,3,7,8,9 HxCDD

Table 16 lists the 17 dioxin/furan congeners and their respective target SDL values. The reported SDLs for individual samples may differ from those in Table 16 because they are determined by signal to noise ratios and changes to final volumes. Typical sample detection limits are shown.

Table 16. Dioxin/furan Solids Sample Detection Limit Goals (pg/g) and Lower Calibration Limit Goals

Parameter	Typical Detection Limit/SDL	LMCL based on Low Cal./RDL
Dioxins		
2,3,7,8 TCDD	0.5	2.0
1,2,3,7,8 PeCDD	0.1	5.0
1,2,3,4,7,8 HxCDD	0.1	5.0
1,2,3,6,7,8 HxCDD	0.1	5.0
1,2,3,7,8,9 HxCDD	0.1	5.0
1,2,3,4,6,7,8 HpCDD	0.1	5.0
OCDD	0.5	10.0
Furans		
2,3,7,8 TCDF	0.05	1.0
1,2,3,7,8 PeCDF	0.5	5.0
2,3,4,7,8 HxCDF	0.1	5.0

Parameter	Typical Detection Limit/SDL	LMCL based on Low Cal./RDL
1,2,3,4,7,8 HxCDF	0.1	5.0
1,2,3,6,7,8 HxCDF	0.1	5.0
1,2,3,7,8,9 HxCDF	0.1	5.0
2,3,4,6,7,8 HxCDF	0.1	5.0
1,2,3,4,6,7,8 HpCDF	0.1	5.0
1,2,3,4,7,8,9 HpCDF	0.1	5.0
OCDF	0.55	10.0

Note: based on EPA method 1613b, AXYS Analytical Services method MLA 017
SDL - Sample Detection Limit
LMCL - Lower Method Calibration Limit
RDL - Reporting Detection Limit

Quality control samples include method blanks, OPR samples, and surrogate spikes. Method blanks and OPR samples are each included with each batch of samples. Surrogate spikes are labeled compounds that are included with each sample. The sample results are corrected for the recoveries associated with these surrogate spikes as part of the isotope dilution method. In addition, a laboratory duplicate will be conducted with each batch of samples. Note that a matrix spike and matrix spike duplicate are not required, nor meaningful under Method 1613b. Method 1613b has specific requirements for method blanks that must be met before sample data can be reported (see Section 9.5.2 of Method 1613b). The OPR samples must show acceptable recoveries, according to Method 1613b, in order to samples to be analyzed and data to be reported. A summary of the quality control samples are shown in Table 17. If sample is extracted from the filter bag, a method blank and an OPR sample will be analyzed with the sample(s). A laboratory duplicate will not be analyzed.

Table 17. Dioxins/Furans QA/QC Frequency and Acceptance Criteria

	Method Blank	Lab Duplicate (RSD)	OPR (% Recovery)	Surrogate Spikes
Frequency	**1 per batch [a]**	**1 per batch [a]**	**1 per batch [a]**	**Each sample**
Dioxins/Furans	<LMCL[b]	RPD <50%	laboratory QC limits [c]	laboratory QC limits [c]

[a] batch = 20 samples or less prepared as a set
[b] EPA Method 1613B blank criteria (see Table 2 of the published method) is to be below the Minimum Levels: 0.5, 1.0, and 5 pg/g for the tetra, penta through hepta, and octa respectively
[c] The laboratory's performance-based control limits that are in effect at the time of analysis will be used as quality control limits.
LMCL = Lowest Method Calibration Limit
RSD = Relative Standard Deviation
OPR = Ongoing Precision and Recovery

5 DATA VALIDATION, REPORTING AND RECORD KEEPING

This section presents the data validation, reporting, and record keeping for the samples collected under this SAP.

5.1 Data Validation

Chemical data generated during this study will be validated according to accepted EPA guidelines (EPA 2001, 2004 and 2005), where applicable. KCEL will develop "QA 1 (Ecology 1989) or EPA Stage 2a data packages allowing for this level of validation. This level of validation includes reviews of holding times, method blanks, and QA/QC samples. An EPA Stage 2b validation will be performed on approximately 20% of the metals and organic batches. This level of validation includes a review of summary forms for calibrations, instrument performance, and internal standard summaries. Dioxin/furan data will undergo a Level III data validation. All necessary data needed for independent review of dioxin/furan data will be provided by AXYS. All other chemical analysis and associated conventional water quality data will be validated against requirements of the reference methods as well as the requirements of this SAP. Data validation will be performed by the King County WLRD for all data generated by KCEL. Data validation for dioxin/furan data will be conducted by an outside party for this study. Data validation memoranda will be produced and maintained along with the analytical data as part of the project records.

5.2 Reporting

All data collected associated with this SAP from the Green River and its four tributaries and any supporting information will be documented in a data report. All sediment trap and filtered solids data will be reported in dry weight using sample specific percent solids. Data validation memoranda will be included in the data report, as will copies of COC forms. In addition, if appropriate data fields can be generated in Ecology's FSU database, data will be submitted for loading into the EIM database.

5.3 Record Keeping

All hard-copy field sampling records, custody documents, raw lab data, and laboratory summaries and narratives generated by KCEL will be archived according to KCEL policy for LDW Superfund records. These records will include both hard copy and electronic data. Conventional, trace metals and trace organics analytical data produced by the KCEL will be maintained on its LIMS database in perpetuity. AXYS will provide electronic deliverables of data and associated quality control results to King County. While KCEL will maintain a copy of deliverables from AXYS, copies of full data packages pertaining to King County samples analyzed by AXYS will be maintained by AXYS for 10 years from the analysis date.

6 REFERENCES

APHA 1998. Standard Methods for the Examination of Water and Wastewater, 20th Edition. American Public Health Association. Washington, D.C.

Ecology. 1989. Puget Sound Dredged Disposal Analysis Guidance Manual - Data Quality Evaluation for Proposed Dredged Material Disposal Projects. Prepared for the Washington State Department of Ecology by PTI Environmental Services. Bellevue, Washington

EPA. 1994. Method 1613, Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS. United States Environmental Protection Agency, Office of Water. Washington, D.C

EPA. 2001. USEPA Contract Laboratory Program National Functional Guidelines for Low Concentration Organic Data Review. United States Environmental Protection Agency. Washington, D.C.

EPA. 2004. USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review. Available at: http://www.epa.gov/superfund/programs/clp/download/inorgfg10-08-04.pdf

EPA. 2005. National functional guidelines for chlorinated dibenzo-p-dioxins (CDDs) and chlorinated dibenzofurans (CDFs) data review. OSWER 9240.1-51. EPA 540-R-05-001. Office of Superfund Remediation and Technology Innovation, U.S. Environmental Protection Agency, Washington, DC.

Federal Register Appendix D 2007: Federal Advisory Committee on Detection and Quantitation Approaches Single Laboratory Procedure v2.4 of the Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Act Programs Final Report 12/28/07.

Gries and Sloan. 2009. Contaminant Loading to the Lower Duwamish Waterway from the Suspended Sediment on the Green River. WA Department of Ecology. Olympia WA. Publication No 09-03-028.

King County. 2007. Water Quality Statistical and Pollutant Loading Analysis – Green Duwamish Water Quality Assessment. Prepared for the King County Department of Natural Resources by Herrera Environmental Consultants, Inc., Seattle WA.

King County. 2011. Green River Loading Study – Sampling and Analysis Plan. Prepared by Deb Lester, Richard Jack, and Debra Williston. Water and Land Resources Division. Seattle, Washington.

King County. 2012. Stream Sediment Monitoring Sampling and Analysis Plan Green River Basin. Prepared by Dean Wilson, King County Water and Land Resources Division. Seattle, Washington.

KCEL SOP #731. King County Environmental Laboratory Standard Operating Procedure. Analysis of Semivolatile Compounds by GC/MS, King County, WA.

KCEL SOP #757. King County Environmental Laboratory Standard Operating Procedure. Analysis of PCB Aroclors by GC/ECD, King County, WA.

KCEL SOP #624. King County Environmental Laboratory Standard Operating Procedure. ICPMS Analysis of Waters, Sediments and Tissues for Trace Metals by Thermo X II CCT Instrument, King County, WA.

KCEL SOP #604. King County Environmental Laboratory Standard Operating Procedure. Instrumental Analysis for Mercury in Environmental Samples by Cold Vapor Atomic Absorption Spectrometry, King County, WA.

KCEL SOP #337. King County Environmental Laboratory Standard Operating Procedure. Total Organic Carbon in Sediments and Soils, King County, WA.

KCEL SOP #307. King County Environmental Laboratory Standard Operating Procedure. Total Solids and Total Volatile Solids, King County, WA.

KCEL SOP #318. King County Environmental Laboratory Standard Operating Procedure. Particle Size Distribution Analysis of Sediments by ASTM D422, King County, WA.

KCEL SOP #350. King County Environmental Laboratory Standard Operating Procedure. Particle Size Distribution (PSD) by Laser Diffraction (LD) and Sediment Concentration (SC), King County, WA.

KCEL SOP #109. King County Environmental Laboratory Standard Operating Procedure. Removal of Excess Overlying Water from Sediment Trap Samples, King County, WA (In-prep).

Windward Environmental, LLC 2010. Final Remedial Investigation Report, Lower Duwamish Waterway. Prepared for Lower Duwamish Waterway Group for submittal to U.S. Environmental Protection Agency, Seattle, WA and Washington Department of Ecology, Bellevue, WA, Prepared by Windward Environmental, Seattle, WA

APPENDIX A:
CHAIN-OF-CUSTODY FORM

KING COUNTY DNR ENVIRONMENTAL LABORATORY *322 West Ewing Street Seattle, WA 98119*

LABORATORY WORK ORDER

Project Name: LDW In-line Solids

Project Number:

Laboratory Project Manager: Fritz Grothkopp

684-2327

Sampler:_____

					Parameters									
Lab SAMPLE #	LOCATOR	MATRIX	COLLECT DATE	COLLECT TIME	BNALL	PCBLL	ICP Metals	Mercury	Total Solids	TOC	PSD		No. of Containers	Comments
Additional Comments:										Total # of Containers:				

RELINQUISHED BY	Date	RECEIVED BY	Date
Signature		Signature	
Printed Name	Time	Printed Name	Time
Organization		Organization	

APPENDIX B:

KCEL TRACE ORGANICS PERFORMANCE-BASED QC LIMITS FOR SEDIMENTS

Performance-based control limits are statistically derived, reviewed and potentially updated on an annual basis. The limits below are current as of July 2012.

Table B-1

Laboratory QC Limits for Sediment BNAs analyzed by Method SW846 3550B/8270D **– Matrix Spike Recoveries**

Parameter	Lower Limit (%)	Upper Limit (%)	Parameter	Lower Limit (%)	Upper Limit (%)
1,2,4-Trichlorobenzene	22	95	Chrysene	47	141
1,2-Dichlorobenzene	20	110	Di-N-Butyl Phthalate	64	150
1,4-Dichlorobenzene	20	105	Di-N-Octyl Phthalate	43	150
2,4-Dimethylphenol	27	126	Dibenzo(a,h)anthracene	39	150
2-Methylnaphthalene	22	109	Dibenzofuran	49	135
2-Methylphenol	21	126	Diethyl Phthalate	71	130
3-,4-Methylphenol	24	129	Dimethyl Phthalate	66	128
Acenaphthene	37	129	Fluoranthene	53	144
Acenaphthylene	44	134	Fluorene	52	150
Anthracene	37	150	Hexachlorobenzene	51	149
Benzo(a)anthracene	52	149	Hexachlorobutadiene	20	133
Benzo(a)pyrene	62	136	Indeno(1,2,3-Cd)Pyrene	41	150
Benzo(b,j,k)fluoranthene	48	135	N-Nitrosodiphenylamine	58	140
Benzo(g,h,i)perylene	27	150	Naphthalene	20	112
Benzoic Acid	20	150	Pentachlorophenol	35	134
Benzyl Alcohol	28	111	Phenanthrene	51	136
Benzyl Butyl Phthalate	27	150	Phenol	21	142
Bis(2-Ethylhexyl)Phthalate	54	150	Pyrene	59	143

Table B-2

Laboratory QC Limits for Sediment BNAs analyzed by Method SW846 3550B/8270D **– Blank Spike Recoveries**

Parameter	Lower Limit (%)	Upper Limit (%)	Parameter	Lower Limit (%)	Upper Limit (%)
1,2,4-Trichlorobenzene	39	94	Chrysene	45	150
1,2-Dichlorobenzene	44	105	Di-N-Butyl Phthalate	71	142
1,4-Dichlorobenzene	40	103	Di-N-Octyl Phthalate	43	150
2,4-Dimethylphenol	20	121	Dibenzo(a,h)anthracene	41	150
2-Methylnaphthalene	20	128	Dibenzofuran	52	133
2-Methylphenol	20	123	Diethyl Phthalate	75	131
3-,4-Methylphenol	se	119	Dimethyl Phthalate	70	129
Acenaphthene	43	126	Fluoranthene	56	143
Acenaphthylene	45	132	Fluorene	57	150
Anthracene	48	149	Hexachlorobenzene	53	150
Benzo(a)anthracene	51	150	Hexachlorobutadiene	20	135
Benzo(a)pyrene	61	140	Indeno(1,2,3-Cd)Pyrene	42	150
Benzo(b,j,k)fluoranthene	45	143	N-Nitrosodiphenylamine	57	136
Benzo(g,h,i)perylene	28	150	Naphthalene	28	109
Benzoic Acid	20	92	Pentachlorophenol	25	135
Benzyl Alcohol	26	111	Phenanthrene	47	141
Benzyl Butyl Phthalate	36	150	Phenol	26	136
Bis(2-Ethylhexyl)Phthalate	61	150	Pyrene	60	144

Table B-3

Laboratory QC Limits for Sediment BNAs analyzed by Method SW846 3550B/8270D **– Surrogate Recoveries**

Parameter	Lower Limit (%)	Upper Limit (%)
2,4,6-Tribromophenol	45	150
2-Fluorophenol	20	136
d5-Phenol	20	142
d5-Nitrobenzene	22	126
d4-2-Chlorophenol	20	127
2-Fluorobiphenyl	22	135
d14-Terphenyl	25	150

Table B-4

Laboratory QC Limits for Sediment BNAs analyzed by Method SW846 3550B/8270D **– SRM Recoveries**

Parameter	Lower Limit (%)	Upper Limit (%)
Benzo(a)anthracene	48	127
Benzo(a)pyrene	48	119
Benzo(b,j,k)fluoranthene	50	126
Benzo(g,h,i)perylene	42	141
Chrysene	64	150
Dibenzo(a,h)anthracene	54	200
Fluoranthene	56	137
Indeno(1,2,3-Cd)Pyrene	40	130
Phenanthrene	49	124
Pyrene	58	123

Table B-5

Laboratory QC Limits for Sediment PCBs as Aroclors Matrix Spike Recoveries

Parameter	Lower Limit (%)	Upper Limit (%)
Aroclor 1242	57	111
Aroclor 1260	33	105

Table B-6

Laboratory QC Limits for Sediment PCBs as Aroclors Blank Spike Recoveries

Parameter	Lower Limit (%)	Upper Limit (%)
Aroclor 1242	23	92
Aroclor 1260	52	103

Table B-7
Laboratory QC Limits for Sediment PCBs Surrogate Recoveries

Parameter	Lower Limit (%)	Upper Limit (%)
Decachlorobiphenyl	55	120
2,4,5,6-Tetrachloro-m-xylene	20	115

Table B-8
Laboratory QC Limits for Sediment Metals
Laboratory Control Sample Recoveries: Buffalo River Sediment (MI-15-30)

Parameter	Lower Limit (%)	Upper Limit (%)
Arsenic	80	120
Cadmium	76	116
Chromium	40	80
Copper	n/a	n/a
Lead	71	111
Nickel	80	120
Silver	n/a	n/a
Vanadium	10	44
Zinc	69	109

Table B-8
Laboratory QC Limits for Sediment Metals
Laboratory Control Sample Recoveries: ERA Soil (M-12-026)

Parameter	Lower Limit (%)	Upper Limit (%)
Arsenic	80	120
Cadmium	80	120
Chromium	80	120
Copper	80	120
Lead	80	120
Nickel	80	120
Silver	66	134
Vanadium	77	123
Zinc	80	120

APPENDIX C: EQUIPMENT BLANK METHODS AND MDLS

Target Analytes and Detection Limits

PCB Aroclors®

Equipment blanks will be prepared by liquid-liquid extraction as detailed in method SW846 3520C, and analyzed for PCB Aroclors® by method SW846 8082A GC/ECD), KCEL SOP 757. The following table lists the PCB Aroclors® and their respective target MDL and RDL goals for the equipment blanks. These MDL/RDLs are based upon extraction of 1000 mL of sample and concentration to 1.0 mL final volume. The reported MDLs and RDLs for individual equipment blanks may differ from those shown below due to changes in the volume of sample extracted or the final extract volume. Every effort will be made to meet these limits, however depending upon the organic content of the samples it may not be possible to obtain this concentration factor.

Method = SW846 3520C / 8082A (GC/ECD) (µg/L)

Analyte	MDL	RDL
Aroclor 1016	0.025	0.05
Aroclor 1221	0.025	0.05
Aroclor 1232	0.025	0.05
Aroclor 1242	0.025	0.05
Aroclor 1248	0.025	0.05
Aroclor 1254	0.025	0.05
Aroclor 1260	0.025	0.05

SVOCs

Equipment blanks will be prepared by liquid-liquid extraction as detailed in method SW846 3520C, and analyzed for semivolatile organics by method SW846 8270D (GC/MS), KCEL SOP 731. Semivolatile organics analyzed in the equipment blanks will consist of the compounds included in the KCEL Base-Neutral-Acid-Sediment Management Standards (BNASMS) list type. The LIMS product is BNASMS. The following table lists the BNASMS compounds and their respective target MDL and RDL goals for the equipment blanks. These MDL/RDLs are based upon extraction of 1000 mL of sample and concentration to 1.0 mL final volume. The reported MDLs and RDLs for individual equipment blanks may differ from those shown below due to changes in the volume of sample extracted or the final extract volume. Every effort will be made to meet these limits, however depending upon equipment blank volume it may not be possible to obtain this concentration factor.

Method = SW846 3520C / 8270D (GC/MS) (µg/L)

Analyte	MDL	RDL	Analyte	MDL	RDL
1,2,4-Trichlorobenzene	0.30	0.50	Chrysene	0.30	0.50
1,2-Dichlorobenzene	0.30	0.50	Dibenzo(a,h)anthracene	0.80	1.50
1,4-Dichlorobenzene	0.30	0.50	Dibenzofuran	0.50	1.00
2,4-Dimethylphenol	0.50	1.00	Diethyl Phthalate	0.50	1.00
2-Methylnaphthalene	0.80	1.50	Dimethyl Phthalate	0.20	0.30
2-Methylphenol	0.50	1.00	Di-N-Butyl Phthalate	0.50	1.00
3-,4-Methylphenol	0.50	1.00	Di-N-Octyl Phthalate	0.30	0.50
Acenaphthene	0.20	0.40	Fluoranthene	0.30	0.60
Acenaphthylene	0.30	0.50	Fluorene	0.30	0.50
Anthracene	0.30	0.50	Hexachlorobenzene	0.30	0.50
Benzo(a)anthracene	0.30	0.50	Hexachlorobutadiene	0.50	1.00
Benzo(a)pyrene	0.50	1.00	Indeno(1,2,3-Cd)Pyrene	0.50	1.00
Benzo(b,j,k)fluoranthene	0.80	1.50	Naphthalene	0.80	1.50
Benzo(g,h,i)perylene	0.50	1.00	N-Nitrosodiphenylamine	0.50	1.00
Benzoic Acid	2.00	3.00	Pentachlorophenol	0.50	1.00
Benzyl Alcohol	0.50	1.00	Phenanthrene	0.30	0.50
Benzyl Butyl Phthalate	0.30	0.50	Phenol	2.00	3.00
Bis(2-Ethylhexyl)Phthalate	0.30	0.50	Pyrene	0.30	0.50

Note: LIMS MDL and RDL limits may change annually due to MDL studies. Any limits that are increased due to an MDL study will be noted in a data anomaly form (DAF).

Note equipment blanks will be run with these QC samples: method blank, spike blank and spike blank duplicate. The surrogate and spike blank control limits will be based upon the lab derived limits for liquid matrices.

Metals and Mercury

Equipment blanks will be analyzed by EPA Method 200.8 / 6020A (Inductively Coupled Plasma-Mass Spectrometry [ICP-MS]), KCEL SOP 624 and analyzed for the metals shown below. Mercury will be analyzed by EPA Method 245.1/7470A CVAA), KCEL SOP 604, mid-range. The following table lists the metals and their respective target MDL and RDL goals for the equipment blanks. ICP-MS MDLs are based upon digesting a 50 mL sample aliquot and diluting the resultant solution to a final volume of 50 mL. The CVAA MDL is based upon digesting a 100 mL sample aliquot, resulting in a final volume of 100 mL.

Method = EPA 245.1 (CVAA) (µg/L)

Analyte / Range	MDL	RDL
Mercury / Mid Range	0.05	0.15

Method = EPA 200.8 (ICP-MS) (µg/L)

Analyte	MDL	RDL
Arsenic	0.1	0.5
Cadmium	0.05	0.25
Chromium	0.2	1
Copper	0.4	2
Lead	0.1	0.5
Nickel	0.1	0.5
Silver	0.04	0.2
Vanadium	0.075	0.375
Zinc	0.5	2.5